EUROPEAN SYMPOSIUM ON ATOMIC SPECTROMETRY 2012
XXTH SLOVAK-CZECH SPECTROSCOPIC CONFERENCE

BOOK OF ABSTRACTS

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Preface

Dear colleagues,

I would like to warmly welcome you all to the joined event of the European Symposium on Atomic Spectrometry 2012 and the XXth Slovak-Czech Spectroscopic Conference organized by Slovak Spectroscopic Society and Ioannes Marcus Marci Spectroscopic Society in Tatranská Lomnica, October 7-12, 2012.

For us, it is both honour and privilege that the International Scientific Committee of the European Symposium on Atomic Spectrometry decided to organize this year Symposium in Slovakia and agreed to join it with the Slovak-Czech national conference. These conferences take place every 2 years and are organized jointly by both national spectroscopic societies (this year for the third time) as a result of the long-time productive cooperation. The last conference was the 14th Czech-Slovak spectroscopic conference organized by Ioannes Marcus Marci Spectroscopic Society and Slovak Spectroscopic Society in Litomyšl, Czech republic in 2010; and the first was the XIXth Slovak-Czech spectroscopic conference in Častá-Papiernička, Slovakia in 2008. The numbering according to the previous conferences in the both countries is retained.

On behalf of the Organizing Committee I would like to thank for the interest of well-known scientists as well as the other participants from 19 countries from various institutions, universities, laboratories, and commercial companies, who created together very professional program worth seeing. The conference programme covers the full range of atomic and molecular spectroscopy, and special spectroscopic techniques. This year Conference will be hosting about 216 persons, the scientific program consists of 4 honorary and 25 invited lectures, 57 oral presentations, 97 poster displays, and 12 commercial presentations.

The scientific as well as the social programme will take place in Grandhotel Praha in Tatranská Lomnica, located in the middle of Slovakia´s highest mountains. The hotel combines the elegance of the old world with the perks of modern age. A cableway trip to the astronomical observatory on Lomnický štít, which is one of the highest peak in the High Tatras, as well as a visit to former royal free city Kežmarok, which is one of Slovakia's most important urban heritage reservations with rich history, will also belong to unforgettable experiences.

I should like to take this opportunity to thank for the support of Allianz Slovenská poisťovňa, a.s. and ROKO, a.s. as the partners, Thermo Fisher Scientific, Inc. and Pragolab, s.r.o. as the general sponsors, Shimadzu Europa, GmbH and Analytik Jena, AG as the ESAS sponsors and the other supporters.

I believe that we will create pleasant and inspirational atmosphere and just the right conditions for you to work, discuss and receive new ideas as well as meet new interesting people for future cooperation. You will also take advantage of the natural beauty and the option to relax in the High Tatras.

With my best regards

Jana Kubová
Chair of the organizing committee

PROGRAMME

SUNDAY, OCTOBER 07, 2012

14.00-22.00	Registration
18.00-20.00	Dinner
20.00-22.00	Get together and Welcome “bottle” party

MONDAY, OCTOBER 08, 2012

07.00-10.00	Breakfast
08.30-20.00	Registration
08.30-20.00	Installation of posters (Poster session I)
08.30-09.00	Opening ceremony

Chairpersons: E. Bulska, V. Kanický, M. Miglierini

09.00-09.30	**T. Kántor** History of ESAS and related meetings: a personal view
09.30-10.00	**E. Plško** Some personal recollections concerning the development of spectroscopy in Slovakia
10.00-10.30	**B. Strauch** From history of Czechoslovak and JMM Spectrosopic Society
10.30-11.00	**K. Flórián** 50 years of atomic spectroscopy on TU in Košice, celebrating his 60th anniversary: past – presence and future perspectives

11.00-11.30	Coffee/Tea break

SESSION A1

Chairperson: G. Záray

11.30-12.00	**R. Salzer** Spectroscopic imaging of biological samples
12.00-12.30	**E. Bulska** Atomic and mass spectrometry in clinical applications
12.30-13.00	**M. Holčapek** Comprehensive lipidomic characterization of biological samples using LC-MS

SESSION B1

Chairperson: J. Humlíček

11.30-12.00	**B. Vlčková** Cooperation between plasmonic nanoparticles generation by laser ablation and SERS spectroscopy
12.00-12.30	**P. Mojzeš** Kinetic studies on the formation of SERS-active systems

12.30-13.00 **P. Matějka** The influence of temperature on surface-enhanced vibrational spectra: how significantly does it affect spectral data obtained?

13.00-14.30 Lunch

SESSION A2

Chairperson: B. Dočekal

14.30-15.00 **G. Schlemmer** Academic versus industrial research and development: A view on today´s enhancements in optical atomic spectroscopy

15.00-15.20 **D. Katskov** The application of low resolution continuum source electrothermal atomic absorption spectrometry for simultaneous multi-element analysis of underground water

15.20-15.40 **Z. Kowalewska** Determination of nickel in non-decomposed organic samples using graphite furnace atomic absorption spectrometry: new outlook on old problems

15.40-16.00 **A. Alajtal** Determination of some inorganic metals in olive and vegetable oils by atomic absorption spectrophotometry

16.00-16.20 **E. Baranyai** Trace element level in whole and protein separated blood serum of patients with Systemic lupus erythematosus and Syögren syndrome

SESSION B2

Chairperson: P. Matějka

14.30-15.00 **J. Humlíček** Resonances of infrared local fields and negative-refraction in anisotropic metamaterials

15.00-15.20 **K. Šišková** SERRS spectral behavior of modified Tollens method prepared Ag nanoparticles and the effect of HCl

15.20-15.40 **I. Šloufová** Resonance Raman and surface-enhanced resonance Raman excitation profiles of $[Fe(tpy)_2]^{2+}$ on Ag nanoparticle surfaces

15.40-16.00 **M. Člupek** Advanced chemometric models for evaluation of SERS spectroscopic data describing the influences of the metal and excitation wavelength

16.00-16.20 **M. Kokošková** Surface-modified luminescence and SERRS excitation profiles of Ru(II) $(bpy)_2(dcbpy)$ complex chemisorbed on Ag nanoparticles

16.20-16.50 Coffee/Tea break

SESSION A3

Chairperson: G. Schlemmer

16.50-17.20 **B. Dočekal** Direct solid sampling electrothermal atomic absorption spectrometry – why and how? – A personal view

17.20-17.50 **V. Krivan** Performance comparison of potential routine solid sampling methods for bulk analysis of high and ultrahigh purity materials

17.50-18.10 **V. Vojteková** Z-GFAAS with variable magnetic field in the solution and solid sample analysis

18.10-18.30 **K. Elsherif** Direct and simultaneous determination of Bi, Sb and Cd in biological samples by multi-element graphite furnace atomic absorption spectrometer

SESSION B3

Chairperson: R. Salzer

16.50-17.20 **M. Boča** X-ray photoelectron spectroscopy as a tool for identification of fluorine atoms with different bonding properties

17.20-17.50 **M. Liška** Glass structure study by Raman spectroscopy combined with thermodynamic modeling

17.50-18.10 **I. Němec** Molecular crystals for non-linear optics – vibrational spectroscopic aspects

18.10-18.30 **I. Matulková** Phase transitions in novel NLO materials – vibrational and diffraction study (*in Czech*)

18.30-20.00 Dinner

20.00-22.00 Poster session I with Slovak beer tasting

TUESDAY, OCTOBER 09, 2012

07.00-10.00 Breakfast

09.00-20.00 Registration

09.00-20.00 Installation of posters (Poster session II)

SESSION A1

Chairperson: E. Beinrohr

09.00-09.30 **J. Dědina** Progress in trace elemental and speciation analysis based on volatile species generation with atomic absorption/fluorescence detection

09.30-09.50 **J. Kratzer** In-atomizer trapping of hydrides for AAS – last advances

09.50-10.00 **R. Cibula** iCAP-Q – new dimension in ICP/MS spectrometry *(in Slovak)*

10.00-10.20 **Š. Eichler** Speciation analysis of selenium in urine by HPLC and ICP/MS hyphenation *(in Czech)*

10.20-10.40 **K. Mališová** Speciation analysis of mercury in terrestrial plants and food of plant origin *(in Czech)*

SESSION B1

Chairperson: B. Vlčková

09.00-09.30	**J. Sitek** Present state of Mössbauer spectroscopy applications
09.30-10.00	**M. Miglierini** Mössbauer spectrometry of iron in biological tissues
10.00-10.20	**L. Machala** Mössbauer spectroscopy in studying of thermal decomposition of iron containing compounds
10.20-10.40	**E. Plško** Assignment of a chemical property to the value of a spectroscopic analytical signal *(in Slovak)*

10.40-11.10	Coffee/Tea break

SESSION A2

Chairperson: J. Dědina

11.10-11.40	**E. Beinrohr** Electrochemical hydride generation for atomic spectroscopy
11.40-12.00	**H. Matusiewicz** Ultrasonic nebulization/dual-mode sample introduction system for the determination of metal volatile species in analytical samples by microwave induced plasma spectrometry (USN/MSIS-CVG-MIP-OES)
12.00-12.20	**T. Matoušek** Arsenic speciation analysis at (ultra)trace levels by hydride generation and/or HPLC with ICP MS detection – pros, cons and principal limitations of individual approaches
12.20-12.40	**J. Hraníček** A determination of gold by electrochemical generation of volatile form with quartz atomizer-AAS detection (optimization and characterization)
12.40-13.10	**H. Gleisner** Determination of fluorine using high-resolution continuum source molecular absorption spectrometry (HR CS MAS)
13.10-13.20	**M. Zavadil** Elemental analysis in the industry and research *(in Czech)*

SESSION B2

Chairperson: V. Krivan

11.10-11.40	**M.T.C. de Loos-Vollebregt** Electrothermal vaporization plasma emission and mass spectrometry
11.40-12.00	**K. Flórián** Solid-sampling atomic spectroscopic determination of impurity elements in catalysts based on Pd with various supports *(in Slovak)*
12.00-12.20	**J. Schram** Determination of rare earth elements in electronic waste using ICP-OES spectrometry
12.20-12.40	**A. Krejčová** The efficiency of the ICP-OES introduction systems
12.40-13.00	**M. Zeiner** ICP-AES determination of selected nutrients in Aronia (*Aronia melanocarpa*) berries and infusions
13.00-13.20	**M. Kröppl** Plant nutrients in different grain size fractions of biomass fly ashes

13.20-14.50	Lunch

SESSION A3

Chairperson: M.T.C. de Loos-Vollebregt

14.50-15.20	**T. Černohorský** TOF-ICP-MS spectrometry – historical overview and latest developments
15.20-15.40	**L. Husáková** Multi-elemental analysis of milk by ICP-oa-TOF-MS after matrix modification by oxalic and nitric acid
15.40-16.00	**I. Urbanová** Elimination of chloride interferences in ICP-oa-TOF-MS analysis
16.00-16.20	**M. Reijnen** Understand interferences within the application needs
16.20-16.40	**M. Elbagermi** Biomonitoring of heavy metals using soft drinks from Misurata City – Libya
16.40-17.00	**R. Koplík** Trace metals and phosphorus speciation in digested food: a way of elements' availability estimation? *(in Czech)*

SESSION B3

Chairperson: M. Boča

14.50-15.20	**M. Sabo** Using corona discharge ion mobility-mass spectrometry for monitoring of volatile organic compounds
15.20-15.40	**M. Michl** Plasmonics in fluorescence spectroscopy
15.40-16.00	**F. Sohbatzadeh** Spectroscopic characterization of atmospheric pressure plasma plum regarding geometrical aspects
16.00-16.20	**U. Oppermann** Characterization and quantification of TiO_2-nano particles in body care products using laser diffraction and ICP-OES spectrometry
16.20-16.40	**L. Novosád** Behaviour of analytical spectral lines emitted by plasma pencil operated in a continuous and in a pulsed mode
16.40-17.00	**A. Hrdlička** Influence of analyzed solutions on the plasma pencil discharge *(in Czech)*

18.00-20.00	Dinner
20.00-22.00	Poster session II with Slovak wine tasting

WEDNESDAY, OCTOBER 10, 2012

07.00-10.00	Breakfast
08.00-18.00	Excursion to Skalnaté pleso and Lomnický štít astronomical observatory
09.00-20.00	Registration
09.00-20.00	Installation of posters (Poster session III)
12.00-14.00	Lunch or packed lunch

18.00-20.00 Dinner

20.00-22.00 Poster session III with Slovak spirit/liquor tasting

THURSDAY, OCTOBER 11, 2012

07.00-10.00 Breakfast

09.00-20.00 Registration

SESSION A1

Chairperson: J. Schram

09.00-09.30 **D. Günther** New capabilities in laser ablation-ICP-mass spectrometry

09.30-09.50 **B. Wagner** Analytical strategy for multi-elemental laser ablation ICP MS investigations of pigments from unique, historical objects

09.50-10.10 **T. Vaculovič** Laser ablation in analytical chemistry *(in Czech)*

10.10-10.30 **V. Helán** Tenders for laboratory equipment *(in Czech)*

SESSION B1

Chairperson: H. Dočekalová

09.00-09.30 **Y. Bazeľ** Development of new sample pretreatment techniques before spectrometric detection

09.30-09.50 **I. Hagarová** Surfactant-based extractions: application to ultratrace determination of metals

09.50-10.10 **M. Tüzen** Solid phase extraction of lead and copper on a novel block copolymer disk and flame atomic absorption spectrometric determination of its in water and food samples

10.10-10.30 **L. Macháčková** The possibilities of toxic elements trace analysis in natural waters by combination of atomic spectrometry methods with a sample preparation techniques *(in Slovak)*

10.30-11.00 Coffee/Tea break

SESSION A2

Chairperson: T. Černohorský

11.00-11.30 **V. Kanický** Laser-assisted plasma spectrometry techniques – development and applications

11.30-11.50 **T. Kratochvíl** The use of laser-induced breakdown spectroscopy for the quantitative analysis of fluorine

11.50-12.10 **K. Novotný** Simultaneous system of DP-LIBS and laser ablation ICP-OES *(in Czech)*

SESSION B2

Chairperson: J. Sitek

11.00-11.30 **T. Liptaj** Residual dipolar couplings constants in NMR

11.30-11.50 **J. Posta** A new spectrometric method and instrument to follow thermal processes

11.50-12.10 **P. Lubal** Development of optical chemical sensors/sensor arrays

12.10-14.00 Lunch

14.00-19.30 Excursion to Kežmarok

20.00-24.00 Conference dinner (banquet) with live music band and prizes giving

FRIDAY, OCTOBER 12, 2012

07.00-10.00 Breakfast

09.00-12.00 Registration

SESSION A1

Chairperson: D. Günther

09.00-09.30 **T. Kántor** Laser ablation ICP-MS: interpreting the effects of increasing carrier gas flow rate

09.30-09.50 **T. Warchilová** Study of molten fluoride salts treatment on metallic samples by means of LA-ICP-MS

09.50-10.10 **K. Štěpánková** Comparison study of laser ablation based methods for analysis of kidney stones

10.10-10.30 **N. Gardenová** Determination of major and trace elements in natural silicate minerals using LA-ICP-MS

SESSION B1

Chairperson: S. Akman

09.00-09.30 **G. Záray** Aerosol studies in urban environment

09.30-09.50 **O. Zvěřina** Mercury associated with size-fractionated urban particulate matter: three years of sampling in Prague, Czech Republic

09.50-10.10 **A. Kleckerová** Dandelion (*Taraxacum officinale*) as bioindicator for urban metal pollution *(in Czech)*

10.10-10.30 **L. Bednárová** Antibacterial peptides from eusocial bee *Halictus sexcinctus* interacting with model membranes *(in Czech)*

10.30-11.00 Coffee/Tea break

SESSION A2

Chairperson: M. Liška

11.00-11.20	**O. Dogan** Measurement of the fluorescence cross sections of YBCO superconductor materials using EDXRF technique
11.20-11.40	**M. Ozcan** Evaluation of calibration techniques in the determination of Pb in glass samples by direct solid sampling atomic absorption spectrometry
11.40-12.00	**A. Plško** Quantitative analysis of oxide glasses by X-ray fluorescence analysis *(in Slovak)*

SESSION B2

Chairperson: R. Koplík

11.00-11.20	**B. Dočekal** Diffusive gradients in thin film (DGT) technique in characterization of environmental systems
11.20-11.40	**M. Gregušová** Characterization of atmospheric particulate matter by diffusive gradient in thin film (DGT) technique
11.40-12.00	**H. Dočekalová** Diffusive gradient in thin films technique for assessment of copper bioavailability to radish (*Raphanus sativus*) (*in Czech*)

12.00-12.30	Closing ceremony with prizes giving
12.30-14.00	Lunch

POSTER SESSION 1

Monday, October 08, 2012, 20.00-22.00

Chairpersons: K. Flórián, T. Kántor, E. Plško, B. Strauch

P-01 **S. Akman** A new approach for the determination of fluorine in water samples via molecular absorption of barium mono-fluoride using HR CS ETAAS

P-05 **A.A. Asweisi** A new cross-shaped graphite furnace for reduction of interferences in atomic absorption spectrometry

P-06 **N.R. Bader** Determination of trace amounts of cadmium by flame atomic absorption spectrometry after pre-concentration using silica gel coated with Schiff's bases

P-13 **S. Cadore** Optimization of meat sample pretreatment by factorial design for cadmium determination for the official food control

P-15 **P. Coufalík** The determination of mercury species using thermal desorption analysis in AAS

P-17 **R. Červenka** Determination of methylmercury in soil samples by GC-AFS

P-18 **B. Demirata Ozturk** Determination of sulphur dioxide and antioxidants in wine by spectroscopic methods

P-20 **R. Dobrowolski** Study of platinum adsorption onto modified SBA-15 with respect to analytical application

P-21 **R. Dobrowolski** Determination of bismuth in soils and sediments by slurry sampling GFAAS using chemical modifiers

P-25 **A. Eswayah** Heavy metal removal from aqueous solution using Libyan natural zeolite and activated carbon

P-26 **M. Fehér** Determination the elemental uptake of barramundi (*Lates calcarifer*) larvae fed by Co, Zn and Mn enriched *Artemia nauplii* using atomic absorption spectrometry

P-29 **B. Godlewska-Żyłkiewicz** Ultrasound assisted sequential extraction for determination of bioavailable fraction of cadmium and lead in soil by ETAAS - green sample pretreatment

P-32 **I. Hagarová** Coacervative extraction of lead from natural waters prior to its determination by electrothermal atomic absorption spectrometry

P-35 **M. Hlodák** Spectrometric assessment of phytoavailability and ecotoxicological effects of mercury in the soil-plant system (*Hordeum vulgare* L.) under laboratory conditions

P-42 **Z. Jakubíková** RTG fluorescence spectroscopy study of glass melting filter dust composition

P-44 **N. Kamakura** Determination of Cr(III), Cr(VI), and Cr(acac)$_3$ in water by ion-exchange disks/metal furnace atomic absorption spectrometry

P-48 **G. Khayatian** Development of ultrasound-assisted emulsification solidified floating organic drop microextraction for determination of trace amount of iron and copper in water, food and rock samples

P-49 **G. Khayatian** Directly suspended droplet microextraction and determination of trace amount of iron and copper in water, fruit, vegetable and rock samples

P-52 **M. Konečná** Determination of trace metals in phthalocyanine-containing materials by atomic absorption spectrometry

P-56 **J. Laštincová** Proficiency testing in wine analysis

P-57 **B. Leśniewska** On-line SPE-FAAS method for determination of chromium in water samples

P-58 **L. Macháčková** Removal of heavy metals from the aqueous solutions and acid mine drainage at the Smolnik locality by *Aspergillus niger* wild type strains

P-59 **A. Manová** Electrochemical hydride generation atomic absorption spectrometry for the determination of some inorganic elements

P-60 **S. Matějková** Elemental analysis of systems based on gold nanoparticles using of X-ray fluorescence and inductively coupled plasma - optical emission spectroscopy

P-61 **P. Matúš** Investigation of dissolved cationic aluminium species sorption on some nano-sized metal oxides for analytical purposes using atomic spectrometry methods

P-63 **Z. Melichová** The AAS analysis of selected toxic metals in natural waters and soils from an area affected by mining activities (Špania Dolina, Slovakia)

P-73 **J. Pagáčová** Quantitative analysis of B_2O_3 content in glasses by X-ray fluorescence spectroscopy

P-83 **M. Rybínová** Determination of selenium using photochemical volatile compounds generation coupled with atomic absorption spectrometer

P-90 **J. Šrámková** Elemental analysis of identification taggants by F-AAS using slurry sampling technique

P-95 **V. Vojteková** Sono-extractive isolation of metals from the solid sample matrix

P-96 **A.N. Zacharia** Graphite “filter-furnace” application at electrothermal atomic absorption analysis of some food and environmentals

P-97 **E. Zambrzycka** Determination of ruthenium in environmental samples by ETAAS after its separation on a new ion imprinted polymers

POSTER SESSION 2

Tuesday, October 09, 2012, 20.00-22.00

Chairpersons: K. Flórián, T. Kántor, E. Plško, B. Strauch

P-02 **V. Anan'ev** Non-polarized light absorption in pure, doped with the nitrite ions, and photolyzed KNO_3 crystals

P-07 **D. Bauer** Direct determination and quantification of sulphur species in solid fuels by ETV-ICP OES – economical and environmentally friendly

P-08 **M.E.A. Benamar** Selenium content in wheat and estimation of the selenium daily intake in different regions of Algeria

P-11 **K. Boriová** Quantification of bioaccumulation and biovolatilization processes using ICP OES and CV AAS

P-16 **L. Čanecká** Sorption study of P(V), As(V) and Sb(V) on Fe (oxy)hydroxides during the thermal transformation and change of their surface properties

P-22 **R. Dobrowolski** Direct determination of trace metals in suspension fertilizers by slurry introduction inductively coupled plasma optical emission spectrometry

P-23 **J.M. Dubrovkin** Optimization of spectrochemical analysis of "white" multicomponent mixtures using direct calibration

P-24 **J.M. Dubrovkin** Estimation of the minimum uncertainity of quantitative spectrochemical analysis

P-28 **K. Gardošová** Selenium determination in two/three-component cultivation system (fungus/humic acid/mineral phase) by ICP OES

P-33 **L. Havránek** Spectroelectrochemical study of 4-aminobenzenethiol on copper, silver and gold: What is the role of the metal on the reactivity of the adsorbed species?

P-34 **M. Heželová** DC arc spectroscopic studies of evaporation processes of important elements in various Pd based catalysts

P-36 **G. Holéczyová** Mono-standard calibration for analysis of solid environmental samples using SS-DCA-OES method

P-38 **M. Huleihel** Fourier transform infrared microspectroscopy (FTIR-M) as an effective tool for identification of virally infected cells and cells contaminated with bacteria or fungi

P-40 **M. Chromčíková** Thermodynamic model and principal component analysis of Raman spectra of $15(Na_2O,K_2O).10(CaO,ZnO).75(ZrO_2,SiO_2)$ glasses

P-47 **G. Keşan** DFT, FT-IR and Raman investigations of 1-pyrrolidino-1-cyclopentene

P-51 **M. Kokošková** Surface-modified luminescence of Ru(II) polypyridine complexes

P-54 **J. Kubová** Inductively coupled plasma optical emission spectrometry used in sorption study of platinum and palladium onto nanometer-sized titanium dioxide

P-62 **I.V. Mazepa** Distribution of manganese in the soil-water-plant in the zone of Burshtyn thermal power station

P-64 **J. Mihalčová** Determination of water content in oil with the application of FTIR spectrometry

P-66 **C. Nadejde** On the spectral behavior of rifampicin molecules in solutions and ferrofluids

P-67 **C. Nadejde** Molecular modeling and spectral investigation on some triphenyltetrazolium chloride derivatives

P-71 **J. Ortyl** Application of 5-phenyl-3-amino-2,4-dicyanobenzoates as spectroscopic probes for monitoring in real time photopolymerization processes

P-72 **J. Ortyl** Developing of fluorescence probes based on acenaphthene for monitoring of photopolymerization processes by fluorescence spectroscopy

P-74 **C. Parlak** Vibrational spectroscopic analysis of some Hofmann type complexes

P-78 **P. Puliš** Comparison of solid-sampling spectrographic and spectrometric method at their utilization for determination of impurity elements in Pd-C catalysts

P-80 **D. Remeteiová** Possibilities of modern spectrometric method (SS-DCA-OES) for the catalysts trace analysis: 2. Optimization of calibration

P-81 **M. Rimár** Reliability of determination of some analytes in oil by RD OES

P-82 **S. Ružičková** Possibilities of direct spectrometric method (SS-DCA-OES) for the catalysts trace analysis: 1. Optimization of evaporation

P-84 **F. Sohbatzadeh** Investigation of microwave plasmoid at atmospheric pressure by optical emission spectroscopy

P-85 **F. Sohbatzadeh** Investigation of additive gases to the argon gas on the plasma jet length in dielectric barrier discharge apparatus

P-91 **E. Terpáková** FTIR method as a guideline to study degradation of composite building materials

P-92 **E. Terpáková** The importance of multidisciplinary analytical approach to solving problems of biocorrosion in civil buildings

P-94 **T. Vogt** Direct determination of boron in silicon-materials by ETV-ICP OES – an easy way?

POSTER SESSION 3

Wednesday, October 10, 2012, 20.00-22.00

Chairpersons: K. Flórián, T. Kántor, E. Plško, B. Strauch

P-03 **M. Anguš** Optical emission spectroscopy of PE and PE HF CVD process of carbon nanotubes growth

P-04 **M. Anguš** Study of hydrogen-argon helical RF discharge

P-09 **E. Bencúrová** Molecular analysis of possible ligands and receptors responsible for interaction between *Francisella* and brain microvascular endothelial cells

P-10 **M. Bhide** Development of simple and rapid elution methods for proteins from various affinity beads for their direct MALDI-TOF downstream application

P-12 **R. Brodzka** Determination of trace elements in quartz filters by LA-ICP-MS technique

P-14 **W. Cegiełkowska** Chemical and biological studies of the distribution and speciation of zinc in *Plantago lanceolata* L.

P-19 **P. Diviš** Application of ICP-MS and chemometrics for determination of the wine origin

P-27 **M. Fišera** Determination and speciation of arsenic compounds in fishes

P-30 **M. Gregušová** New modification of diffusive gradient in thin film technique (DGT) for determination of metals in sediments

P-31 **Z. Grolmusová** Stable isotope ratio mass spectrometry of water samples from Dunaj and Morava rivers in Bratislava, Slovakia

P-37 **M. Horňáčková** Determination of Si/Al molar ratio in microporous zeolites using calibration free laser induced breakdown

P-39 **S. Hušková** Provenance study of archeological raw material using LA-ICP-MS

P-41 **D. Iwahata** New metal tag reagent for highly selective and sensitive analyses of amino acids and dipeptides by LC-ICP-MS

P-43 **B. Janasik** Arsenic speciation in urine by HPLC-ICP-MS technique

P-45 **A. Kaňa** Software solution for post-column isotope dilution HPLC-ICP-MS

P-46 **J. Karasiński** On the use of chromatography followed by mass spectrometry for speciation of zinc in plants

P-50 **M. Kociánová** Elemental analysis of bentonites using CF-LIBS

P-53 **A. Krata** Effect of chemical form of mercury on the quality of results of mercury content in natural water by ICP-QMS

P-55 **E. Kurek** On the use of mass spectrometry for the investigation of biotransformation of selenium towards designing the functional food

P-65 **M. Michalska-Kacymirow** Analytical scenario for the investigation of biotransformations of selenium in plants

P-68 **J. Návesník** oaTOF-ICP-MS analysis of gadolinium in algae, surface and waste water

P-69 **J. Návesník** Multielemental analysis of horse hair by oaTOF-ICP-MS

P-70 **H. Nováková** ICP-MS for analysis of fish scales and otoliths of perch (*Perca fluviatilis*) and bream (*Abramis brama*)

P-75 **I. Petry-Podgórska** Bioanalytical ICP-MS method for quantification of potassium changes in the cells and supernatants after action of CyaA toxin

P-76 **J. Pořízka** Influence of the different farming systems on elemental content of *Vitis vinifera* and on antioxidant properties of wine

P-77 **M. Průšová** Elemental analyses of textile structures by LIBS

P-79 **J. Rakovský** Self-absorption effect used in multi layer plasma modeling for element density determination in LIBS analysis

P-86 **M. Stanisławska** Determination of chromium species in the workplace air using HPLC-ICP-MS technique

P-87 **J. Sysalová** Size-distribution and mobility assessment of Hg and other risk elements in urban particulate matter and amended soils

P-88 **J. Száková** Variability of total and mobile element contents in the ash after biomass combustion

P-89 **A. Šípková** Affinity of selected elements to individual fractions of organic matter

P-93 **J. Tremlová** Arsenic compounds in less common species of vegetable determined with HPLC-ICPMS

50 YEARS OF ATOMIC SPECTROSCOPY ON TU IN KOŠICE, CELEBRATING HIS 60TH ANNIVERSARY: PAST – PRESENCE AND FUTURE PERSPECTIVES

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The lecture should give an overview about activities in atomic spectroscopy on TU in Košice during 50 years. Fundamental studies in this field of instrumental analytical chemistry are described with focus on the use of statistical methods (later chemometrics and information theory) in computerized spetrochemical evaluation. Besides classical methods of powders analysis (today = solid sampling) also solution methods were used and performed, e.g. the use of capillary or rotating disk electrodes. Very important was the international cooperation, first of all with Hungary in evaluation of photographically registered spectra, later with Germany in validation of modernized DC-arc-OES as well as ETV-ICP-OES methods in analysis of advanced ceramics. The interest was focused in last periods on solid sampling analysis of samples with environmental relevancy, there also alternative methods were evaluated and tested. Special attention was paid for problem of analytical calibration process, having their specialities in solid sampling analyses.

Acknowledgement: The research presented in this lecture was since 1990 supported by Slovak Grant Agencies VEGA (projects: 1852/94, 1/4365/97, 1/7418/20, 1/7437/20, 1/7460/20, 1/0214/03, 1/0386/03, 1/3149/06, 1/0461/08, 1/0764/08, 1/0236/11) and APVV (projects: 20-0022-02, 20-0094-04), by more bilateral Hungarian-Slovak and German-Slovak projects as well as by DAAD. The gratitude of authors should be expressed for these supports.

HISTORY OF ESAS AND RELATED MEETINGS: A PERSONAL VIEW

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The major aim of this "honorary" presentation is the complementation of the list of the historical overview provided by the Organizers (very laudably) with photos of the participants. The projection of photos will be intermitted by brief notes about some characteristics of the particular meetings (e.g. new or emphasized topics). It is important to note that the photos were made quite randomly, which means that the selection do not represent necessarily VIP considerations. However, it is intended to present at least one named photo for the regular participants of these meetings. (Sorry for the unsuccessful cases.)

In the list of series 18 meetings are accounted, and these are too many to project pictures for all of them within a reasonable time. Therefore it is decided to start with the "East European Furnace Symposium" (1994) that was a milestone to generate interest of the whole atomic spectrometry community. In the former five "solid sampling GF-AAS" meetings (10 years), the communication was not extensive enough in this respect. Starting from 1994, the number of photos had to be restricted to 4-8 for each meeting, do not exceed the total number of 80, which is probably the highest limit for a presentation in 30-40 min.

In addition to the meetings listed by the Organizers it seemed logical to document with photos also those "internationally participated" national and CSI meetings which had highly populated GF-ETA/ETV sections. Accordingly, the following meetings will be considered: Warsaw (1994), StPetersburg (1996), Debrecen (1997), Prague (1998), Budapest (1998), Podbanske (1998), Bled (1999), Nevsehir (1999), Ankara (1999), Podbanske (2000), Merseburg (2000), Pretoria (2001), Blagoevgrad (2002), Zaragoza (2003), Balatonföldvar (2004).

It is noted that all photos of these 15 meetings were made with the use of photographic films, copied on photographic paper (i.e. made on the classical way), and the photographs were electronically scanned for power point presentation. The direct electronic recording of pictures could be started by the author from 2005, which makes the collection of pictures much easier. Easier and with higher perfection, as it is exemplified by the collection of photos of the ESAS-2010 (Wroclaw) meeting, by Piotr Bienkowski, in the journal Analityka (Poland).

SOME PERSONAL RECOLLECTIONS CONCERNING THE DEVELOPMENT OF SPECTROSCOPY IN SLOVAKIA

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The beginning of spectroscopic investigations in our country started already in the 19th century with the study of astronomical objects by the world known scientist Nicolaus Konkoly Thege who in his astrophysical observatory situated in Stará Ďala (now Hurbanovo, southern Slovakia), measured, identified and described more than 2000 spectra of different bright stars, 23 comets as well as reflexion spectra of Moon rocks compared with the terrestrial ones. He published in german also several books on spectroscopy. These results belonged practically to the first spectroscopic activities of this kind all over the world.

Spectrochemical analysis of industrial, geological and other samples started in our country during the Second world war. The first Slovak spectroscopic publications appeared in 1947 and for the further development of spectroscopy the Czechoslovak Spectroscopic Society was founded in 1949. The results obtained in this scientific field needed their presentation and this occurred in Slovakia for the first time in 1959 during the Spectrographic Congress held in this very Grandhotel Praha in Tatranská Lomnica. The conference was organized by Prof. M. Matherny and it presents the start of till now existing conferences like this one as well as each two years organized Conferences of Analytical Atomic Spectroscopy (CANAS). The Seminar on the spectra excitation organized in 1963 by me in Smolenice presents the first contacts between eastern and western spectroscopists. These contacts have presented scientifically high valuated series of spectroscopic conferences organized in our country.

Our tasks in spectrochemical analysis cannot be valuated separately because they belong to a complex development of the whole science forming an immanent part of culture. My endeavour not to separate different parts of analytical chemistry according to separate methods, analytical signal, instrumentation etc. but to find common features of the whole analytical chemistry has led to extraction of procedures common for all parts of analytical chemistry including also spectrochemical analysis. This progressive approach to spectrochemical analysis forms so a part of a higher complex called by me as "General analytical chemistry" and described in details in my book of this title comprising the following chapters: Adequacy of the method to the requirement, Taking and processing of sample, Measuring of analytical signal, Assignment of a property to the signal value, Valuation of the analytical signal. All the cited items form the basis of all analytical procedures inclusive spectroscopic analysis regardless the method, procedure, instrumentation etc. Their knowledge helps so to a correct and reliable performing of spectroscopic investigations too and vouches the quality of obtained results which will be presented also in the program of this conference.

FROM THE HISTORY OF CZECHOSLOVAK AND JMM SPECTROSCOPIC SOCIETY

Bohuslav Strauch

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On the beginning, formation and development of Czechoslovak Spectroscopic Society and its branches after the 2nd World War and on introducing of special courses and trainings in spectroscopic methods till the present.

DEVELOPMENT OF NEW SAMPLE PRETREATMENT TECHNIQUES BEFORE SPECTROMETRIC DETECTION

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Despite significant advances in analytical chemistry, mainly in the field of instrumental techniques, the sample preparation is yet often considered as the weakest part of the analytical procedure. The liquid – liquid extraction is probably the oldest and most-known preconcentration technique. Since it possess several drawbacks related to the use of large amounts of organic solvents used, its contribution to environment pollution, or harmful effect on the health of laboratory personnel and extra operational costs associated with the elimination of generated waste, there were new separation techniques developed in the second half of the 20th century, for example solid-phase extraction and solid-phase microextraction. However, in the mid-to-late 1990´s, the scientific community has turned back to the liquid – liquid extraction with the aim of its miniaturization, replacement of toxic reagents by non-toxic ones and automation. As a result, novel preconcentration techniques have been developed based on conventional LLE with the difference that only microliter volumes of solvents have been used (single-drop microextraction, hollow-fiber liquid – phase microextraction, dispersive liquid – liquid microextraction), from which the most frequently used and studied is the dispersive liquid – liquid microextraction.

Our research group has been also dealing with this problem and as a result, there have been several novel approaches developed that allow the employment of solvents lighter than water in DLLME [1-6], which will be the subject of the presentation.

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ELECTROCHEMICAL HYDRIDE GENERATION FOR ATOMIC SPECTROSCOPY

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The electrochemical generation of hydrides of some semi-metals and metals seems to be an interesting alternative to the “classical” chemical generation by means of sodium tetrahydroborate reagent. Potential advantages such as the elimination of the unstable and expensive reducing reagent, simpler experimental design and reducing of some interferences are the main driving forces for this research.

A special flow-through cell was designed for the generation of hydrides of arsenic, selenium and antimony. The corresponding hydrides are generated in a porous glassy carbon electrode which ensures high efficiency and sufficient selectivity. The resulting solution is mixed with argon gas and after separation of the gas phase the hydrides are measured in a heated quartz tube by atomic absorption. The analytical figures of merit, possible interferences and their elimination and potential application areas are discussed in the paper.

X-RAY PHOTOELECTRON SPECTROSCOPY AS A TOOL FOR IDENTIFICATION OF FLUORINE ATOMS WITH DIFFERENT BONDING PROPERTIES

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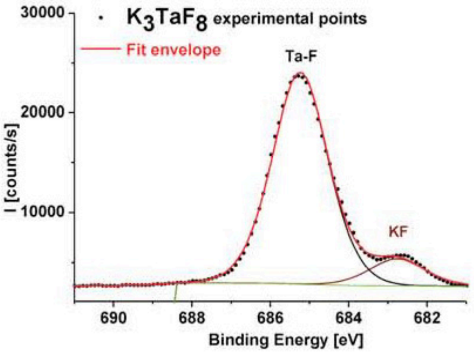
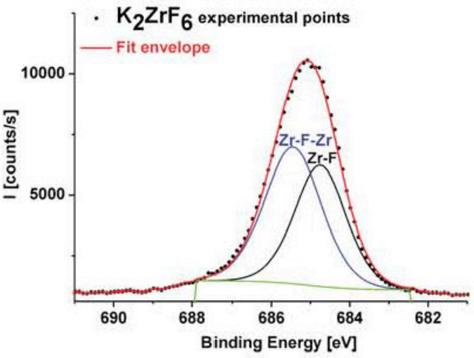
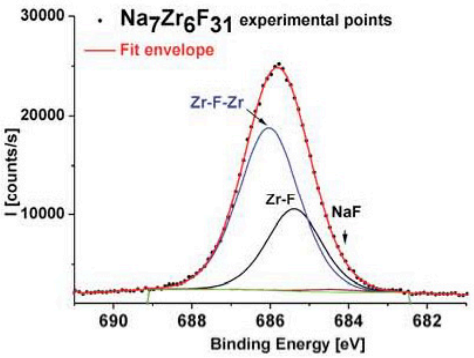
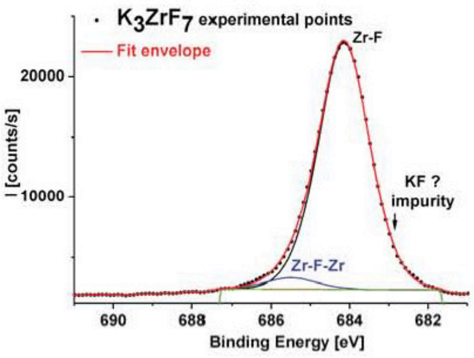
X-ray photoelectron spectroscopy was applied for identification of differently bonded fluorine atoms in series of compounds NaF, K_2TaF_7, K_3TaF_8, K_2ZrF_6, $Na_7Zr_6F_{31}$ and K_3ZrF_7. Three different types of fluorine atoms were described qualitatively and quantitatively. Uncoordinated fluorine atoms (F^-) provide signals at lowest binding energies, followed by signals from terminally coordinated fluorine atoms (M—F) and then bridging fluorine atoms (M—F—M) at highest energy. Based on XPS signals assigned to fluorine atoms in compounds with correctly determined structure it was suggested that fluorine atoms in K_3ZrF_7 have partially bridging character.









ATOMIC AND MASS SPECTROMETRY IN CLINICAL APPLICATIONS

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Besides the commonly used analytical methods for the routine inspection of various parameters of blood and urine performing by clinical laboratories, in the last years a more attention is paid to extend the set of instrumental methods which could be used for supporting clinical investigations. In fact the role of modern analytical techniques in this field cannot be over-estimated as the knowledge on the chemical composition of various human tissues supports those investigations.

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 blood and urine as well as various tissues, e.g. brain, ovary, uterus or liver.

Various data were collected including elemental and molecular composition of the tissues as well as element's distribution over the selected area of the inspected organs. In all cases the samples were obtained from the hospital and all were well labeled in respect of the clinical diagnosis. The control group of selected healthy patients was always investigated in parallel; therefore it was possible to correlate the chemical information with the clinical description of the samples.

In order to investigate the chemical composition selected tissues were digested or were exposed to various extraction media. ICP MS was used for the determination of the elemental composition. In order to evaluate the molecular composition various means of chromatographic separation were used, namely HPLC ICP MS or gel electrophoresis followed by LA ICP MS inspection. The late technique, LA ICP MS also was used for the evaluation of the distribution of critical elements over the selected organs.

TOF-ICP-MS SPECTROMETRY - HISTORICAL OVERVIEW AND LATEST DEVELOPMENTS

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ICP MS instruments are commonly equipped with quadrupole (low resolution, routine systems) or sector field mass analysers (high resolution systems). Quadrupole and scanning sector field mass analysers are working as “mass filter” devices and are not able to analyse simultaneously the different isotopes (m/z) or analyse set of isotopes, which are sampled from plasma in one time. This is main disadvantage when the measurement of precise isotope mass ratio is required or when the fast time dependent signals are generated (ICP MS with Laser Ablation, ETA, FIA or CE). One solution is use of Multicolector ICP MS instrument, but these instruments are very expensive and the number of simultaneously measured isotopes is limited. Other technique is Mattauch-Herzog sector field mass spectrometers with multichannel detector; this technique is really new and the number of references for real samples is very limited. Third available technique is use of Time of Flight mass analyser (TOF). TOF ICP MS instruments are available on the commercial available more than 15 years, but the real penetration in university and routine laboratories is visible only in past 8 years. TOF ICP MS instruments are offering some advantages, which can offer good performance for measurement of transient signals, especially when the measurement of high number of isotopes is required or isotope mass ratio for high number of isotopes is important. Another advantage is ability to measure high number of isotopes from small volume, which is important for forensic analysis, analyse of small biological samples and many other applications.

First part of lecture gives historical overview on the development of Time of Flight ICP MS instruments. The main differences between common TOF instruments for organic analysis and ICP MS TOF instruments are described. The construction details like ion beam formation, orthogonal acceleration or ion blanking technology are discussed.

Second part deals with some latest developments and frequently asked questions regarding TOF ICP MS technology like interferences, sensitivity and real detection limits. The examples based on our eight year experience with TOF ICP MS technology will demonstrate data for real samples such urine, beer, biota, horse hairs and etc.

ELECTROTHERMAL VAPORIZATION PLASMA EMISSION AND MASS SPECTROMETRY

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Electrothermal vaporization (ETV) sample introduction of solutions, slurries and solid samples in inductively coupled plasma-atomic emission spectrometry (ICP-AES) and -mass spectrometry (ICP-MS) has been used successfully in a variety of applications [1] and will now be discussed in view of recent advances and new developments. One of the clear advantages of ETV sample introduction is the possibility of matrix removal during the pyrolysis step, similar to what is normal practice in electrothermal atomic absorption spectrometry (ETAAS). However, the situation is more complex because the transportation of the sample vapor to the plasma is related to the vapor composition and the sensitivity of ETV-ICP-AES and ETV-ICP-MS may change accordingly [2]. Due to the somewhat higher analyte concentrations used in AES, the situation is less critical than in MS. The typical behavior of ETV pyrolysis curves will be discussed. In addition to being a useful sample introduction technique for solid and slurry samples, ETV has proven to be a nice tool for the introduction of small sample volumes in the plasma, e.g. for application in single-drop micro-extraction methods [3]. The processing of short transient signals in multi-element analysis using an ICP-AES instrument with CCD detection system in Paschen-Runge mount has recently been described and the applicability of the approach will be demonstrated [4].

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PROGRESS IN TRACE ELEMENTAL AND SPECIATION ANALYSIS BASED ON VOLATILE SPECIES GENERATION WITH ATOMIC ABSORPTION/FLUORESCENCE DETECTION

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Detection power of atomic spectrometry detectors can be substantially improved employing generation of volatile species (VSG) of elements since separation from the sample matrix and high efficiency analyte transfer from sample to spectrometer are involved. In addition, it makes analyte preconcentration easy. All these factors result in a superior sensitivity. VSG is therefore ideally suited for trace and ultratrace elemental/speciation analysis.

This presentation will briefly overview the recent developments and perspectives of individual approaches to trace and ultratrace elemental/speciation analysis based on atomic absorption (AAS) and atomic fluorescence (AFS) detection coupled to VSG. It will be shown that the combination of VSG with AAS or AFS can bring substantial benefits for elemental as well as speciation analysis of those elements that can be converted to analytically useful volatile species. VSG with AAS or AFS can thus substitute or even surpass conventional approaches to elemental and speciation analysis based on the liquid phase sampling inductively coupled plasma mass spectrometry which generally serves as a trademark of unparalleled sensitivity.

The applicability of the combination of VSG with AAS or AFS will be illustrated on our recent results:

- hydride trapping in quartz tube atomizers for AAS for ultratrace elemental determination of hydride forming elements, namely in the presence of very high concentrations of other hydride forming elements;
- generation of substituted arsines followed by cryogenic trapping and atomization in the multiatomizer for AAS for speciation analysis of As in extremely difficult matrixes and in liver homogenate slurry;
- generation of substituted arsines followed by cryogenic trapping and atomization in the flame-in-gas-shield atomizer for AFS for ultratrace analysis of toxicologically important As species.

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DIRECT SOLID SAMPLING ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY – WHY AND HOW ? – A PERSONAL VIEW

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

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

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NEW CAPABILITIES IN LASER ABLATION-ICP-MASS SPECTROMETRY

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Laser ablation-inductively coupled plasma mass spectrometry has been successfully applied to a wide variety of solid samples for major, minor, trace element analysis or isotope ratio determinations. Beside remaining limitations it has been shown that the precision and accuracy in direct solid analyses improved continuously over the last decade. This has mainly to do with progress in laser technology and the fact that sampling, aerosol transport and excitation processes have been studied in great detail, leading to improved quantification strategies.

The most recent trend in LA-ICP-MS is focused on quantitative, high spatial resolution elemental mapping, which is required to reconstruct the trace element distribution in tissues, in stalagmites or in alloys and steel samples, meteorites and many others. Therefore, low dispersion and sample-geometry independent ablation cells have been developed, which allow monitoring minimum changes in trace element concentrations. Some most recent ablation cell geometries will be discussed and their features on selected applications will be shown. A recently introduced atmospheric sampling system, currently in the third generation, allowing the analysis of samples without an airtight ablation cell will be explained and some promising applications will be discussed in detail [1].

Besides a lot of improvements, the lack of reference materials requires the use of non-matrix matched calibration materials for quantification. However, this quantification approach is not generally applicable and the results differ in accuracy. Therefore, laser-generated aerosols and single particles were introduced into the ICP and studied by using optical emission spectroscopy, particle imaging velocimetry and laser light scattering. These studies will demonstrate that the onset of particle vaporization is one of the most crucial parameters for accurate and precise quantification in LA-ICP-MS.

Furthermore, various strategies for producing well defined and matrix matched calibration materials were investigated. Especially the production of precious metals containing samples was tested. Preliminary results, including homogeneity studies on the newly synthesized materials will be discussed.

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COMPREHENSIVE LIPIDOMIC CHARACTERIZATION OF BIOLOGICAL SAMPLES USING LC-MS

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Lipidomics is used in clinical studies to improve the understanding how lipids function in biological systems and for the elucidation of the mechanism of lipid-related diseases including cardiovascular diseases, cancer or other serious human diseases. We have developed a comprehensive lipidomic approach based on a combination of several well optimized analytical methods. Total lipid extracts are fractionated using hydrophilic interaction liquid chromatography (HILIC) in the first dimension, which enables the isolation of more than twenty individual lipid classes, such as different classes of phospholipids, glycerolipids, sphingolipids, sterols, fatty acids, etc [1]. Fractions of lipid classes are then analyzed by (U)HPLC/MS methods developed for both polar [1] and non-polar lipids [2] in the off-line 2D-LC/MS mode. Phospholipids and sphingolipids are separated in reversed-phase UHPLC systems with sub-2 μm or core-shell particles. Silver-ion HPLC is useful for the separation of non-polar lipid species differing in the double bond number, geometry and regioisomerism [3,4]. The chiral HPLC/MS is applied for triacylglycerol enantiomers together with new synthetic procedure for their synthesis. The novel method on the non-targeted quantitation of multiple lipid classes in parallel will be presented based on HILIC-HPLC/MS and the response factors calculated for individual lipid classes. The potential of our detailed lipidomic characterization will be illustrated in the search for lipid biomarkers in plasma (HDL, LDL and VLDL), erythrocytes or tissue of patients with cardiovascular diseases and cancer.

Acknowledgement: This work was supported by the project No. 203/09/0139 sponsored by the Czech Science Foundation.

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RESONANCES OF INFRARED LOCAL FIELDS AND NEGATIVE-REFRACTION IN ANISOTROPIC METAMATERIALS

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The infrared optical response functions can vary very strongly due to the varying weight of the polarizability caused by free charge carriers, polar vibrations and interband electronic transitions. Using suitable combinations of the optical response and geometrical form of flat or curved interfaces can lead to a strong enhancement of local fields, related to sharp spectral resonances. The resonances are strongly polarization-dependent, and can occur at single interfaces or in (nanostructured) metamaterials. We present a classification of the resonant phenomena in inhomogeneous systems and examine their manifestation in infrared ellipsometry. We report mid-infrared ellipsometric spectra of a doped semiconductor metamaterial, exhibiting negative refraction. The resonance is responsible for a strong anisotropy and the interesting behavior of refracted light is found to lead to characteristic features in the ellipsometric spectra, most notably in the relative phase shift between the p- and s-polarized waves.

LASER-ASSISTED PLASMA SPECTROMETRY TECHNIQUES - DEVELOPMENT AND APPLICATIONS

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Techniques of laser-assisted plasma spectrometry (LAPS) are convenient for direct analysis of solids where either spatially resolved information is required or solution analysis is troublesome due to complex and/or incomplete sample dissolution. Elemental mapping and local microanalysis may provide important information on technological materials, biological tissues, geological materials such as individual mineral grains in rocks, archaeological findings and objects of cultural heritage including authentication and provenance determination.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) represents significant analytical tool for such analyses and is frequently combined with physical methods of surface analysis and complementary methods for molecular imaging. Laser-induced breakdown spectroscopy (LIBS) represents less expensive alternative for elemental mapping. Double pulse (DP) LIBS brings improved detection limits for some elements in comparison to the single pulse LIBS.

Development of LAPS as well as its applications is presented. Simultaneous DP-LIBS and LA-ICP-OES system was designed to study the influence of DP conditions on the LIBS properties and aerosol generation. Laser ablation-LIBS (LA-LIBS) instrumentation arrangement was designed and tested.

Elemental mapping of uroliths was studied by LA-ICP-MS including calibration which was confirmed by electron microscopy and EPXMA. Simultaneous measurement of urolith pellets with LIBS and LA-ICP-OES has been accomplished using original instrumental setup, and (LA-LIBS) has been used, too. LA-ICP-MS quantitative 2D-mapping for the description of compositional changes on nickel-based alloys throughout the depth of the corrosion-affected layer formed by the action of the molten mixture of LiF and NaF at high temperature has been developed. Obsidian artifacts and raw materials from various sites have been studied by means of LA-ICP-MS and analytical data have been processed using multivariate statistics for classification of provenance. A host rock for radioactive waste repositories has been examined by LA-ICP-MS from the viewpoint of penetration of isotopes into the environment. LA-ICP-MS elemental mapping tumour tissue as well as some other examples of mapping is presented. Obsidian artefacts provenance has been studied using LA-ICP-MS and advanced statistical methods.

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LASER ABLATION ICP-MS: INTERPRETING THE EFFECTS OF INCREASING CARRIER GAS FLOW RATE

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The LA-ICP-OES/MS methods utilize the sample introduction technique based on the generation of an aerosol from sample surface by a laser beam and its streaming into the spectroscopic source. The influences of operating parameters (wavelength, pulse-time, energy density, atmosphere, carrier gas flow rate, etc.) on the analytical signals are important in optimization, and further on, the exploration of the physical background of these effects is the key to methodical and instrumental developments.

The effects of several operating parameters on ICP-MS signals of eight elements in fused silica were studied in [1], the influence of carrier gas flow rate is of present interest. The general observation was that the signals changed according to maximum curves in the range of 0.4-1.4 l/min Ar. By surpassing the signal maxima (at 1.1-1.3 l/min Ar), a sharp decrease of ionization efficiency was implicated. The broad enhancement period of signals was explained with decreasing ICP gas-temperature which resulted in reduced radial diffusion of sample vapor and following signal increments.

In this laboratory [2], optimization of carrier gas flow rate (Ar) was made to a closed ablation cell (commercial UP-213 system) applying two kinds of flow conditions: (1) variation of total carrier gas flow rate and (2) variation of the carrier gas flow rate in the ablation cell alone, while keeping the total carrier gas flow rate constant (in the transport tube and in the ICP). The surprising observation was that the signals of brass components (Cu, Zn, Ni) increased very similarly with the two kinds of flow conditions in the 0.4-1.3 l/min Ar range. The important conclusion follows that the increase of MS signals was due primarily to changes of aerosol formation in the ablation cell.

The classical theory of aerosol formation (Kelvin or Gibbs-Thomson equation) is accounted for explaining the literature data of particle size distributions, supposing also the importance of "vapor condensation on foreign particles" (e.g., Zn vapor on more stable Cu nuclei). To explain signal enhancements it is supposed that intensification of the cooling of sample vapor is attained at higher flow rates, resulting in more effective nucleation and condensation on stable particles.

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PERFORMANCE COMPARISON OF POTENTIAL ROUTINE SOLID SAMPLING METHODS FOR BULK ANALYSIS OF HIGH AND ULTRAHIGH PURITY MATERIALS

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For analysis of high and ultrahigh purity materials, analytical methods providing LODs between 0.1 µg/g (5N) and 10 pg/g (9N) are needed. The applicability of all methods involving digestion is seriously limited and is decreasing with increasing material purity grade. Therefore, ultratrace analysis of solids has become a growing domain of direct solid sampling methods. The potentials and limitations of the most important methods are discussed and compared from the viewpoint of their application to routine analysis.

For ultratrace analysis of conductive materials, glow discharge mass spectrometry (GDMS) is by far the most powerful one of all currently available methods. It provides an exeptionally simple and highly universal calibration method using the main elements as internal standards, the highest simultaneity, matrix universality, and LODs at sub-ng/g levels. Several sample preparation/introduction techniques have been developed enabling to achieve reasonable performance of GDMS also for non-conductive materials. Pressing the sample onto a high purity indium sheet, its addition to high purity gallium and its introduction into a cavity of a tantalum supporting electrode have proved to be the most important sample preparation techniques.

During the last about 15 years, direct solid sampling graphite furnace atomic absorption spectrometry (SoS-GF AAS) and solid sampling electrothermal vaporization inductively coupled plasma optical emission or mass spectrometry (SoS-ETV-ICP-OES/MS) have been established as routine techniqes for material analysis on the ultratrace level. Matrix specific methods have been developed for a large number of materials. Good accuracies have been obtained by using calibration curves measured with aqueous standard solutions in the determination of almost all analytes in various materials. For most analytes, SoS-GF AAS provides the lowest LODs of all current methods - down to the lower 10 pg/g range, whereas the LODs of the SoS-ETV-ICP-OES are roughly two orders of magnitude higher. Therefore, despite its pronounced monoelement character, SoS-GF AAS is to be considered an important supplementary solid sampling technique or, in special cases, the technique of choice. The SoS-ETV-ICP-OES/MS methods are interesting for multielement ultratrace analysis at narrow sample diversity. Sometimes occurring problems with spectral interferences or incomplete release of the analytes from the matrix can for the most part be avoided by using an adequate modification.

Results on precision, accuracy and LODs obtained for five different high purity materials by these three techniques as well as their feasibility for routine analysis will be discussed and compared.

RESIDUAL DIPOLAR COUPLINGS CONSTANTS IN NMR

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Interactions of NMR active spins exhibit a profound anisotropy with respect to the orientation of the external magnetic field. In standard liquid samples this anisotropy is effectively removed by an intensive isotropic thermal movement of dissolved molecules. As a consequence, relatively simple high resolution spectra are obtained in isotropic solutions. The penalty paid for this simplicity is a partial lost of important structural information.

It is well known, that a part of lost information can be retrieved back if a sample is dissolved/merged in an orienting medium. Besides the other effects, this is associated with the reappearance of dipolar couplings that are bearing very valuable structural information.

Reappeared dipolar coupling interactions (referred to as Residual Dipolar Couplings, RDC) are scaled down according the degree orientation, from full value in fixed orientation to zero in isotropic solution. In order to obtain tractable spectra, it is important be able to control the degree of molecular orientation and keep it relatively small (~ 0.1%) to keep RDC in range of Hz or tens of Hz.

Suitable weakly oriented media became available a decade ago. Initially they were applied to the structure refinement of biological macromolecules in aqueous solution. Numbers of aqueous suitable weakly orienting media were soon developed. [1-3]. Later weakly orienting media suitable for organic solvents were developed also [4]. The most universal approached is based on the use of stretched polymer gels, in which the alignment of molecules can be to certain degree controlled by mechanical stress applied to the polymer gel [5].

RDC's contain a new type of structural information accessible from liquid state spectra. It is a kind of the "long-range" information that allows comparison of configuration of distant part of molecules.

In the lecture, basic aspects of exploitation of RDC in NMR structural analysis will be illustrated on practical examples.

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GLASS STRUCTURE STUDY BY RAMAN SPECTROSCOPY COMBINED WITH THERMODYNAMIC MODELING

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The method of analysis of glass Raman spectra based on the thermodynamic modeling is presented. First the number of linearly independent spectral active components is obtained by Principal Component Analysis (PCA) of baseline subtracted Raman spectra. Then the thermodynamic model of Shakhmatkin and Vedishcheva is constructed. Within this model, the studied glass is considered as an ideal solution of system components defined by the stoichiometry of stale crystalline phases of particular system. The correlation analysis of equilibrium molar amounts of individual components is performed to identify the independent spectral active components in accord with the result of PCA analysis. Finally the least squares decomposition of experimental spectra on the partial Raman spectra (PRS) is performed using the equilibrium molar amounts of linearly independent components. The physical meaning of individual PRS is deduced from the correlations between equilibrium molar amounts of individual components. The proposed method was applied on the As_{20}-Sb_{20}-$S_{(60-x)}$-Se_x glasses.

THE INFLUENCE OF TEMPERATURE ON SURFACE-ENHANCED VIBRATIONAL SPECTRA: HOW SIGNIFICANTLY DOES IT AFFECT SPECTRAL DATA OBTAINED?

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Surface-enhanced Raman scattering (SERS) and surface-enhanced infrared absorption (SEIRA) are fundamentals of surface-enhanced vibrational spectroscopy (SEVS) [1]. Both SERS and SEIRA spectra are measured typically under ambient laboratory conditions. An initial study of temperature effect on SERS spectra of pyridine demonstrated no significant change in the band intensities on copper and gold substrates, while in the case of the Ag substrate an initial growth of the 1006-cm^{-1} band on warming with a final dramatic decrease of SERS intensities at laboratory temperature was referred [2]. Published results of several studies are still controversial; sometimes, a significant increase of enhancement at elevated temperatures (50°C [3]) is reported while other studies demonstrate (e.g. [4]) a dramatic enhancement of spectral signal caused by the decrease of temperature. Thus, we decide to develop temperature-controlled sample holders both for SERS and SEIRA spectroscopy and to perform systematic spectroscopic/chemometric studies of the influence of substrate temperature on the SEVS spectra obtained on three coinage metals, i.e. Ag, Au and Cu. We have designed tailored temperature-controlled holders of SEVS-active samples to record large arranged spectral sets suitable for evaluation by chemometric methods. (Bio)-organic analytes (e.g. vitamins [5]) and mixtures extracted from plant leaves have been deposited on electrochemically prepared Ag, Au and Cu surfaces. The SEVS spectral datasets in the range 5 – 50 °C exhibit evident relationships to temperature variations. A tuning of temperature can improve the detection limit and/or data repeatability.

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MÖSSBAUER SPECTROMETRY OF IRON IN BIOLOGICAL TISSUES

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Iron is an essential element for biological cells. It exists in living organs in a form of ferritin – an ubiquitous intracellular protein. The function of ferritin is to store iron in a non-toxic form, to deposit it in a safe form, and to transport it to areas where it is required. Possible malfunctions may seriously affect the living conditions of the cells. While low ferritin content enhances the risk of anemia, its high concentration produces excess iron. Here, we present the results of our study which is aimed in identification of iron and its deposits in selected biological tissues. We concentrate on specification of structural positions and forms of iron using mainly Mössbauer spectrometry which is a powerful tool for identification of iron ions. Its huge diagnostic potential enables to describe individual positions of the resonant atoms by the help of their hyperfine interactions. Thus, both chemical states as well as structural positions can be described. Results from Mössbauer spectrometry obtained from the investigations of human and horse spleens, and from human brains are complemented by SQUID magnetometry experiments.

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KINETIC STUDIES ON THE FORMATION OF SERS-ACTIVE SYSTEMS

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Surface-enhanced Raman spectroscopy (SERS) takes advantage of an immense signal enhancement of generally weak Raman scattering, provided that the analyte molecules are located in a close proximity of metal nanostructures, constituting so called SERS-active system. The SERS effect amplifies Raman scattering of all molecules adsorbed on the metal surface, nevertheless the most important contribution comes from those trapped in "hot-spots", i.e. junctions or gaps between closely spaced and confined metallic nanostructures. In the case of colloids, the most frequently employed SERS substrates, constitution of the SERS-active system and formation of the hot-spots comprise physisorption or chemisorption of the analyte to the surface of the nanoparticles (NPs) and their aggregation mediated by the analyte itself or by an aggregating agent, respectively. Both processes may have important consequences for structural and spectral properties of the analyte and often affect its photophysics and photochemistry. Reorientation of the analyte at the surface and changes of electromagnetic field in dynamically evolving hot-spots cause temporal alterations in the SERS spectra which complicate their analysis and proper interpretation. Even though SERS activity is dynamic by its nature, a common practice is to deal with static SERS spectra of fully evolved systems, ignoring informational richness hidden in their temporal evolution.

The aim of the present contribution is to shed light on the dynamics of the SERS activity and to provide better insight into the hot-spots formation. Using several analytes differing in their spectral properties and abilities to form SERS-active systems, temporal evolution of their SERS spectra after sudden addition into the colloid will be analyzed by advanced multivariate statistical methods. Interesting effects of tight aggregation and hot-spot formation controlled by addition of chlorides will be demonstrated by decomposing temporal spectral series taken with acquisition times easily accessible to common CCD detectors. We would like to demonstrate that distinct spectral forms can be revealed in the evolving SERS systems by relatively simple tools, provided that short-exposure temporal series are taken instead of information-leveling long-exposure acquisitions. Besides the kinetic measurements in the large-scale samples, formation of the hot-spot at microscopic level will be demonstrated by using Raman microspectroscopy and microfluidic devices. Effect of the hot-spot formation to the SERS enhancement, spectral features of the analyte and signal stability, as well as morphology of the active sites speculated from the time-evolution of the analyte spectra will be presented and discussed.

USING CORONA DISCHARGE ION MOBILITY-MASS SPECTROMETRY FOR MONITORING OF VOLATILE ORGANIC COMPOUNDS

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The capability of corona discharge (CD) ionization source for monoaromatic volatile organics compounds (VOC) monitoring by ion mobility spectrometry interfaced to Time of Flight mass spectrometry (IMS-TOFMS) will be presented in this work [1]. The two-dimensional (2D) IMS-TOF spectra of VOC was recorded in nearly real time as the time required for analysis was less then 5 minutes [1].

Among the other factors the separation in IMS depends on the mass of the ions and their geometry [2]. Thus the IMS allows separation of the isometric ions. The implementation of CD ionization source to IMS-TOFMS technique allowing generation of neutral NO what results in higher NO^+ yield. The generation of NO^+ is important for monoaromatic VOC monitoring like the benzene, toluene and m-xylene (BTX) are. The two dimensional map of BTX molecular and NO^+ adducts ions measured in zero air is depicted on figure 1. [1]. The sensitivity of IMS for 20% NO^+ adduct ions of BTX compounds is 1.5, 1.4 and 2.6 ppb respectively while for molecular ions was up to 20 times higher (37, 41 and 72 ppb). The possibility of CD to generate up to 50% of NO^+ will be for the first time presented.

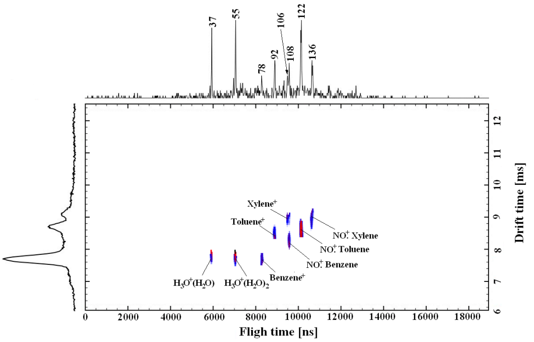

Figure 1. 2D map of BTX molecular and NO^+ adducts ions measured in zero air.

An important feature of the IMS-TOF instruments is the ability to record 2D IMS-MS spectra. In the 2D spectra, for particular classes of the chemicals, correlations in mobility-mass spectra exist, also called trend lines. In order to improve selectivity, sensitivity and acquisition time the application of dopant gas for IMS-TOFMS will be also demonstrated.

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SPECTROSCOPIC IMAGING OF BIOLOGICAL SAMPLES

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Various techniques are established for chemical characterization of biological samples, several other methods based on new technology are under development [1]. Well-established instrumental techniques like magnetic resonance imaging (MRI), X-ray tomography, or mass spectrometric imaging (MSI), are capable of identification and localization of minute details within biological samples. As the existing technologies are exploited to their limits, new instrumental approaches are required. Vibrational spectroscopy techniques (both Raman and infrared) complement the standard methods for biomedical diagnostics [2].

Both infrared and Raman spectroscopy can provide a biochemically based profile of tissue in real time and without requiring additional contrast agents [3]. Potential and limitations of infrared and Raman spectroscopic imaging shall be compared to other imaging techniques for biological samples. Marker-free techniques are particularly considered, because they avoid any perturbation of the sample under investigation. Promising approaches include Raman fiber techniques and non-linear Raman methods. Raman fiber techniques can easily be combined with commercial endoscopes. Of the non-linear Raman methods, Coherent Anti-Stokes Raman Scattering (CARS) attracts the greatest research interest. Infrared spectroscopy is already being used in the operating theater to examine freshly resected tissue while the surgery is going on.

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ACADEMIC VERSUS INDUSTRIAL RESEARCH AND DEVELOPMENT: A VIEW ON TODAY´S ENHANCEMENTS IN OPTICAL ATOMIC SPECTROSCOPY

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Optical Atomic Spectroscopy Techniques are assumed to be mature since more than a decade. The new developments, such as Continuum Source AAS, multi-element-graphite furnace AAS or transverse heated atomizers in Atomic Absorption, high resolution, fast access to line intensities of the complete spectrum, economic operation of the plasma source, and mathematical models for spectra correction in ICP-OES have all been published 2 decades ago. A part of the research of the heyday years has found broad commercial application, some of the ideas have disappeared from routine use again, a couple of brilliant concepts have almost been forgotten. Today, compared with more modern fields of research in analytical chemistry, predominantly in life science, molecular spectroscopy and separation techniques, the number of publications in optical elemental spectroscopy is in minority.

Specific applications, such as e.g. direct analysis of elemental ultra- traces in solids, determinations with a minimum of chemical agents, improvements in sample introduction and ionization, speciation, the determination of anions, subtle ways of calibration and chemometric methods are pursued in academia. Industrial R&D is investing predominantly into the improvement of existing concepts by making use of modern construction material, novel optical components, detector technology, power and micro- electronics and micro fluidics. This has resulted in important steps forward in analytical performance of instruments, ruggedness, laboratory space requirement and economical use of consumables and supplies.

In this contribution the state of the art in optical spectroscopy including accessories will be discussed with the help of a few examples from the fields of AAS/ AFS and ICP-OES. The examples demonstrate that there is still plenty of room for academic research and industrial engineering to improve the existing equipment and techniques.

PRESENT STATE OF MÖSSBAUER SPECTROSCOPY APPLICATIONS

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Mössbauer spectroscopy was established as an analytical method fifty years ago and still is of current interest. Areas of research where Mössbauer spectroscopy is contribution are metals and alloys, magnetic materials, chemical compound, oxidation states, nanoparticles, mineralogy, archeology and biological materials. Synchrotron radiation is special kind of application .

At present Mössbauer spectroscopy is used by analysis of environmental materials as zeolites, volcanic tephra and compounds containing Fe [6]. Nanocrystalline materials as FINEMET, NANOPERM and HITPERM are analysed under different external influence of neutron irradiation or external strong and weak magnetic field.

Potassium white micas in sheared basement and cover rocks from the Central Western Carpathians were investigated. Chemical and spectroscopic characteristics were specified, which allow distinction between celadonite-poor (muscovitic) and celadonite-rich (phengitic) white mica formed during a polystage evolution. Phase analysis of Kosice meteorite confirmed that it belongs to chondride H. Magnetic and non-magnetic parts were analysed in details.

Analytical potential of Mössbauer spectroscopy is still large, but is limited with demand that samples must contain iron. Up to now most of works were done with iron isotop because other isotop application is experimentally complicated.

COOPERATION BETWEEN PLASMONIC NANOPARTICLES GENERATION BY LASER ABLATION AND SERS SPECTROSCOPY

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Ag and Au nanoparticles (NPs) and their assemblies are one of the most frequently employed substrates for SERS (surface-enhanced Raman scattering) spectroscopy. Very early after the first ablation experiments, SERS spectroscopists recognized plasmonic nanoparticles prepared by laser ablation of a plasmonic metal target in ultrapure water as unique SERS substrates with chemically pure surfaces [1]. Chemical purity of the surfaces has offered the possibilities of a purposeful functionalization of the plasmonic NPs by the target adsorbates [2] as well as by molecular spacers [3] which attract target molecules towards the NP surface, and simultaneously, prevent their denaturation by a direct interaction with the metal NP surface. On the other hand, generation of a SERS active AgNP/adsorbate system by laser ablation of Ag in an adsorbate solution [4] opened new research possibilities for SERS spectroscopy in terms of controlling the outcome of an in-situ functionalization of plasmonic nanoparticles by various chemical species in the course of laser ablation. Recently, a new exciting possibility to employ SERS spectroscopy for probing of not only the outcome, but also the progress of the intermittent laser ablation of Ag in aqueous solutions of specifically selected adsorbates has been demonstrated [5]. The selected adsorbates act as SERS probes of adsorption sites (neutral or cationic) available on Ag NP surfaces and/or of the factors affecting the adsorbate stability. The wavelengths of laser pulses employed for ablation as well as the type of Ag NP surface-adsorbate bonding emerge as the most important factors affecting the adsorbate stability during laser ablation.

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AEROSOL STUDIES IN URBAN ENVIRONMENT

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The mass concentration and the chemical composition of airborne particulates have a decisive influence on the air quality of cities and the health of their habitants. From 1 January 2010 a target value (25 μg/m^3) was introduced for the mass concentration of PM2.5 fraction in the member countries of the European Community. Presently, there is not target value for selected chemical compounds in this aerosol fraction, therefore the knowledge of its chemical composition and the toxicity of different compounds is necessary to establish a target or limit value for the most dangerous chemical elements and compounds.

The PM2.5 fractions of urban aerosols were collected in the city center of Budapest (Széna square) and the city border (Pestlőrinc) applying high-volume samplers and quartz fiber filters. The sampling site in the city center had high traffic density (approximately 80000 cars/day), while the other sampling site was practically a rural area. Samples were collected monthly for 96 hours on 4 consecutive workdays from June 2010 to May 2012. During the 96 hours sampling period 2880 m^3 air was transported through the filter.

The analytical work included i) gravimetric determination of PM2.5 mass concentration; ii) trace element determination (Bi, Cd, Co, Cr, Cu, Fe, Ga, Li, Mn, Mo, Ni, Pb, Pt, Rb, Sb, Sn, Te, Tl, U, V, Zn) after microwave–assisted *aqua regia* and sonication–assisted water extraction by inductively coupled plasma sector field mass spectrometry; iii) evaluation of major anions (SO_4^{2-}, NO_3^-, Cl^-) as well as NH_4^+ concentrations in the aerosol samples subjected to sonication–assisted water extraction by ion chromatography and spectrophotometry, respectively; iv) assessment of total, water–soluble and elemental carbon by a C/N analyzer in the samples.

On basis of our investigations the following conclusions can be drawn:

- The average mass concentration of PM2.5 fractions remained below the target value set by the European Commission.
- The total carbon content amounted to about 40%.
- The water soluble parts of carbonaceous compounds were about 25%. Due to photochemical reactions the solubility was higher in summer time.
- Among the traffic related elements Fe > Zn > Pb were present in the highest concentrations and Pb had a homogeneous distribution in the city.
- Cd and Pb had a seasonal change. (About 3 times higher concentrations during the winter time compared to summer.)

Seasonal changes were observed for NO_3^-/PM2.5, SO_4^{2-}/PM2.5, as well as for WSC/TC mass concentration ratios. During the winter, NO_3^-/PM2.5 had a maximum, while the SO_4^{2-}/PM2.5 and the WSC/TC ratios had minimum values.

DETERMINATION OF SOME INORGANIC METALS IN OLIVE AND VEGETABLE OILS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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Heavy metal pollution is a consequence of activities such as chemical manufacturing, painting and coating, mining, extractive metallurgy and the nuclear industry. This study using flame atomic absorption spectrophotometry was performed on some samples of edible oils available in the market of Misurata city, including olive oil, corn oil and sunflower oil, to determine the concentration levels of some heavy metals (lead, copper, zinc, manganese and iron) and to compare these concentrations with the permissible limits. The results indicate that the levels of heavy metals in local edible oils collected were found to be higher than the permissible maximum value.

TRACE ELEMENT LEVEL IN WHOLE AND PROTEIN SEPARATED BLOOD SERUM OF PATIENTS WITH SYSTEMIC LUPUS ERYTHEMATOSUS AND SYÖGREN SYNDROME

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The elemental concentration of human blood is often used for building up diagnosis in the clinical practice. However, only a few studies are in the literature concerning the trace element and protein level of blood serum in case of autoimmune diseases and no information is available about the quantity of these essential trace elements binded to the main transport proteins [1], [2]. Therefore the aim of recent study was to determine the concentration of K, Ca, Mg, Zn, Cu, Fe and Mn in whole blood serum and to further investigate the quantitative distribution of these elements between Immunoglobulin G and three other high abundant protein fractions in blood serum of patients with Systemic lupus erythematosus (SLE) and Sjögren syndrome (SS).

Anion exchange chromatography was used to separate blood serum samples into protein fractions and high abundant protein components were identified by UV-VIS spectrophotometry. Both whole blood serum samples and diluted protein fractions were digested by a microwave assisted system prior to analysis. K, Ca, Mg and Zn concentration of samples were determined by flame atomic absorption spectrometry (FAAS) while Zn, Cu and Fe concentration were measured by graphite furnace atomic absorption spectrometry (GFAAS). Statistical analysis was carried out to evaluate the results. The distribution of trace elements among the gained protein fractions are calculated in percentage.

There were no significant difference ($p>0.05$) in Mg and Fe concentration between the control, SS and SLE groups. Significantly lower concentration ($p<0.05$) of K and Ca was measured in SS and SLE groups compared to the control. The concentration of Zn was found to be significantly decreased ($p<0.001$) in SS and SLE groups than in the control, while the concentration of Cu significantly increased ($p<0.001$) in both groups.

Alterations were also observed in the quantitative distribution of elements among protein fractions containing Immunoglobulin G, Transferrin, Albumin and Ceruloplasmin of SS and SLE groups compared to the control. In control group the highest Cu concentration was determined in the protein fraction containing Cer (62.1% of total), while in SS and SLE groups in the fraction containing Alb (SS: 37,7%; SLE: 36,7%). The concentration of Zn decreased in the Alb containing fraction (SS: 18,3%; SLE: 24,6%) and increased significantly in the IgG (SS: 33,9%; SLE:27,4%) and Cer containing protein fractions (SS: 29,5%; SLE: 35,8%) compared to the control.

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ANTIBACTERIAL PEPTIDES FROM EUSOCIAL BEE *Halictus sexcinctus* INTERACTING WITH MODEL MEMBRANES

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There are many already known antimicrobial peptides (AMPs) with considerable therapeutic potential but their exact mechanism of action still remains a matter of controversy. AMPs interact with cytoplasmatic membrane and their amphiphatic structure plays an important role in this process. Simple models of membrane penetration involve formation of pores or dissolving membrane in a detergent-like manner. These processes lead to breakdown of the transmembrane potential causing leakage of cell content and finally the cell death. The mechanism of antibacterial action probably includes recognition and specific interaction with bacterial cell membranes inducing lipid clustering or lipid phase separation.

Halictine-1 (Hal-1) a linear antibacterial dodecapeptide isolated from the venom of the eusocial bee *Halictus sexcinctus* – has been subjected to a detailed spectroscopic study including circular dichroism, fluorescence and vibrational spectroscopy. We investigated Hal-1's ability to adopt an amphiphatic α-helical structure upon interaction with model lipid based bacterial membranes (phosphatidylcholine/phosphatidyl- glycerol based large and small unilamellar vesicles, sodium dodecylsulfate micelles) and/or helix inducing components (trifluoroethanol). It was found that Hal-1 responds sensitively to composition of the membrane model and to peptide/lipid ratio. Amphipathic nature of the helical Hal-1 seems to favour flat charged surfaces of the model lipid particles over the non-directional interaction with trifluoroethanol. Increasing fraction of polyproline II type conformation was detected at low peptide/lipid ratios.

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iCAP-Q - NEW DIMENSION IN ICP/MS SPECTROMETRY

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With an all-new, user-inspired design, advanced engineering and ground-breaking technology, the iCAP™ Q is an evolutionary jump in ICP-MS. The iCAP Q is simple to use, easier to maintain, and delivers more performance than any other system — giving you total confidence in your results, whether you perform routine analyses or state-of-the-art research.

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ADVANCED CHEMOMETRIC MODELS FOR EVALUATION OF SERS SPECTROSCOPIC DATA DESCRIBING THE INFLUENCES OF THE METAL AND EXCITATION WAVELENGTH

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Surface-enhanced Raman scattering (SERS) is an optical phenomenon used for detection and identification of trace amounts of analytes situated in the vicinity of a nanostructured surface of proper substrate. Suitable SERS-active substrates possess enhancements of several order of magnitude of acquired Raman signal. The band intensities of analytes can be affected by a huge number of more or less controllable factors. Chemometric models can be developed to clarify the role of various factors. The crucial factors examined in this study are the metal substrate (silver, gold and copper) and the excitation wavelength (1064, 785, 633 and 488 nm). Each substrate with deposited analyte was examined repeatedly with the use of above-mentioned series of excitation wavelengths to obtain data matrix of sufficient size.

To ensure data compatibility, all the large-scale SERS-active substrates were prepared by similar electrochemical procedures based on cathodic reduction of the selected metal on platinum target in an appropriate electrochemical bath. A regular monolayer of an organic analyte was formed on all substrates. All experimental spectra were accumulated under the same experimental conditions at stabilized laboratory temperature. Both raw spectra and preprocessed ones (e.g. baseline corrected, noise filtered and/or normalized) were evaluated using several chemometric methodologies. The exploratory approach was based on principal component analysis (PCA). Classification methods comprised SIMCA modeling and discriminant analysis. Furthermore, the combination of PCA and control charts was applied using an algorithm previously developed [1].

The results show rather complicated chemometric models with contributing influences of many factors. In addition to the proposed effects of selected metal and excitation wavelength, a significant role of the composition of the electrochemical preparation bath was found out.

The set of applied chemometric methods forms a group of complementary results where different influences originated in both preparation and measurement steps are resolved.

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DIFFUSIVE GRADIENTS IN THIN FILM (DGT) TECHNIQUE IN CHARACTERIZATION OF ENVIRONMENTAL SYSTEMS

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DGT technique (Diffusive Gradients in Thin films technique) is known to be capable of quantitatively measuring in situ labile metal species concentrations in natural waters, metal fluxes in sediments and soils, and also estimates of metal concentrations in pore waters [1-5]. This technique employs two layers of hydrogel. In one layer, typically a specific ion-exchange resin with bound iminodiacetic groups (Chelex 100) is embedded. The second layer of ion-permeable hydrogel of well-defined thickness and porosity covers the resin hydrogel. After diffusing through the ion-permeable gel, metal ions are rapidly immobilized by the resin gel. Provided the resin sink is not saturated, the DGT probe reflects the actual metal concentration at the surface. The Fick´s first and/or second law of diffusion controls the metal ion transport. The metal flux and subsequently the in situ metal concentration in the solution can be calculated from the its mass accumulated in the resin, determined by using suitable elution and analytical procedures.

DGT technique was employed in characterization of sewage sludge amended soils in the Czech Republic, for assessment of mobile forms of heavy metals and their accessibility to plants. The influence of the soil moisture content, the deployment time and the DGT-sink demand on in situ response of the soils were investigated. The maximum heavy metal re-supply fluxes were estimated. Biological relevance, phytoavailability, and leachability of heavy metals are discussed.

New modification of DGT piston and sediment probes with respect to selectivity of uptake and spatial distribution in sediments is also described. A new specific sorbent with bound 8-hydroxyquinoline groups is used for selective sorption of U in aquatic systems. Results of comparative interference studies are shown. Design and performance of a new modified segmented sediment probe for depth profiling is described and examples of employment of this probe are discussed.

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DIFFUSIVE GRADIENT IN THIN FILMS TECHNIQUE FOR ASSESSMENT OF COPPER BIOAVAILABILITY TO RADISH (*Raphanus sativus*)

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The aim of this study was to assess the copper uptake of radish (*Raphanus sativa)* and to test the capability of DGT to predict phytoavailability of the metals for this plant. Radish was grown in pots filled with control-uncontaminated and artificially contaminated soils differing by copper content. Copper concentrations in plant root were compared with soil metal concentrations obtained by common leaching procedures and free ion metal concentrations in soil pore water, and effective concentration measured by DGT.

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MEASUREMENT OF THE FLUORESCENCE CROSS SECTIONS OF YBCO SUPERCONDUCTOR MATERIALS USING EDXRF TECHNIQUE

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Measurement of the K shell fluorescence cross sections have been investigated in $YBa_2Cu_3O_7$ superconductor compound. $\sigma_{K\alpha}$ and $\sigma_{K\beta}$ have been measured at room temperature and liquid nitrogen temperature for the Y, Ba and Cu elements. $YBa_2Cu_3O_7$ samples were prepared by the usual solid-state reaction method from high method from high purity starting powders Y_2O_3, $BaCO_3$ and CuO . Results of the XRD measurements displayed which series S1 (not heated, calcining and pulverizing procedures) did not showed the typical orthorhombic symmetry. Series S1 was excited and counted at the room temperature and liquid N_2 temperature. Series S2 showed the typical orthorhombic symmetry, which agrees well with previously published data for $YBa_2Cu_3O_{7-y}$. No additional phases such as Y_2BaCuO_5 or $BaCO_2$ were found. These series also counted at room and liquid N_2 temperature. Kα and Kβ fluorescence cross-sections and K shell fluorescence yields of Cu, Y, and Ba in $YBa_2Cu_3O_7$ have been measured at room temperature and liquid N_2 temperature. The samples were excited using 59.5 keV gamma rays from an Am-241 radioisotope source of strength 50 mCi. Measurements of the K_α and K_β x-rays fluorescence cross-sections have indicated that there are two effects on $\sigma_{K\alpha}$ and $\sigma_{K\beta}$ as the temperature and structural. K x-rays fluorescence cross-sections at room temperature were found higher than under the liquid N_2 temperature.

SPECIATION ANALYSIS OF SELENIUM IN URINE BY HPLC AND ICP/MS HYPHENATION

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Owing to selenium's fundamental importance to human health, there is continuing interest in monitoring of the selenium status populations. Preferred biomarkers are total selenium or specific selenium species in readily obtainable body fluids like urine. A method for determination of common selenium species in urine (selenite, selenate, selenourea, trimethylselenonium ion, selenomethionine, selenoethionine, selenomethylselenocystine) using ion-pair reversed-phase chromatography with inductively coupled plasma mass spectrometric (ICP/MS) detection was developed. A mobile phase was consisted of 2,5 mmol/l sodium butansulfonate, 4 mmol/l malonic acid and 8 mmol/l tetramethylamonium hydroxide. The determination of selenium species was complicated by difficult matrix and it was necessary to find optimal parameters of chromatographic and detection system. It was used some internal standards (Ge, Rh, Ar) by different technics of addition. The method was validated and different types of calibration were compared. Stability of the selenium compounds at concentrations 50 µg/l in human urine, stored in dark at -35°C, -5°C, or ambient temperature 25°C, without addition of any stabilizing reagent was evaluated. The developed method was used for monitoring of selenium species in urine taken from five volunteers (men and women 25-55 years old) after ingestion dietary supplements containing selenium. Two types of dietary supplements were compared and it was shown that there are many differences in efficiency between the supplements, which differ in a content of selenium species.

BIOMONITORING OF HEAVY METALS USING SOFT DRINKS FROM MISURATA CITY - LIBYA

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Some 50 canned soft drink specimens collected from supermarkets across several regions in Misurata-Libya were analyzed for Pb, Fe, Cu, Zn and Cd using inductively coupled plasma-mass spectrometry (ICP-MS) following digestion with an HCl and HNO_3 mixture (aqua regia) and H_2O_2.

The mean levels (± SE) of lead, iron, copper, zinc, and cadmium were found to be 0.170 ± 0.038 mg/kg, 0.436 ± 0.333 mg/kg, 0.187 ± 0.181 mg/kg, 1.300 ± 0.751 mg/kg, and 0.006 ± 0.0016 mg/kg, respectively, in the soft drinks. Our data revealed that lead, iron, copper, zinc, and cadmium mean levels found in all soft drinks, collected from several regions in Misurata-Libya, were within the Libyan National Centre for Standardization and Metrology (LNCSM) values.

Additionally, the results were compared with other studies and discussed. According to these results, to prevent this heavy metal pollution threat in the soft drink in Libya.

DIRECT AND SIMULTANEOUS DETERMINATION OF Bi, Sb, AND Cd IN BIOLOGICAL SAMPLES BY MULTI-ELEMENT GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETER

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Direct and simultaneous determinations of Bi, Sb, and Cd in different biological samples using a multi-element electrothermal atomic absorption spectrometer (Perkin-Elmer SIMAA 6000) are described. Two kinds of modifiers; $Pd(NO_3)_2$ + $Mg(NO_3)_2$ mixture modifier and Ir-permanent modifier were tested. The electrothermal behaviour of the elements in single-element and multi-element mode (with and without modifiers) was studied. The pyrolysis and atomization temperatures for the simultaneous determination using the mixture modifier were 600 and 1900°C and using permanent modifier were 550 and 1900°C. The detection limits were 0.86-1.5 $\mu g.l^{-1}$ for Bi, 0.79-2.5 $\mu g.l^{-1}$ for Sb, and 0.01-0.025 $\mu g.l^{-1}$ for Cd. The Characteristic masses were 62.9-88 pg for Bi, 46.3-67.7 pg for Sb, and 1.8-3.3 pg for Cd. A standard reference material (Seronorm Trace Elements Urine) was used to find the optimal temperature program. The reliability of the entire procedure was confirmed by analysis of certified reference materials as Trace Elements Urine Sample (from Seronorm 05115459), Bovine Liver (from NIST 1577b), Pig Kidney (from BCR 186), and Pork Liver (from GBW 08551). A standard additions method was used to determine Bi, Sb, and Cd in the samples simultaneously. Results of analysis of standard reference materials were in agreement with certified values.

SOLID-SAMPLING ATOMIC SPECTROSCOPIC DETERMINATION OF IMPURITY ELEMENTS IN CATALYSTS BASED ON Pd WITH VARIOUS SUPPORTS

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Pt group elements, especially Pd based catalysts, are often applied in hydrogenation technological processes. Hydrogenation process, except of experimental conditions, can be influenced by impurities, which come from added PdO either directly from the used support (carbon or SiO$_2$). With regard to character of the given supports, methods of the solid sampling atomic spectrometry are appropriate for this analytical task. Atomic emission spectrometry with excitation in the direct current arc – DCA (free-burning but also a modern electronically controlled) was applied. Qualitative analysis shows the presence of accompanying/ contaminating elements Al, Fe, Cr, Cu, Mg, Ni, Si and Ti. First step was devoted to the determining process at the direct analysis - perfect evaporation and subsequent excitation of studied elements. The best results were obtained using so-called high-resistance electrodes (SW material) at a relatively low sample weight (7 mg in the crater of the electrode). Details will be presented elsewhere (poster). Analytical calibration was performed using synthetic calibration samples (CRMs are not available). At the second (re) calibration, Pd catalyst component was included in the group of studied elements. Experiments were carried out in parallel spectrographic (spectrograph PGS-2) and spectrometric technique (CID-Echelle spectrometer Atomcomp-2000 with an integrated, computer-controlled DCA). Comparison of both technique will be presented separately (poster). The results of the calibration, validation and analysis of real samples will be presented in a lecture.

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DETERMINATION OF MAJOR AND TRACE ELEMENTS IN NATURAL SILICATE MINERALS USING LA-ICP-MS

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Major elements (Al, Si, K, Fe), as well as trace elements (Ga, Ge, In, Sn, Tl) were determined in whole rock samples and in major rock-forming minerals, such as quartz, feldspars, micas and amphiboles. The prime interest was observation of twins Al/Ga and Si/Ge, which should be the indicator of different magmatic (e.g. source of the parental melt and the degree of its fractionation) and hydrothermal processes (e.g. greisenization). The second one was determination of differences in contents of these elements among individual mineral species - differences based on crystal structure.

Whole-rock content of Ga ranges from 8 to 77 mg.kg^{-1}. All the less and moderately fractionated rock types fall in the interval of 15 – 35 mg.kg^{-1}. The highest values are found in strongly fractionated granites. The Al/Ga ratio generally decreased during magmatic fractionation.

Whole-rock content of Ge contents varies from 1.1 – 8.8 mg.kg^{-1}. Most of the moderately fractionated granitoids ranges from 1.5 to 2.5 mg.kg^{-1}, the highly fractionated from 2.5 to 5 mg.kg^{-1}. The Si/Ge ratio in most cases decreased during magmatic fractionation.

Content of Ga and Ge in individual minerals has shown that the highest contents among all common granite-forming silicate minerals are found in micas of the biotite-zinwaldite series. Values of Ga range from about 60 – 100 mg.kg^{-1} in Cínovec and between 100 – 150 mg.kg^{-1} in the Western Erzgebirge, but without clear correlation to the fractionation grade. Also the highest content of Ge was found in samples from Cínovec (15 – 25 mg.kg^{-1}). There are only small differences in the Ga- and Ge- contents of feldspars among particular plutons. Quartz generally contains only about 1.0 – 1.5 mg.kg^{-1} Ge and less than 0.5 mg.kg^{-1} Ga.

The Al/Ga ratio was in well negative correlation with Rb/Sr and Y/Ho ratios.

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DETERMINATION OF FLUORINE USING HIGH-RESOLUTION CONTINUUM SOURCE MOLECULAR ABSORPTION SPECTROMETRY (HR-CS MAS)

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With the introduction of the principle of HR-CS AAS in the last decade of years, the chance is given to overcome the limitation of traditional AAS for non-metal determination.

Especially for fluorine determination the spectroscopic methods like ICP-OES and -MS are not practicable because of high ionization potential and resonance wave lengths are below 100 nm. Other analytical methods for detecting fluorides dominating today are the ion chromatography and the use of ion-selective electrodes (ISE). Both detection methods have in common that they only response to ionic dissolved fluorides. Solids and other fluorine species (covalent bonded) are not directly detectable.

A suitable alternative is the detection of fluorine using high temperature molecular absorption spectrometry (MAS) with the commercial available high resolution continuum source atomic absorption spectrometer (HR-CS AAS). This analytical method uses the MAS based on the formation of stable mono-fluorides (AlF, GaF, InF, CaF). These diatomic molecules can just like atoms absorb defined energy from a continuous spectral radiation source. The molecular absorption spectra correspond to the molecular transitions between the different molecule states. The line width of various molecular absorption lines is roughly equal to that of atomic absorption lines and can thus be mainly resolved and used for the analysis in the HR-CS AAS.

For analytical purpose the most sensitive GaF molecule band head at 211,248 nm was used for optimization. A 10% Ga solution is used as molecule forming reagent in combination with several modifier substances. Thermal modifier pretreatment was used to activate the Pd/Mg- modifier for Ga stabilization. The best results were achieved with a permanently Zr-coated graphite tube with platform, a pyrolysis temperature of 550°C and a molecule formation temperature of 1550°C. On the basis of these conditions a detection limit of 0.26 $\mu g\ l^{-1}$ F was determined (3 σ) [1].

Different lower sensitive molecular absorption wavelengths of GaF were tested for analytical applicability for measuring of high fluorine concentrations in solids with direct solid sampling and to avoid high dilution factors for liquid sampling mode. Resulting a simple fast and robust method for the detection of fluorine in different liquid and solid samples like drinking water [2], brunches and leaves, tooth pastes and different high-tec materials is presented. Analytical results for direct solid sampling as for liquid sampling HR-CS AAS are discussed and compared with each other.

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CHARACTERIZATION OF ATMOSPHERIC PARTICULATE MATTER BY DIFFUSIVE GRADIENT IN THIN FILM (DGT) TECHNIQUE

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The increase of automobile emissions relates to the rapid growth of urbanization and industrialization. Toxicity of heavy metals associated with atmospheric particulate matter depends also on solubility, speciation and kinetics of metal release from solid phase. The diffusive gradient in thin films (DGT) technique is an in situ technique which can be used in measurement of kinetics of mobilization fluxes of metals.

In this study, characteristics of heavy metal contamination in road dust collected from urban area with heavy traffic in Brno, Czech Republic were investigated. The DGT probes were exposed in aqueous suspensions of particulate matter for different time periods to monitor responses of the sample matter. The road dust and DGT sorption gels were decomposed by microwave assisted extraction and analyzed by inductively coupled plasma mass spectrometry for estimation of trace metals contents.

The results revealed that the traffic appears to be responsible for the high levels of Cu, Pb, Ni and Sb and also that DGT technique, as alternative to conventional extraction procedures is a useful tool for characterization of metals mobility.

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SURFACTANT-BASED EXTRACTIONS: APPLICATION TO ULTRATRACE DETERMINATION OF METALS

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This lecture is dedicated to the surfactant-based extractions such as cloud point extraction (CPE) and coacervative extraction (CAE) that provide distinct advantages for separation and preconcentration of ultratrace metals prior to their determination by spectrometric methods.

Surfactants are amphiphilic molecules that comprise distinct hydrophobic and hydrophilic moieties – a polar or ionic group connected to a long hydrocarbon tail (linear, branched or containing aromatic rings). In aqueous solutions, at concentration above critical aggregation concentration (CAC), sufractants begin to form aggregates that are in equilibrium with monomers in the bulk aqueous solution. The number of monomer surfactants in the aggregate form (called aggregation number), the shape and the size of aggregates vary greatly. Depending on the surfactant structure and solution conditions, the amphiphilic molecules may form e.g., spherical or cylindrical micelles, reverse micelles, vesicles, planar or flexible bilayers.

In surfactant-based extractions, solutions of surfactant aggregates are separated into a surfactant rich phase of small volume and a diluted aqueous phase (in which the surfactant concentration is close to CAC). While in CPE, the phase separation of neutrally charged (non-ionic or zwitterionic) surfactants induced by the temperature is produced, in CAE, phase separation of ionic amphiphiles induced by other parameters (e.g., addition of electrolytes, pH change, addition of organic co-solvent, or simple mixing of oppositely charged amphiphiles) is reached [1].

In the case of ultratrace metal ions, separation and preconcentration in the form of their hydrophobic complexes is mainly accomplished. While CPE is used for sample preparation in trace metal analysis since its introduction and many papers about its application to this field are published, CAE is mainly used for separation and preconcentration of various organic analytes [2] and just few applications to ultratrace metal analysis can be found.

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

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TENDERS FOR LABORATORY EQUIPMENT

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The purpose of public tenders is to choose proper laboratory equipment for science, research and education and to save public expenditure. Public tender must be transparent, placed at equal conditions and without discrimination.

According to our opinion in many cases the choice was done in forward and the condition of the tender are fixed that way to choose only one equipment or supplier.

People preparing the tender may be trying honestly to choose the instrument that they consider to be the best one. But sometimes they choose well known instrument or manufacturer because they are lazy to learn new things and not brave enough to try new equipment. And sometimes this is even the case of bribery.

A DETERMINATION OF GOLD BY ELECTROCHEMICAL GENERATION OF VOLATILE FORM WITH QUARTZ ATOMIZER-AAS DETECTION (OPTIMIZATION AND CHARACTERIZATION)

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Electrochemical generation approach as a gaseous phase sampling technique in AAS is nowadays sufficiently examined for typical hydride forming elements (such as As, Se, Sb, Te, ...). On the other hand, there are many other analytical useful volatile compounds (including transition and noble metals) for electrochemical generation, which have not been investigated. This study is focused on the possibilities of continuous electrochemical generation of gold volatile species with on-line quartz atomizer-AAS detection. Arslan at al. performed chemical generation approach resulting to characterized gold species as nanoparticles [1].

Experimental setup (including electrolytic cell, carrier gas, transporting system, gas/liquid separator) was used the same as it is common for generation of hydrides from hydride forming elements [2]. Three different designs of electrolytic cell and five chemically different materials for working electrodes were tested. Preliminary experiments were performed to optimize relevant working parameters (type and concentration of electrolyte, carrier gas flow rate, electrolyte flow rate, value of generation electric current, atomization temperature). Under the optimal working conditions, calibration and other characteristics were found for the optimal designs (thin-layer) and cathode materials (Cu). The limit of detection 2.4 $\mu g\ ml^{-1}$ was obtained for this arrangement. The different kinds of gas/liquid separator and experimental setup modifications were tested. Additionally the influence of oxygen introduced in different part of experimental setup on sensitivity enhancement was investigated. Small amount of Triton X-100 and DDTC (sodium diethyldithiocarbamate) added into the catholyte stream increase the sensitivity more than 5 times. Atomic absorption spectrometry with flame atomization was used for determination of the analyte concentration in the waste solution to estimate the conversion efficiency from the liquid form (nearly 65%). It was observed, that appreciable amount of the analyte was reduced on the cathode surface. For characterization of analyte form on the cathode surface the scanning electron microscope with BSE and SE detector was used.

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INFLUENCE OF ANALYZED SOLUTIONS ON THE PLASMA PENCIL DISCHARGE

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Plasma pencil is a radiofrequency (13.56 MHz) plasma jet running under atmospheric pressure in argon or helium flowing through a narrow quartz tube. It has been investigated for many years and patented in 1998 by M. Klíma et al. Except for some archaeological and industrial applications including mainly surface modifications of artifacts, textile and other products it has been recently demonstrated that this type of discharge can be successfully employed as an excitation source for atomic emission spectrometry. Herein we show an influence of analyzed water solutions containing elements in acid matrices on both the discharge physical characteristics and the excitation capabilities. It is well known that the presence of acids in solutions depresses measured lines intensities. Acids viscosity can worsen the nebulisation efficiency and the presence of acids in the discharge together with abundant water consume a non-negligible amount of the delivered electrical energy. These phenomena result in a decrease of the intensities of measured atomic emission lines of elements in the introduced solution. The determination of the elements in acid matrices is less sensitive than in pure water solutions. This behaviour is also recognizable in case of the presented plasma pencil. Experiments were realized with three single element containing solutions. The selected elements were Cu, Mg and Zn in the concentration range of 1 – 100 mg l^{-1} and the contents of 70% nitric acid of 2, 10, 20 and 50 ml per 100 ml flask. A decrease of the slopes of the calibration lines depends on the particular spectral line and ranges from about 10 to 20% for the acid concentration change from 2 to 20 ml per 100 ml flask. These results are supported by changes in the rotational temperature calculated from OH radicals, excitation temperature from a set of Ar lines and electron number density from the Stark effect on hydrogen H beta line. Despite the sensitivity decrease the discharge stability was not very influenced by the presence of the acid which is in contrast to the influence of the pure water. It was also proven that the plasma pencil is capable of reliable determination of zinc content in a commercial multivitamin tab in presence of other matrix substances.

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MULTI-ELEMENTAL ANALYSIS OF MILK BY ICP-OA-TOF-MS AFTER MATRIX MODIFICATION BY OXALIC AND NITRIC ACID

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Modification of the sample preparation procedure by precipitation of milk samples with oxalic acid prior to analysis by inductively coupled plasma orthogonal acceleration time-of-flight mass spectrometry (ICP-oa-TOF-MS) was found to offer advantages for some elements whose assay is more difficult when using conventional quadrupole instruments like As, Se, Co or Ni. Oxalic acid enables the elimination of spectral interferences originating from different calcium containing species for the above mentioned elements through the separation of calcium as precipitated non-soluble oxalate. The use of nitric acid for precipitation of proteins is essential for better separation of solid and liquid phase of modified samples. The methodology serves, in addition, as a fast and sensitive alternative for the determination of some other elements. After that, direct, reliable and simultaneous determination of 16 elements at trace and ultra-trace levels in milk can be performed without dilution under optimum instrumental conditions and by using Rh as an internal standard. Accuracy and precision was assessed by measuring NCS ZC73015 Milk Powder control standard, yielding results in agreement with certified values and RSD < 10%. The accuracy was also checked by comparison of the results of the proposed method with those found by a method based on a microwave-assisted digestion of real samples.

THE APPLICATION OF LOW RESOLUTION CONTINUUM SOURCE ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY FOR SIMULTANEOUS MULTI-ELEMENT ANALYSIS OF UNDERGROUND WATER

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The methodology of simultaneous multi-element electrothermal atomic absorption spectrometry (SMET AAS) is based on pulse vaporization of the sample in a fast heated tube atomizer, detection of transitory radiation from continuum source within 200-410 nm wavelength range and calculation of absorption at the selected wavelengths. The experimental setup includes Ocean Optics CCD spectrometer (1200 mm^{-1} groove density; 5 μm slit width; 3648 pixels (190-410 nm); 4 ms data collection time), xenon arc lamp and small fast heated (10 K/ms) graphite tube atomizer. The data from 80 spectra acquisitions are collected during the atomization step and processed using specially developed software. The calculation algorithm provides visualization of temporally resolved or integrated spectra as well as background correction, modification and integration of measured absorbance for the spectral lines of various analytes. The measurements for number of elements are performed using single sampling. . The results obtained for the multi-element solutions show opportunity of direct determination of individual analytes within 3-5 orders of magnitude concentration range and limits of detection close to μg/L level About 1-2 minutes is needed for the measurement and calculation independent of number of elements to be determined. The instrument is simple and compact.

Five samples of underground borehole water collected from locations around Pretoria, South Africa were used to reveal prospects and potential problems related to practical application of the instrument. In order to highlight possible sources of errors the samples were not exposed to any chemical treatment or modification. The results show that the samples contain various concentrations of Al, Ca, Cu, Cr, Fe, K, Mg, Mn, Na and Ni above the detection and quantification levels. Concentrations of some elements (e.g. Al and Fe) in various samples differed within 2-3 orders of magnitude. For the low concentrations the results correlate with limits of detection. For higher concentrations the results obtained from multiple element lines using respective reference calibration curves for individual analytes typically demonstrate less than 20% deviation. Beside of atomic lines the spectrum contains multiple molecular species, e.g. AlCl, AlF, MgCl, MgF, SiO, CS and some other sulfur containing species. For each sample a specific combination of atomic and molecular spectra is characteristic. Easy visualization of the integrated or time resolved spectra helps in the optimization of temperature program or temporal detection interval to provide lower error or better LOD. Instant observation of molecular spectra can also help for *in situ* chemical modification of the sample to reduce the release of molecular species. Otherwise, molecular spectra can be employed for the determination of sulfur or halogens using the molecular bands.

DANDELION (*Taraxacum officinale*) AS BIOINDICATOR FOR URBAN METAL POLLUTION

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To examine the metal content of dandelion leaves and roots in relation to environmental metal levels, the concentrations of cadmium, mercury, lead and copper were analyzed in plant parts and soil samples collected at five sites in the city of Brno differentially impacted by pollution. Soils and plants were collected in November 2009, March 2010 and April 2011. The highest values of metal contents (Cd: 0.747 ± 0.022 $mg.kg^{-1}$, Hg: 0.707 ± 0.231 $mg.kg^{-1}$, Pb: 78.2 ± 3.6 $mg.kg^{-1}$, Cu: 44.1 ± 1.2 $mg.kg^{-1}$) were found in the soil sampled at Opuštěná Street, a heavily polluted locality with high traffic density situated in the city centre. The higher content of mercury, lead and copper in the leaves rather than in roots in all localities illustrated a contribution of significant atmospheric deposition. Higher cadmium content was found in underground part of the plants that indicated soil contamination. High correlations were found between the amount of cadmium ($r = 0.781$) in the soil and in the dandelion roots and between the amount of lead ($r = 0.978$), mercury (0.763) and copper ($r = 0.978$) in the soil and in the dandelion leaves. The content of heavy metals both in the dandelion and in the soil should be seen as a good indicator of natural urban environmental pollution.

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SURFACE-MODIFIED LUMINESCENCE AND SERRS EXCITATION PROFILES OF RU(II) (BPY)$_2$(DCBPY) COMPLEX CHEMISORBED ON Ag NANOPARTICLES

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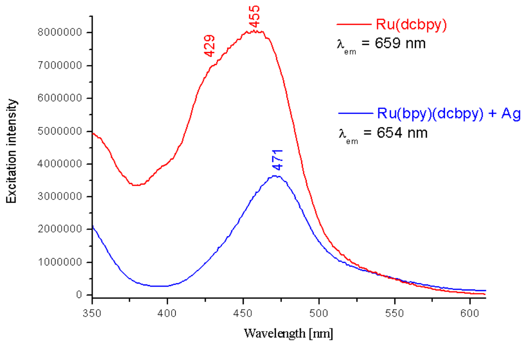
The growing interest in heteroleptic Ru(II) polypyridine complexes stems from the exciting possibility to affect the bonding properties of one of the ligands as well as the electronic structure of the complex by introduction of various peripheral substituents, which in turn, promotes applications of these complexes e.g. as sensitizers in dye-sensitized solar cells. In this study, we have selected Ru (bpy)$_2$(dcbpy) / Ru(II) bis(2,2'-bipyridine)(4,4'-dicarboxy-2,2'-bipyridine) complex/ as a model chromophore and luminophore for investigation of surface-modified luminescence and SERRS (surface-enhanced resonance Raman scattering) of species chemisorbed on Ag nanoparticle (NP) surfaces. First, we obtained SERS and SERRS spectral evidence of chemisorption of the complex on Ag NP surface in Ag NP hydrosol/ Ru(bpy)$_2$(dcbpy) systems via at least one of the carboxylate groups of the (dcbpy) ligand. Secondly, we have constructed SERRS/SERS excitation profiles from SERRS and SERS spectra measured at five different excitation wavelenghts. We found out that the profiles of SERRS spectral bands of the Ru(bpy) structural unit peak at 457 nm, i.e. while those of the Ru(dcbpy) unit maximize at 488 nm. Furthermore, we measured and compared excitation spectra of ^{3}MLCT phosphorescence (max. 655 nm) of the complex in aqueous solution and in Ag NP hydrosol/ Ru(bpy)$_2$(dcbpy) system (Fig.). While the excitation spectrum of the free complex is virtually identical with its absorption spectrum, the excitation spectrum of the chemisorbed complex shows a distinct new maximum at 470 nm. Both the SERRS/SERS excitation profiles and the phosphorescence excitation spectra (Fig.) indicate an energy decrease of the MLCT transition Ru(II)→(dcbpy) upon chemisorption of the complex on Ag NP surface via the COO$^-$ group(s) of the (dcbpy) ligand. The energy decrease is attributed to a substantial increase of the electron-withdrawing ability of the COO$^-$ group(s) upon their bonding to Ag$^+$ adsorption sites present on Ag NP surface.



Our results demonstrate the potential of luminescence excitation spectra to provide information about changes of electronic transition energies in molecular species upon their chemisorption on plasmonic NP surfaces.

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TRACE METALS AND PHOSPHORUS SPECIATION IN DIGESTED FOOD: A WAY OF ELEMENTS' AVAILABILITY ESTIMATION?

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The estimation of biological availability or toxicity of trace elements has been an important reason for elements speciation studies in food and biological samples. The chemical state of elements in food belongs to the factors influencing biological accessibility of the element from diet. Nevertheless, the actual efficiency of element absorption in gastrointestinal system strongly depends on the biological factors of the individual consumer such as the total element store in the body, the adequacy of nutrients dietary intakes in recent months as well as the sex and age of the consumer. Moreover, the chemical composition of diet affects the biological availability of elements significantly. This includes the content of proteins and dietary fibre and namely the presence of the specific compounds acting as enhancers (e.g., ascorbic acid, cysteine, histidine) or inhibitors (e.g., phytic acid, plant phenolic compounds) of elements absorption. Speciation analysis of elements in food could give valuable data concerning distribution of element content among the fractions of soluble or insoluble, low- or high-molecular and inorganic or organically bound species.

To find out the chemical state of elements in digested food, we applied a sample treatment by *in vitro* simulated enzymatic digestion followed by SEC-ICP-MS fractionation of element species. The digestion was carried out at 37°C and included two steps (firstly with pepsin in 0.02 M HCl, secondly with pancreatin at pH=7.5) corresponding to the gastric and the duodenal process, respectively. We focused on the analysis of cereal products and legume-derived foods, as they are important nutrient sources with limited bioavailability of some essential elements (Ca, Zn, Fe). High content of phytic acid (inositol-hexakisphosphate) is often considered as the main cause of low bioavailability of metallic elements. Therefore, the chromatographic fractionation of phosphorus was performed together with that of trace metals. We fractionated the elements species using SEC (Superdex 75 column and 0.02M Tris-HCl, pH=7.5 as the mobile phase) hyphenated with ICP-MS. For phytic acid and phosphate determination, we applied phosphorus speciation method based on ion-paired reversed phase chromatography hyphenated with ICP-MS.

The results showed a time dependence of soluble portion of phosphorus and copper during sample hydrolysis as well as the distribution of soluble species among inorganic metal ions (the main form of Mn) and various chelates ranging in molecular mass from 1–2 kDa (typical for Cu, Zn, Ni, Co) to >150 kDa (Fe).

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DETERMINATION OF NICKEL IN NON-DECOMPOSED ORGANIC SAMPLES USING GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY: NEW OUTLOOK ON OLD PROBLEMS

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Graphite furnace atomic absorption spectrometry (GFAAS) belongs to the most important analytical techniques for nickel determination at trace level. The technique is also used for analysis of various organic samples, for example: edible oils and fats, crude oil and various its products as well as biofuels and biocomponents. The samples can be analysed in an aqueous solution after decomposition or without decomposition: directly, after dilution in an organic solvent or in a form of emulsion or microemulsion. Although such an analyses have been performed since 70-ies, the last technical and methodological progress enabled to reveal some problems (inaccurate results), which were unrecognizable so far. The technical tools, used for detection and explanation of the problems were: application of high-resolution continuum-source GFAAS, various ways of GF heating, atomization from a wall or from a platform and from uncoated or pyrolytically coated graphite. Inorganic or organic Pd modifiers (applied in various ways) and oxidizing chemical modifiers were also tested. Investigations of various groups of chemical forms of Ni as well as samples of various matrixes were carried out.

The most important findings are as follows:

- The inaccuracy errors of order (orders) of magnitude can be unrecognizable in recovery studies and by analysis of CRMs;
- A pyrolysis curve course does not reveal effects that take place over the entire investigated pyrolysis temperature range, e.g. some volatile chemical forms of Ni can be lost even at the solvent evaporation phase;
- There are some rules of behavior of organic Ni compounds during GFAAS analysis and the behavior depends on the organic part of an Ni molecule;
- The presence of volatile (probably porphyrins) and non-volatile Ni forms in crude oil and its products can be distinguished using GFAAS (fractionation by differential volatilization);
- Interaction with graphite affects evaporation of Ni compounds, which can be present in graphite furnace at the temperature much higher than their boiling points; the interactions depend on Ni form and matrix; some interactions lead to increase of Ni signal, some others to decrease of the signal (carbides formation);
- Formation of volatile $Ni(CO)_4$ should be taken into account, when analyzed sample contains Ni atoms bound by O atoms (especially in carbonyl group).

It is possible to overcome the considered problems and GFAAS can be successfully utilized for reliable, fast and automatic (autosampler) Ni determination. A characteristic mass of 6.5 pg and detection limit below 1 ng g^{-1} can be reached.

THE USE OF LASER-INDUCED BREAKDOWN SPECTROSCOPY FOR THE QUANTITATIVE ANALYSIS OF FLUORINE

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The aim of this work was to develop an effective, rapid and simple method for the quantitative analysis of fluorine in Glass Ionomer Cement (GIC).

The influence of the He atmosphere and the gate width to the signal of fluorine emission lines was investigated in details in this work. The measurements were realized by using two double-pulse LIBS devices with different parameters (experimental arrangements and gate widths of detector).

The use of the He atmosphere in the working chamber had a significant influence on the intensity of fluorine emission lines in the 673 – 697 nm wavelength range. An increasing of the intensity of fluorine lines and decreasing of the background was observed on both devices with He flow. The change from the air to the He atmosphere caused a more noticeable decreasing of background in the case of device with the large gate width.

The model samples of CaF_2 with $CaCO_3$ (both purity per analysis) were used to obtain the calibration curves. The emission lines F(I) 683.4 nm, F(I) 685.6 nm, F(I) 687.02 nm and F(I) 690.2 nm were selected for analysis. The model samples were prepared in the calibration range 1.25 to 15 wt.%.

Calibration curves describing the relationship between the fluorine concentration and the corresponding intensity of LIBS signal, were constructed for both LIBS devices, with and without He flow also. F(I) spectral line of 685.6 nm was found to be considerably sensitive and provided the linear calibration. The best LOD value was obtained for the device with the short gate width (5 µs) in He atmosphere.

Obviously, the collinear arrangement is more suitable for measurement of powder samples on the tape than the orthogonal arrangement. In the case of an orthogonal set second (excitation), the laser pulse can be interrupted by the contact with unevenness on the sample surface, and it can reduce intensity of the excitation pulse or even the pulse can be interrupted.

The results show that the compact commercial LIBS system with fixed gate width is less suitable for LIBS analysis of fluorine (non-easily ionizable elements), than the table-top set with adjustable gate width.

The proposed method was successfully used for the quantitative analysis of fluorine in GIC. The LIBS methodology developed in this work is fast and precise and can be employed on a routine basis for fluorine determination in samples.

IN-ATOMIZER TRAPPING OF HYDRIDES FOR AAS – LAST ADVANCES

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A compact trap-and-atomizer device based on a quartz multiatomizer was shown to be a powerful tool for ultratrace determination of hydride forming elements (As, Sb, Bi, and Se). It allows rapid and efficient in-atomizer preconcentration of the analyte prior to its detection by atomic absorption spectrometry (AAS). Oxygen rich atmosphere is used to remove hydrogen evolved during chemical hydride generation to reach efficient trapping of the analyte in the inlet arm of the multiatomizer. On the contrary, hydrogen rich atmosphere is used to efficiently volatilize trapped species. In this work, generation, atomization and preconcentration conditions have been optimized for another important hydride forming element - lead. Plumbane is efficiently retained in the trap at temperatures below 300°C in the presence of oxygen. Subsequently, the trapped analyte can be completely volatilized employing temperature above 800°C and 100 $ml.min^{-1}$ of hydrogen. Plumbane trapping in the trap-and-atomizer device can be routinely used for lead determination at ultratrace levels reaching a detection limit of 0.21 ng ml^{-1} Pb (30 s preconcentration time, sample volume 2 ml). Among other hydride forming elements, bismuth was found as the strongest interferent. A carrier free ^{212}Pb radioactive indicator, prepared by us, was used to verify the plumbane generation and preconcentration conditions as well as to investigate the mechanism of the interference caused by bismuth. Plumbane generation efficiency of 95% was found under the optimized conditions in the presence of $K_3[Fe(CN)_6]$. Complete plumbane trapping as well as analyte volatilization were confirmed by the radioactive indicator resulting in the overall preconcentration efficiency of 100%. Larger surface area is required for plumbane trapping compared to other hydrides as found by autoradiography. Around 75% of the analyte is retained in the trap whereas the remaining 25% of the analyte can be found trapped in the optical arm of the trap-and-atomizer device under the optimized conditions for analyte collection. In spite of the large surface area required up to 200 ng of Pb can be trapped in the device without change in the trapping efficiency. As a consequence, the trap capacity is more than sufficient for trace determination since 1-5 ng of Pb is typically trapped (30 s preconcentration time, sample volume 2 ml). Bismuth presence in the sample does not affect plumbane generation efficiency as found by ^{212}Pb radioactive indicator. Also the plumbane trapping efficiency is not decreased due to the co-trapped bismuthane (at least up to 800 ng of Bi). The nature of the Bi interference on Pb determination was found to be the volatilization interference.

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THE EFFICIENCY OF THE ICP-OES INTRODUCTION SYSTEMS

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A commonly used sample introduction system for the ICP OES consists of a nebulizer transforming liquid samples into an aerosol and a spray chamber selecting the maximum drop size of aerosol further introduced into the plasma. The interferences are often given to the relation with the plasma because the excitation and ionization processes will are affected. Nevertheless, additional instrumental aspects and variables influencing the aerosol generation and transport contribute in a very significant way. The sample aerosol injected into the plasma modifies its thermal characteristics[1,2,3].

The influence of several combinations of nebulizing devices and spray chambers on the matrix effects in the ICP OES was tested. Study was carried out using model samples. Interfering agents were chosen from easily ionised ions (Na, Ca, Ba), decomposing and conserving reagents (nitric acid), organic matter (urea) and their mixture on concentration levels approaching the real concentrations in samples routinely analysed. Recoveries of analysis for selected spectral lines (Cd II 228.802 nm, Cd I 214.438 nm, Cu I 324.700 nm, Cu I 324.754 nm, Ni II 231.604 nm, Cr II 283.604 nm, Mn II 257.61 nm, Pb II 220.353 nm, Zn I 231.856 nm) were evaluated for various matrix loads tested. Without an internal standardisation, the recovery was found to be 93 – 95% for the microconcentric nebulizer coupled with the small inner volume spray chamber. For the concentric and microconcentric nebulizers with the large volume spray chamber the recoveries 88 – 93% were obtained. The V-groove nebulizer plus the large volume spray chamber provided unsatisfactory recoveries 70 – 110% given by eye-noticeable fluctuations of the aerosol produced. This work confirms a significant contribution of the sample introduction system to these effects apparently due to the various sample loads to the plasma for the single instrumental arrangements.

Matrix effects relating to the plasma were evaluated using the Mermet factor (Mg II 280.270 nm / Mg I 285.213 nm) and the ionic/atomic ratio for Cd (Cd I 214.438 nm / Cd II 228.802 nm).

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PLANT NUTRIENTS IN DIFFERENT GRAIN SIZE FRACTIONS OF BIOMASS FLY ASHES

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As biomass counts to the renewable energies, it is CO_2-neutral when transportation and pre-treatment of the biomass are not taken into account. Biomass is therefore a good alternative to the usage of fossil based fuels. Especially wood is increasingly used for the generation of heat and electricity.

During the incineration process all the organic compounds are converted into gases. The remaining ashes (1-3% of the input biomass) contain nutritive elements for soils and plants (e.g. phosphorus, potassium, calcium and magnesium). The best way to recycle them is therefore by their usage as soil enhancers as it is often done with bottom ashes collected at the bottom of the incinerator.

But especially fly ashes collected in the gas cleaning system of the incinerator are often very loaded with harmful heavy metals which restrict in most cases the application of the fly ash on soils and so they are usually disposed.

In this investigation, fly ashes from an Upper Austrian biomass incinerator have been separated with a laboratory air classifier into different grain size fractions (2-55 μm). The distribution of nutrients in the fractions has been investigated. As it is known from other investigations that the biggest amounts of heavy metals are concentrated in the finer ash fractions, also the distribution of Cadmium was determined in the different grain size fractions as it is the most limited heavy metal in the Austrian recommendation for the usage of biomass ashes on soils with a limit of 8 mg/kg.

The original fly ash as well as the separated grain size fractions were digested in a microwave assisted digestion unit with hydrochloric acid and nitric acid at around 200°C. For the determination of metals ICP-OES (inductively coupled plasma optical emission spectroscopy) and IC (ionic chromatography) were used.

It could be found that most nutrients, as for example magnesium, are distributed homogeniously in the different grain size fractions of the fly ash. Only potassium showed higher concentrations in the finer ash fractions. Unfortunately – and as expected - the same could be found for cadmium.

Therefore, by separating the finest fly ash fractions and hereby removing high amounts of harmful heavy metals results in a cleaner and on fields recyclable coarser ash fraction but with a reduced content of potassium. Other nutrients, though, as magnesium, manganese or calcium, are still present in the coarser fly ash fraction which makes this ash still a good soil enhancer. The necessary amount of synthetic fertilizers and the costs for disposing of fly ashes can so be reduced.

DEVELOPMENT OF OPTICAL CHEMICAL SENSORS/SENSOR ARRAYS

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The "optical sensor" (molecular probe) can be defined as a chemical entity capable of recordable optical signal change (*e.g.* intensity, luminescence, *etc.*) upon presence of analyte while the "sensor array" is used for an organized set of sensors that renders output in form of a data matrix which can be processed by means of advanced chemometric techniques to unravel possible linkages in combinations of several outputs of non-specific sensors for different analytes[1].

In this contribution, the development of optical sensors for determination of Ln(III) ions[2] and anions (*e.g.* bicarbonate, oxalate, halides – iodide, bromide, chloride, *etc.*) will be presented. The example of combination of several sensors into sensor arrays for anion mixture(s) followed by chemometric analysis of experimental data (*e.g.* Artificial Neural Networks, *etc.*) will also be demonstrated.

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THE POSSIBILITIES OF TOXIC ELEMENTS TRACE ANALYSIS IN NATURAL WATERS BY COMBINATION OF ATOMIC SPECTROMETRY METHODS WITH A SAMPLE PREPARATION TECHNIQUES

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Trace metals are regarded as very significant and highly toxic pollutants in the environment. A need for highly reliable methods for the determination of metals in trace and ultra-trace concentrations has been recognised in analytical chemistry and environmental sciences. In metals analysis, a wide variety of spectrometric techniques as well as separation techniques are commonly used. Despite of the high sensitivity and selectivity of atomic spectrometry techniques, the pre-concentration of metals and simplification of the sample matrix by using different sample preparation procedures is frequently required. However, because of the possible risk of sample contamination and the losses of the analyte during sample preparation, these techniques represent a most critical step in the whole analytical procedures. Therefore, the selection and optimization of appropriate sample preparation technique is very important.

The aim of this contribution is to inform and give attention to the importance of the implementation of sample preparation techniques in analytical procedure for determination of toxic trace elements in natural waters by AAS. In this work, some of the sample preparation techniques, widely used in trace analysis of elements, namely solid phase extraction (SPE) and cloud point extraction (CPE), in combination with atomic absorption spectrometry techniques have been selected for the determination, preconcentration and speciation of vanadium, chromium and beryllium. The optimized methods were used for the analyses of the model water samples as well as the real natural water samples. The accuracy of the proposed methods was verified by the analysis of certified reference materials of waters with relative errors less than 5%. By the using of SPE and CPE techniques the simplification of the sample matrix as well as the significant improvement of the detection limits was achieved.

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MÖSSBAUER SPECTROSCOPY IN STUDYING OF THERMAL DECOMPOSITION OF IRON CONTAINING COMPOUNDS

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Thermal decomposition of iron containing precursors presents a simple and cost-effective way for preparation of iron and iron oxide based materials with interesting properties, often in a nanoparticle form. ^{57}Fe transmission Mössbauer spectroscopy is able to monitor kinetics and mechanism of thermal decomposition. From Mössbauer spectra it is possible to identify and quantify iron containing phases despite of their crystallinity or amorphicity. Moreover we can determine valence and spin states of iron atoms in particular phases and also distinguish between nonequivalent positions of iron atoms in a crystal structure. Several examples of thermal decomposition studies using Mössbauer spectroscopy are presented including thermal decomposition of Prussian Blue, ammonium ferrocyanide, ferrous oxalate dehydrate, ferric chloride hexahydrate and ferric sulphate pentahydrate. In the framework of the mentioned studies, discerning between different Fe_2O_3 polymorphs, which can be formed during the thermal decompositions is introduced.

SPECIATION ANALYSIS OF MERCURY IN TERRESTRIAL PLANTS AND FOOD OF PLANT ORIGIN

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Mercury is one of the most dangerous elements in terms of its impact on the human body. Because the toxicity of mercury varies depending on its chemical species, it is very important to determine the exact amount of each species.

We developed analytical technique for the on-line analysis of mercury species in terrestrial plants and plant-originated food by connection of high performance liquid chromatography (HPLC) and inductively coupled plasma mass spectrometry (ICP-MS). Extraction step, the liquid chromatography (concerning the composition of mobile phase and flow rate) and the generation of cold vapor (CVG) were optimized for the improvement of the limit of detection (LOD).

The plant matrix intralaboratory reference material (IRM) was prepared in order to the method of analysis could be validated. The content of methylmercury and inorganic mercury in IRM was determined in our laboratory and in two independent laboratories. For the determination of incriminated species we have used two methods of calibration: internal standard calibration and isotope dilution method.

Our technique was applied for the speciation analysis of mercury in the weed, which was collected around chlor-alkali plant, and radish.

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ARSENIC SPECIATION ANALYSIS AT (ULTRA)TRACE LEVELS BY HYDRIDE GENERATION AND/OR HPLC WITH ICP MS DETECTION-PROS, CONS AND PRINCIPAL LIMITATIONS OF INDIVIDUAL APPROACHES

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Chronic exposure to arsenic, one of the most potent environmental carcinogens, can cause number of serious diseases. Therefore, a development of analytical methods for (ultra)trace speciation analysis of As is nowadays in great demand.

Several approaches to As speciation analysis are commonly reported in the literature, each having its pros and cons. The most common approach based on HPLC separation followed by ICP MS detection is limited by a matrix- an extraction step is often required prior to analysis. Due to limited applicable sample volume, the sensitivity is also restricted. This does not apply to the approach based on hydride generation and separation of collected methylsubstituted arsines: Here, excellent limits of detection can be achieved, but selectivity is determined by the hydride generation properties of individual species as well as the fact that only four arsines can be distinguished.

Methods based on hydride generation with preconcentration by cryotrapping and AAS (LOD for individual species 2- 9 ng l^{-1} As) or ICP-MS detection (LOD 0.06-2.45 ng l^{-1}) are compared with procedure employing HPLC separation with ICP-MS detection. A development and optimization of postcolumn hydride generation with on-line pre-reduction of pentavalent arsenic species by thioglycolic acid, in order to improve sensitivity of this method, yielded LOD of 9-12 ng l^{-1}.

The results of analyses of reference materials of river water (NRC SLRS-4 and SLRS-5) and sea water (NRC CASS-4, CASS-5 and NASS-5), containing less than 1 μg l^{-1} total As and concentrations of methylated As species in tens of ng l^{-1} obtained by individual methods were found in excellent agreement. Another example will be direct As speciation analysis in exfoliated bladder epithelial cells isolated from human urine, containing 10-1000 pg of As species per sample.

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PHASE TRANSITIONS IN NOVEL NLO MATERIALS – VIBRATIONAL AND DIFFRACTION STUDY

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The thermal behaviour was studied in several semi-organic and organic compounds based on the salts of inorganic or organic acids and electron rich N-containing with delocalized π-electrons organic bases (aniline, amino-1,2,4-triazoles, amino-1,3,4-thiadiazole and biguanides) by crystal structure diffraction and vibrational spectroscopy. Some samples based on aminotriazoles or some biguanides[1] exhibit the glass transition according to a shape of DSC curves and no significant changes were observed by vibrational spectroscopy and crystal structure determination. But the remaining structures exhibit a first order near to the second order phase transition measured on DSC and small changes were observed by vibrational spectroscopy mainly infrared spectroscopy and the crystal structure determination. This type of phase transition was detected as the isostructural phase transition observed in the case of salts of phenylbiguanidium[2], aminothiadiazolium, aminotriazolium[3] and anilinium[4].

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ULTRASONIC NEBULIZATION/DUAL-MODE SAMPLE INTRODUCTION SYSTEM FOR THE DETERMINATION OF METAL VOLATILE SPECIES IN ANALYTICAL SAMPLES BY MICROWAVE INDUCED PLASMA SPECTROMETRY (USN/MSIS-CVG-MIP-OES)

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Based on a novel synergic effect of ultrasonic nebulization (USN) and dual-mode sample introduction system (MSIS) when used in combination has been exploited for efficient generation of conventional hydride elements (As, Bi, Sb, Se, Sn), Hg vapor and volatile molecular Cd species. Ultrasonic nebulizer supplied micro-liters sample to a quartz oscillator, converting liquid into aerosol at the entrance of the MSIS spray chamber. The argon/helium carrier/stripping gas is passed to remove and transport the generated species to a detector, which in this study is an microwave induced plasma optical emission spectrometer (MIP-OES). A univariate approach and simplex optimization procedure was used to achieve optimized conditions and derive analytical figures of merit. Analytical performance of the fully integrated on-line USN/MSIS system was characterized by determination of the limits of detection (LODs) and precision (RSDs) with the USN/MSIS observed at 30 μL min^{-1} flow rate. The experimental concentration detection limits for simultaneous determination, calculated as the concentration giving a signal equal to three times of the standard deviation of the blank (LOD, $3\sigma_{blank}$ criterion, peak height) were 11, 22, 16, 19, 20 11 and 15 μg L^{-1} for As, Bi, Sb, Se, Sn, Cd and Hg, respectively. The method offers relatively good precision (RSD ranged from 3 to 5%) for liquid analysis and micro-sampling capability. The methodology was validated through determination of elements in two Certified Reference Materials (NRCC DOLT-2, NIST 1643e), and by the aqueous standard calibration technique. The measured contents of elements in reference materials were in satisfactory agreement with certified value (As, Sb, Se, Cd, Hg) and added amounts (Bi, Sn).

PLASMONICS IN FLUORESCENCE SPECTROSCOPY

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Plasmonics [1] is a field dealing with properties of so called surface plasmon-polaritons (SPP) and their application to manipulation of electromagnetic field at optical frequencies. The SPPs are quanta of collective oscillations of conduction electrons at metal surfaces coupled to photons. Depending on surface morphology, these electromagnetic modes can be either propagating (on flat surfaces) or localized (on nanostructured surfaces). Thus, the rapid advance in plasmonics is closely connected to the fast progress in nanofabrication [2]. Both types of SPP modes have already found their important application in molecular sciences. Namely, the propagating modes are the core of Surface plasmon resonance sensing [3] and the localized modes are essential for the electromagnetic mechanism of enhancement in Surface-enhanced Raman spectroscopy [4]. In recent years, increasing attention is paid application of plasmonics to widely developed fluorescence spectroscopy methods, particularly to the fluorescence microscopy which has become a real workhorse in biological research [5]. The nature of interaction of a fluorescent molecule with SPP modes of a metallic nanostructure is rather complex and can involve changes in rates of both radiative and non-radiative processes in the molecule [6] together with effects due to spatial localization and intensity enhancement of the electromagnetic field. Various aspects of these phenomena and possibilities of their to exploitation for e.g. preparation of bright fluorophores with short lifetimes, reduction of photobleaching or subwavelength resolution in fluorescence microscopy will be discussed in this contribution.

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MOLECULAR CRYSTALS FOR NON-LINEAR OPTICS - VIBRATIONAL SPECTROSCOPIC ASPECTS

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The progressive study of novel materials for non-linear optics (NLO) is primarily motivated by their applications in the areas of new laser frequency generators, optical communication and optical signal processing, as well as data storage and other information processing tasks. Very interesting group of studied materials are molecular crystals based on selected polarizable organic molecules (carriers of NLO properties). These hydrogen-bonded materials range from uncharged cocrystals to ionic salt crystals and frequently combine nonlinear optical properties (e.g. second harmonic generation - SHG) with other desirable properties (optical transparency, thermal, optical and mechanical stability).

The vibrational spectroscopic methods themselves and especially their combination with other experimental techniques (optical characterization, X-ray diffraction, calorimetry) and quantum chemical computations provide unique information concerning symmetry, molecular and phase composition, bonding interactions, phase transitions etc.

In this contribution we are presenting results concerning application of vibrational spectroscopy (IR and Raman) in the field of characterization of novel NLO materials. The studied hydrogen-bonded molecular crystals are based on selected heteroaromatic amines (e.g. 2-aminopyrimidine; 2,4,6-triaminopyrimidine, 2-amino-1,3,4-thiadiazole) and biguanide derivatives (e.g. phenylbiguanide, guanylurea).

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BEHAVIOUR OF ANALYTICAL SPECTRAL LINES EMITTED BY PLASMA PENCIL OPERATED IN A CONTINUOUS AND IN A PULSED MODE

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Plasma pencil is a universal tool originally developed for solving non-standard problems in the archaeology. It is in fact a narrow quartz tube or capillary with a barrier capacitively coupled discharge boosted by a radiofrequency (RF) sinusoidal wave at 13.56 MHz originally in the continuous mode. However, the RF wave can be modulated by various methods, e. g. by frequency or amplitude modulation. The plasma gas is pure argon or helium under atmospheric pressure in this application. Chemical analysis of liquids with the plasma pencil was simulated using sets of standard water solutions of Na^+, Li^+, Ca^{2+}, Mg^{2+}, Cu^{2+} and Zn^{2+} ions. Excitation capabilities, calibration dependences in the range of 1–100 mg l^{-1} and 3σ detection limits for these elements were acquired in the both continuous and in the pulsed mode. Aqueous solutions of calibration standards (0.6 $ml.min^{-1}$) were delivered into a Scott spray chamber with a concentric nebulizer showing an efficiency about 6%. The produced aerosol was introduced by argon (0.3 l min^{-1}) perpendicularly into the plasma pencil operated in flowing argon (4 l min^{-1}). Electrical input power coming into the plasma was in the range of 120–140 W. To create a pulsed mode the carrying wave 13.56 MHz was internally modulated by a rectangular wave 22 kHz with duty cycle 90%. These electrical parameters guaranteed a high stability of the discharge. Rotational temperatures and electron number densities for the pencil under and without water load and sample load were calculated using OH spectra and H beta line and are very similar for both modes. Atomic lines of the elements above were well observable even if the rotational temperatures are relatively low about 1000 K. Intensities of the calibration lines in the continuous mode are lower than in the pulsed mode. Limits of detection are similar for both modes. Intensities of analytical lines of the elements, rotational temperatures and electron number densities along the discharge tube were acquired in 4 different positions in the range of 11–15 cm from the aerosol entrance. These results indicate that the continuous mode should be rather replaced by the pulsed mode in some applications.

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SIMULTANEOUS SYSTEM OF DP-LIBS AND LASER ABLATION ICP-OES

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The simultaneous DP-LIBS and Laser-Ablation ICP-OES setup was designed by utilizing a modified commercially available laser ablation system UP 266 Macro (New Wave). Laser ablation system UP-266 was used without any modification of the original optic. Specially designed ablation chamber was developed to allow combination LIBS, DP-LIBS and LA-ICP-OES technique. The first (ablation) pulse is fed on the sample surface through a window from above, as in the original configuration of the UP-266 system. The radiation of the second (re-heating) pulse with fundamental wavelength 1064 nm (Brilliant, Quantel) is focused parallel to the sample surface by 80 mm focal length glass lens through a second window from right side. The third window at the front side is then used for collection of laser induced plasma emission. Furthermore, ablation chamber is equipped with stage for sample height alignment. Both lasers are externally triggered using two digital delay generators DG 645 (Stanford Research Systems) which are initialized by starting pulses from UP 266 Macro laser module. The laser-induced plasma radiation is transported by a fiber optic system onto the entrance slit of a monochromator Triax 320 (Jobin-Yvon). ICCD detector (Jobin Yvon Horiba) or a photomultiplier (R928 Hamamatsu) gated by a laboratory-built control unit are employed as detectors. For the gate-time delay monitoring and time-resolved signal recording, a digital storage oscilloscope Tektronix TDS 1012 is used. Carrier gas is introduced into the ablation chamber through the mass flow controller and the ablated material is transported by polyamide tubing into the ICP-OES spectrometer iCAP6500 Duo (Thermo).

In preliminary results washout efficiency of new ablation chamber was verified. Basic signal comparison of DP-LIBS and double pulse LA-ICP-OES were studied on the urinary stone cross-section. Results demonstrate high sensitivity for both methods and high spatial resolution.

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CHARACTERIZATION AND QUANTIFICATION OF TiO_2 -NANO PARTICLES IN BODY CARE PRODUCTS USING LASER DIFFRACTION AND ICP-OES SPECTROMETRY

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The Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) was established by the European Commission in 2004 [1], in order to provide scientific advice on the safety of issues requiring comprehensive assessment of risks related to new technologies such as nanotechnology.

Nowadays nanotechnology is present in our daily life and the use of nano particles is common practice in many application fields such as nanotubes for textile applications, nanotechnology for sun screens, and nanoparticles in bodycare products. The influence of silver nanoparticles on the human body is evaluated in recent studies [2].

The distribution of nanoparticles in bodycare products such as sunscreens, shower gels and body lotions is evaluated using a nano particle size analyzer. The IG-1000 is using the induced grating method, which allows the determination of particles in the sub nano range. Thereby no cross-contaminations of foreign particles or agglomerates is influencing the measurements. No refractive index or special pH-value is required.

Furthermore a method has been developed and optimized for the determination of titanium in sunscreen lotions with different sun protection factors using ICP-OES.

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EVALUATION OF CALIBRATION TECHNIQUES IN THE DETERMINATION OF Pb IN GLASS SAMPLES BY DIRECT SOLID SAMPLING ATOMIC ABSORPTION SPECTROMETRY

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Solid Sampling Graphite Furnace Atomic Absorption Spectrometer (SS GFAAS) has developed recently, and samples can be introduced as a solid without dissolving in to graphite furnace directly in this technique. Thus dissolving step of the sample is avoided, the contamination risk, errors and analysis time are reduced.

In all comparative analytical techniques, calibration is one of the most important factors for the quality of the results. Since the matrix may affect the results in direct solid sampling atomic absorption spectrometry, it is a necessity to use suitable calibration material. In the SS GFAAS calibration can be made by using reference solutions or certified solid reference materials. Each of them has their own advantageous and disadvantageous.

In this study, the use of liquid standards and the use of NIST SRM 612 Glass Reference Materials for the calibration in the determination of Pb in glass samples with solid sampling graphite furnace atomic absorption spectrometry are investigated. The advantageous and disadvantageous of both techniques are discussed.

QUANTITATIVE ANALYSIS OF OXIDE GLASSES BY X-RAY FLUORESCENCE SPECTROSCOPY

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For the preparation of glasses and optimization of their properties it is necessary to know their chemical composition. We focused on application of XRF analysis for quantitative analysis of glasses. The samples for analysis were prepared by melting with dilithium tetraborate. The amounts of these chemical elements (expressed in form of congruent oxides) were analyzed: Si, Na, K, Ca, Mg, Pb, Al and Fe. Calibration curves were made by using the standards. To detect the corectness of the analytical method, there were observed the influence of used analytical line for each chemical element, the method used for determination of the intensity of spectral line, matrix effects and also the influence of conditions during the preparation of samples. The significance of listed influences was evaluated by the analysis of variance. Calibration curves were made by using the standards. After selection of appropriate conditions for analytical lines intensity measurement and optimalization of conditions for samples preparation by melting we specified the reliability intervals for particular oxides.

ASSIGNMENT OF A CHEMICAL PROPERTY TO THE VALUE OF A SPECTROSCOPIC ANALYTICAL SIGNAL

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Analytical chemistry represents a scientific branch giving answers to the following chemically aimed questions: **What?** (qualitative analysis), **How much?** (quantitative analysis), **Where?** (local and structural analysis), **How?** (speciation). **Analytical signal** corresponds to the experimentally determined value of a well measurable physical quantity depending on the analysed material property we look for. Owing to the experimental character of this dependence (uncertaity of measurement, its selectivity, ruggidness, etc.) it cannot be of functional character but only of a stochastic one. It therefore cannot be mathematically derived but only experimentally determined using **calibration process** in which the analytical signal of the analysed sample is compared with results obtained using calibration samples of identical type with known values for the analysed component (**Technics with more calibration standards)** or results for the analysed samples with added known amount of analyte (**Standard addition technics**). Absolute analytical procedures not needing any comparison with a known corresponding value for at least one calibration sample do not exist! The calibration plays therefore a crucial role in the whole analytical chemistry and a comprehensive amount of scientific work has allready been devoted to it. In the following lecture I therefore shall present at least in a restricted form some further approaches to the optimisation of calibration in spectrochemical analysis. Analytical calibration dependences should show **linearity** and homoskedasticity. Some linearization procedures and possibilities to ensure homoskedasticity will be presented.

The quality of a given calibration can be judged using the **reliability intervall** of its analytical calibration line. For to obtain a simpler handling the intervall of reliability we introduced the so called one sided generalized (standard deviation = 1 and tabellated value of Student´s distribution at the given probability = 1) reliability intervall. One of its properties enabling to find its minimum value corresponding to the optimal calibration value is that it lies at the arithmetical mean of the concentrations for all the used calibration standards. The choice of optimal calibration parameters in spectrochemical analysis is enabled also by the dynamic range of the calibratation restricted by the used analytical method which has to be selected according to the aim of the analysis. If **chemical characterization** of the samples is needed, methods with high dynamic range (e.g. ICP OES or MS are used) and logarithmic step of calibration sample concentrations (e.g. 1, 10, 100, 1000 etc.) covers a larger concentration range. The use of multielement standard solutions for the preparation of calibration standards is suitable. In the case of **technical control** analysis where approximate concentrations of unic components declared by technical standards are known allready before the analysis, analytical methods with lower dynamic range (AAS, Spectrophotometry etc.) and linear steps (e.g. 1, 2, 3, 4 etc.) in calibration concentrations give better results. The best calibration results can be obtained with standard samples of different concentrations for each element which mean value corresponds to the expected content. The presented advises how to proceed at calibration are supported by corresponding one sided generalized reliability intervalls, forming so a good help for the used calibration standards having for each analysed element the arithmetical mean of concentrations equal to the expected content.

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A NEW SPECTROMETRIC METHOD AND INSTRUMENT TO FOLLOW THERMAL PROCESSES

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The method and an equipment based on a new principle can be used for the continuous following of thermal transformation of solid, liquid and gaseous materials using optical spectrometric method. The applied method is based on that a homodisperse aerosol with particles in the 0 – 1 μm range (nanoparticles) or a gaseous state of a compound is guided through a controlled high temperature space, transformations from solid phase to excited ion occur, in accordance with the characteristic thermal steps of the analyte.

The equipment is a special oven which can be heated to 2000°C in a controlled way and ensures a continuous vertical passing of the tested materials. A nearly homogenous particle size distribution dry or wet aerosol resp. gas is directed upwards between two vertical plane walls made of thermal resistant material which are situated at 10 mm from each other. The sample upwarding between the two vertical walls of the oven is horizontally enlighted by an 1 – 3 mm diameter light beam. Scanning the whole (200 mm) height of the oven with this light beam, the light scattering, molecule formation, atomization and ionization of the materials passing through can be followed. Different chemical materials have different thermal properties (melting point, boiling point, evaporation, sublimation, decompositon temperature, energy of thermal dissociation, atomization, excitation, ionization). These changes and transformations occur at different observation heights which are followed by optical methods.

This is a new thermoanalytical method, to investigate solids, liquids and gases. With this method we can discover a real mechanism of atomization and explain of thermal background of matrix effects in flame, plasma and graphite furnace. Element speciation can also be realized on the thermal differences of compounds of an elements.

The new method was used to follow the thermal decomposition, atomization of inorganic and organic compounds of mercury, cadmium, zinc, lead and sodium.

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UNDERSTAND INTERFERENCES WITHIN THE APPLICATION NEEDS

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The SPECTRO MS is a double-focusing sector field mass spectrometer based on a Mattauch-Herzog geometry with a newly developed ion optic and pioneering detector technology. It is the only instrument available on the market today that is capable of simultaneously measuring the complete mass range used for inorganic mass spectrometry from ^{6}Li to ^{238}U with a permanent ion beam going to the detector.

In this presentation examples are presented of solving interference issues using the unique capabilities of the mentioned instrument.

There is a lot of discussion about the performance of different interference reduction tools used in ICP-MS. The instrument offers numerous analytical benefits to deliver high precision and accuracy of analytical results. With the such analytical instrument the corrections are straight forward and only limited by the application and it’s requirements. The conclusion is that it is important to understand the interferences and find simple and robust solutions within the application needs.

DETERMINATION OF RARE EARTH ELEMENTS IN ELECTRONIC WASTE USING ICP-OES SPECTROMETRY

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Rare earth elements (REE) according to IUPAC definition are a selection of seventeen chemical elements from the periodic table. In contrast to their name the REE are much more present in the earth crust than expected, but because of their geochemical properties rare earth elements are typically dispersed and an economic treatment of rare earth minerals and ores is difficult. Nowadays the biggest ore deposits of REE are located in China (Mongolia) and China is controlling the global REE market.

As REE are required in the electro- and electronics industry the demand for special metals used in the manufacturing of “high tech” products is booming and in European countries the electronics trash could be worth to be recycled in order to be independent from expensive imports [1].

Experimental work has been done on electronic waste material such as mobile phones, notebook PC´s, electronic boards, batteries and more. Samples have been prepared using crushers and mills, homogenized and finally digested in a microwave digestion procedure.

The sample solutions have been measured using qualitative and quantitative analysis on a simultaneous ICP- OES spectrometer. The ICPE-9000 has been optimized for the determination of rare earth elements. Experimental data will be presented in comparison with alternative techniques.

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SPECTROSCOPIC CHARACTERIZATION OF ATMOSPHERIC PRESSURE PLASMA PLUM REGARDING GEOMETRICAL ASPECTS

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There have been several investigations reporting the use of non-thermal atmospheric pressure plasma sources for surface treatments [1,2], medical sterilization [3,4], wound care and cancer therapies. Chemical reactive species play the main role in this surface processing, therefore, identification of the responsible reactive species using optical emission spectroscopy is our task in this work. On the other hand, the geometrical aspects of the plasma head could play important role in such applications. In this work, we investigate the change in radiation emitted by the reactive species as a function of geometrical aspects of the plasma head. In this regard, we measured the emitted intensity from excited states of NO, second positive branch of N_2, singlet oxygen, atomic oxygen, OH, CN and meta-stable argon. It was revealed that the intensity of OH radicals increases after diffusing the plasma jet into the ambient air. The out put nozzle diameter controls the plasma jet length, drastically. We found that there is an optimum value for the ratio between input and out put nozzle diameter in order to maximize the jet length as well as prolongation the emission length. The flow dependencies were also investigated for the different nozzles as well as for a tube plum. It was revealed that in the case of an open tube, the plasma volume as well as radiation intensity is greater than that of a tube having a nozzle.

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SERRS SPECTRAL BEHAVIOR OF MODIFIED TOLLENS METHOD PREPARED Ag NANOPARTICLES AND THE EFFECT OF HCl

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Recently, we have demonstrated the unique properties of silver nanoparticles prepared by modified Tollens method (using glucose as a reductant) and employed them in the surface-enhanced resonance Raman scattering (SERRS) spectral detection of a free-base porphyrin species [1]. In the present contribution, we would like to show a detailed study concerning HCl effect in the final concentration range of 0.1 mM – 0.1 M on the characteristics of these nanoparticles. Indeed, we can directly compare our results obtained on modified Tollens method prepared Ag nanoparticles (using glucose as a reductant) with those previously published on borohydride-reduced nanoparticles [2]. Investigation techniques used by us in the present work have included UV-visible absorption spectroscopy, dynamic light scattering, zeta potential measurements, transmission and scanning electron microscopies, energy dispersive X-ray spectrometry, and surface-enhanced resonance Raman scattering spectroscopy. Namely, the results of the last mentioned spectroscopic technique can be thoroughly discussed. It has turned out that there are distinct differences in HCl effect on modified Tollens method prepared vs. borohydride-reduced Ag nanoparticles. The differences can be related to the specificity of stabilizing species surrounding Ag nanoparticles prepared by two completely different chemical syntheses.

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RESONANCE RAMAN AND SURFACE-ENHANCED RESONANCE RAMAN EXCITATION PROFILES OF $[Fe(TPY)_2]^{2+}$ ON Ag NANOPARTICLE SURFACES

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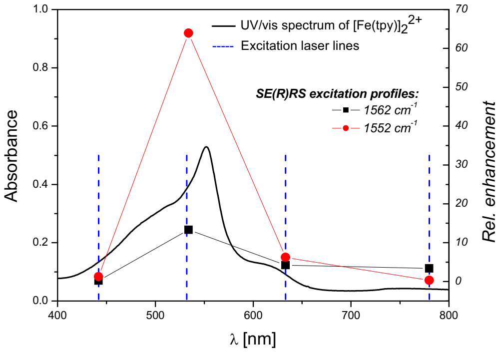
2,2':6',2"-terpyridine (tpy) is known as a suitable chelate ligand for oligomeric components of metallo/supramolecular polymers (MSP). Although the iron (II) - tpy complex is one of the frequently used coupling component in MSP, both the tpy and $[Fe(tpy)_2]^{2+}$ complex belongs to the less studied polypyridine molecule and|or complexes by means of Raman spectroscopy. The $[Fe(tpy)_2]^{2+}$ complex exhibits a broad asymmetric band located around 552 nm, which is responsible for the deep purple colour. This relatively intense band is due to a spin allowed d → π^* ^{1}MLCT (metal-to-ligand charge transfer). According to the analogy with the $[Ru(tpy)_2]^{2+}$ complex, the shoulder at the low energy side can be assigned to direct excitation into ^{3}MLCT states [1]. In this work, the SERRS (surface-enhanced resonance Raman scattering) excitation profiles of $[Fe(tpy)_2]^{2+}$ complex adsorbed on Ag nanoparticles and RRS (resonance Raman scattering) excitation profile of the complex in solution have been studied. Four different wavelengths encompassing both the singlet and triplet MLCT bands as well as the off-resonance state were used (Fig). Excitation profiles of 1552 cm^{-1} and 1562 cm^{-1} bands of Ag colloid/$[Fe(tpy)_2]^{2+}$ system are shown in Fig. Four groups of bands with different excitation profiles were observed: group (i) shows sharp intensity maximum at 532 nm and intensity decrease for higher wavelengths, (ii) shows sharp intensity maximum at 532 nm and intensity increase for 780 nm excitation, with a local minimum at 633 cm^{-1}, (iii) shows monotonic intensity increase toward the red spectral region, (iv) is represented by one band 646 cm^{-1} with maximum of excitation profile at 633 nm. Since the differences between the shapes of excitation profiles are observed also for RR spectra of the complex, they are attributed to the differences in the resonance enhancement experienced by individual vibrational modes upon 532 nm (^{3}MLCT) and 633 nm (^{1}MLCT) excitations. To enable explanation of the different shapes of SERRS and RRS excitation profiles of different spectral bands, the polarization measurements and the depolarization ratios calculations of $[Fe(tpy)_2]^{2+}$ complex were performed.



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COMPARISON STUDY OF LASER ABLATION BASED METHODS FOR ANALYSIS OF KIDNEY STONES

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The distribution of major, minor and trace elements in urinary stones can provide information on their formation. Therefore, analytical methods, which can map the distribution of these elements, should be used. The most common methods include Laser-Induced Breakdown Spectroscopy (LIBS) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS).

Investigated urinary stone were cut, sealed into a resin and the cross-section of the sample was polished and was mapped by laser-ablation based analytical methods. On the base of these measurements, for samples containing whewellit or weddellit (or both of these minerals), the correlation between calcium and carbon distribution was confirmed. The correlation between magnesium and phosphorus can be attributed to the presence of struvite. The correlation between calcium and phosphorus distribution indicates the presence of apatite. The correlation of zinc, sodium or potassium distribution with phosphates was also observed. They are probably the chemical elements that can be associated with apatite. On the other hand increased content of copper was observed in association with uric acid.

Quantification of laser ablation based methods is still very problematic and these methods are often used only for qualitative elemental mapping. There are no commercially available standards, which would correspond to urinary calculi matrix. Internal standardization is also difficult, mainly due to different crystalline phases in one kidney stone.

The aim of next study is to demonstrate the calibration capabilities and limitations of laser ablation based techniques. Calibration pellets were prepared from human urinary calculi with phosphate, oxalate and urate matrix. For this comparative study the most frequently used laser-ablation based analytical techniques were chosen, such as LIBS and LA-ICP-MS. Moreover some unconventional techniques such as simultaneous LIBS – LA-ICP-OES and laser ablation (LA) – LIBS were also utilized.

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SOLID PHASE EXTRACTION OF LEAD AND COPPER ON A NOVEL BLOCK COPOLYMER DISK AND FLAME ATOMIC ABSORPTION SPECTROMETRIC DETERMINATION OF ITS IN WATER AND FOOD SAMPLES

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The determination of trace metal ions in water and environmental samples is restricted by two main difficulties: the very low concentration of heavy metal ions, which may be lower than the detection limit of flame atomic absorption spectrometry (FAAS) and the interfering effects of the matrix. Solid phase extraction is the one of the sensitive, fast and economic preconcentration method for the trace analyte ions in the various materials.

A suspension containing 75 mg of Polyhydroxybutyrate-b-Polydimethyl siloxane (PHB-b-PDMS1), a block copolymer in 50 ml of 5% (w/v) sodium dodecyl sulphate was filtered through a 47-mm-diameter cellulose acetate membrane filter paper with a vacuum pump. The disk was washed with methanol and water successively. The disk was allowed to dry at room temperature. Sudan III dye matter was used as ligand. Various analytical parameters including pH, ligand amount, eluent type and volume, sample volume, flow rates were optimized. The effects of concomitant ions on the retentions of the analytes were also examined. Preconcentration factor was found as 67. Relative standard deviation was found lower than 10%. The accuracy of the method was confirmed by certified reference materials. Optimized method was applied to various water and food samples from Turkey.

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ELIMINATION OF CHLORIDE INTERFERENCES IN ICP-OA-TOF-MS ANALYSIS

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The analysis of samples with complicated matrix of high salt content by using ICP-MS instruments may be difficult due to the formation of polyatomic adducts originating from matrix species and plasma gas. These adducts cannot be differentiated from the analytes of interest using conventional low-resolution mass spectrometers and thus have to be dealt with by either using an expensive double-focusing sector-field analyzer or employing a collision/reaction cell, which even though being commonly used is a time consuming process. In this work, we focused on identification and quantification of polyatomic interferences originating from different chloride matrices encountered on inductively coupled plasma orthogonal acceleration time of flight mass spectrometer (ICP-oa-TOF-MS) and tested both inorganic and organic compounds to suppress them. The selected organic acid was successfully applied to analysis of real samples, namely seawater and urine.

LASER ABLATION IN ANALYTICAL CHEMISTRY

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Laser ablation in connection with inductively coupled plasma mass spectrometry (LA-ICP-MS) represents one of the most sensitive methods for elemental analysis of solids. It allows analysis of all types solid samples regardless of their conductivity/non-conductivity, optical properties... Thus, it can be analyzed wide range of materials; steels, ceramics, geological samples, biological materials (leaves, tumors, teeth, bones...) and archaeological materials.

Contrary to analysis of solutions by means of ICP-MS, LA-ICP-MS allows analysis without decomposition of solid sample, elemental mapping and local microanalysis.

We present application of LA-ICP-MS for analysis of geological samples (mapping granitoids samples), biological samples (mapping tumor tissues), steel samples (study of corrosion processes) and archaeological samples (provenience of obsidians).

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Z-GFAAS WITH VARIABLE MAGNETIC FIELD IN THE SOLUTION AND SOLID SAMPLE ANALYSIS

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The graphite furnace atomic absorption spectrometry with Zeeman effect background correction (Z-GFAAS) is old as a technique [1]. The possibility of the modulation of the magnetic field strength [2] during atomization allows to improve the analytical sensitivity and the linear working range. The Z-GFAAS instrument of the 3rd generation (Analytik Jena ZEEnit 700 AAS) brings the ''three-field mode" or "3-F-mode'' (measurement at zero, maximum and medium magnetic field strength), which allows the sensitivity adaptation for higher element contents. At the 3rd generation instrument device, the magnetic field strength can be freely changed between zero and maximum sensitivity level. Alternatively, it is possible to use the instrument in the two-field mode (2-F-mode), 3-F-mode or dynamic mode (D-mode) [3]. The D-mode is the term for combined (software) evaluation of intensities of 3-F-mode. The 3-F switch mode contains all the information needed for simultaneous evaluation at the 2-F and sensitivity reduced 3-F-mode and its combined intensity evaluation (D-mode) allows the simultaneous measurement and calculation of analytical curves of different sensitivities. By this way, it is possible to expand the usual working range of the AAS spectrometry over 3 orders of magnitude [4,5,6]. Direct solid sampling in the Z-GFAAS methods brings next analytical capabilities of engineering comfort of the routine analytical measurements. In 3-F and D-mode, the higher amounts of elements are possible to determine without wet digestion of solid samples. The measurements were based on calibrations using certified reference materials of appropriate origin. The low matrix effects were observed under the optimized conditions. In this work will be presented the basic information about the technique and basic validation characteristics of the selected elements in the interesting solution and solid sample matrices.

Acknowledgement: Grant project VEGA 1/1096/12//2012-2014.

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ANALYTICAL STRATEGY FOR MULTI-ELEMENTAL LASER ABLATION ICP MS INVESTIGATIONS OF PIGMENTS FROM UNIQUE, HISTORICAL OBJECTS

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Laser Ablation ICP MS is recognized as a micro-destructive method allowing direct sampling from solids, accompanying by its multielemental feature at ultratrace level. Thus LA ICP MS is regarded as very promising analytical methods, which could be applied for the investigation of works of art in respect of their protection and conservation. It could be therefore exploited in analysis of unique objects, from which eventual sampling is acceptable after careful consideration of the influence of the whole analytical procedure on the overall value of the analyzed objects.

Laser ablation can be executed either on the surface of the entire object or on the micro-samples gently taken from the object prior to measurements. Direct laser ablation from objects offers possibility to obtain not only quantitative information about trace, minor or major elements but also their distribution over the selected area at the surface or reconstruction of their depth profiles. The use of micro-samples of the investigated object allows to collect various information by analyzing sampled material by several consecutive instrumental techniques allowing final interpretation of its feature.

In this presentation the development of a multi-instrumental analytical strategy for identification of historic pigments will be presented with special attention to laser ablation ICP MS and its role in the whole analytical protocol. Selected case studies will illustrate the evolution of the final approach of consecutive use of Raman spectroscopy, SEM-EDS and laser ablation ICP MS in chemical identification of pigments from archaeological mural paintings, coffins, icons as well as oil paintings.

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STUDY OF MOLTEN FLUORIDE SALTS TREATMENT ON METALLIC SAMPLES BY MEANS OF LA-ICP-MS

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was applied to the study of corrosion of candidate structural materials for a nuclear reactor cooling circuit. Molten LiF-NaF, LiF-NaF-ZrF_4 salts are examined as a cooling medium in Molten Salts Reactor system (MSR). This new type of nuclear power plant provides greater safety and economic of whole system. The structural materials need to be resistant to high temperatures (~500°C) and extremely corrosive environment, which molten fluoride salts represent.

Different types of structural materials were examined (pure Ni, Ni based alloys, pure Fe with Ni-coating). Tested materials were exposed to molten fluoride salt treatment at temperature of 680°C. Parts of studied materials were cut out, polished by diamond paste and embedded into epoxy resin. The material corrosion changes were studied by mapping the sections of sample walls.

Quantification procedure with external calibration standards is not possible in case of corroded sample due to different ablation rate, hence normalization method which uses a total sum of signals of isotopes was employed. Fluorine signal was calculated from stoichiometry of fluoride salts and Na, Li, Zr counts. Thickness of affected surface was determined and created 2D maps show constituent elements decrease (in case of Li, Na, Zr increase) in the sample (i.e. corrosion). Penetration of molten salts into specimen material was proved.

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ELEMENTAL ANALYSIS IN THE INDUSTRY AND RESEARCH

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HIDEN Analytical – mass quadrupole spectrometers

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ICP-AES DETERMINATION OF SELECTED NUTRIENTS IN ARONIA (*Aronia melanocarpa*) BERRIES AND INFUSIONS

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Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used for the determination of the elemental composition of Aronia berries also called black chokeberries (*Aronia melanocarpa*). Black chokeberries compose high amounts of anthocyanins, phenols, antioxidants, vitamines and minerals. Aronia berries originate from the eastern parts of North America and East Canada and came to Europe occurred around 1900 via Germany to Russia.

Black chokeberry preparations were first used to inhibit chemically induced cancer in esophagus and colon. The berries represent a promising therapeutic source. Whereas the organic compounds are well studied, there are only rare data on the mineral composition of the chokeberries.

Thus the study is focused on the determination of nutrients and toxic elements in aronia fruits and infusions, namely Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr and Zn.

To determine the total amount of nutrients in the whole fruit the Aronia samples were dried, homogenised and digested in a closed microwave assisted digestion system using nitric acid. Infusions were prepared with hot distilled water using different decoction times to find the best extraction conditions for the elements of interest.

The ICP-AES method was validated and optimized for the determination of selected elements in the digest solutions of the berries and in the infusions. The nutrients Ca, K and Mg are present in the fruits (dried matter) at mg/g level, whereas the other elements are in the μg/g level or even below the limit of detection (Cd, Co, Ni, Pb).

Based on the results obtained for the total metal content in the berries and the concentrations of the infusion the extraction yields were calculated. They range from 4 up to 44%. Thus Aronia berries as well as infusions derived from them are a good dietary source of essential metals in addition to the organic compound contained.

MERCURY ASSOCIATED WITH SIZE-FRACTIONATED URBAN PARTICULATE MATTER: THREE YEARS OF SAMPLING IN PRAGUE, CZECH REPUBLIC

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Mercury associated with particulate matter comprises a minor portion of the total atmospheric mercury beside gaseous elemental mercury and reactive gaseous mercury. However, it plays a crucial role in the cycle of this element. The aim of this study was to develop and apply techniques useful for characterization of mercury forms associated with size-fractionated urban particulate matter (PM) collected during three years in Prague.

PM samples were taken in Prague's Congress Centre, which is localized near to busy highway and surrounding air is also affected by local domestic heating. The material was collected from air-condition filters three times in years 2009, 2010 and 2011 with a sampling period of 10 months. The collected material was sieved into separated physical fractions: 507−119 µm, 119−63 µm, <63 µm and sub-fraction <25 µm for the study of distribution of mercury forms among these fractions of particles. Five-step sequential extraction procedure was conducted for separation of mercury compounds into the fractions with similar behaviour. Beside the sequential extraction, thermal desorption from solid-phase was performed for estimation of volatile mercury content as additional technique. Particulate matter was also visualized using electron microscopy.

By sequential extraction procedure, mercury forms were divided into following fractions with similar solubility and thus, similar bioavailability: 1) water soluble mercury, 2) mercury extractable by slightly acid solutions, 3) mercury bound to humic substances, 4) elemental and complex-bound mercury, 5) mercury(II) sulphide and 6) residual mercury. For assurance what species are extracted in each step, artificial samples from pure compounds were prepared and extracted. Interesting results about variability of mercury forms among the sampling periods were obtained. Whilst the water soluble fraction presented the smallest part of mercury contained in all samples, the main form of mercury was in the fourth fraction. In order to distinguish between the elemental and complex-bound mercury which are the main constituents of fourth fraction, thermal desorption was performed. The content of elemental mercury was assessed after its thermal release.

The combination of presented methods provides characterization of mercury contained in samples of particulate matter.

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P-01

A NEW APPROACH FOR THE DETERMINATION OF FLUORINE IN WATER SAMPLES VIA MOLECULAR ABSORPTION OF BARIUM MONO-FLUORIDE USING HR-CS-ETAAS

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This study describes the determination of fluorine in water samples via the rotational fine structured molecular absorption of barium mono-fluoride (BaF) at 495.088 nm using a high-resolution continuum source electrothermal atomic absorption spectrophotometer. In order to generate BaF in the gas phase of graphite furnace, samples were pipetted together with barium as its nitrate form. The effects of experimental conditions and instrumental parameters such as BaF wavelengths, the amount of Ba, graphite furnace program, coating the graphite tube and platform with Zr and Ir and the use of modifier (Pd, Mg and Pd+Mg) on the sensitivity and/or linearity were investigated. In the presence of 40 µg of Ba, a perfect linearity up to 0.1 µg of F was maintained applying a pyrolysis temperature of 900ºC and a molecule forming temperature of 2200ºC in pyrolytically coated platforms. The standard addition curves applied to the water samples were perfectly linear as well and the slopes of the curves i.e. the sensitivity, were not significantly different from that of linear calibration technique. Therefore, 40 µg of Ba was used for the determination of fluorine in real water samples. Using the optimized parameters, the accuracy and precision of the method were tested by analyzing certified reference waste water. The results were in good agreement with certified value. The maximum limit of detection and characteristic mass of the method were 12.0 pg and 8.8 pg of F, respectively which showed small discrepancies from day to day. Finally, F contents of several water samples were determined applying both linear calibration and standard addition techniques. In general, the F concentrations found by the both techniques were not significantly different from each other as well as from the values given on some water bottles.

P-02

NON-POLARIZED LIGHT ABSORPTION IN PURE, DOPED WITH THE NITRITE IONS, AND PHOTOLYZED KNO_3 CRYSTALS

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It is common knowledge that the optical density in biaxial crystal necessary to measure with the polarized light beam directed both parallel and perpendicular to *z* axis. Thus the crystal it is recommended to specifically cut and precisely oriented with respect to the polarized light beam. So, suitable equipment to polarize light and to determine the orientation of optical axes as to polished crystal faces should be available. For practical purposes it would be more convenient to use non-polarized light and the crystals with natural faces. The goal of the present paper is to study non-polarized light absorption in pure, doped with the nitrite ions, and photolyzed biaxial KNO_3 crystals.

Both pure and doped with the nitrite ions KNO_3 crystals were grown by slow evaporation of saturated aqueous solutions. The plates (1 cm × 0.5 cm) were polished parallel to the crystallographic *z*-axis of the KNO_3 crystals.

The samples were photolyzed at room temperature with a low pressure mercury lamp. An analyzing non-polarized light beam was directed perpendicularly to the surface of the plates. The spectra were registered by means of a “Shimadzu UV-2450” spectrophotometer.

Dependencies of optical density in non-polarized light from thickness of pure (registration at 253.7 and 300 nm) and doped with the nitrite ions KNO_3 crystals (registration at 355 nm) are linear when $A < 0.2$ or $A > 0.5$ only. The intercept for linear part of curve in the region of high optical densities is equal to ~0.3. The observed effect concerned with the use of non-polarized light only.

The photolysis of pure KNO_3 crystal results in a new band with its maximum at 350 nm, overlapping the band of the non-photolyzed KNO_3 crystal. The photolyzed time increase leads to the shift of the band maximum. The difference bands calculated as the difference between the photolyzed KNO_3 crystal spectra and the initial spectrum results in the change of the shape in a short-wavelength edge. For the short time of photolysis the shape of spectrum described by Gaussian, but for the long time the one differs from it. Because the photo-induced optical spectrum is single band due to peroxynitrite only, we can state that these effects cause by the non-polarized light used.

The use of non-polarized light beam directed perpendicularly to the *z* axis of a biaxial crystal allows us to determine $\mathbf{K}^{\perp}$ and $\mathbf{K}^{\|}$, separately, without complex equipment. At the same time the analysis of the difference spectrum results in erroneous conclusion about its shape.

P-03

OPTICAL EMISSION SPECTROSCOPY OF PE AND PE HF CVD PROCESS OF CARBON NANOTUBES GROWTH

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Electric arc discharge, laser ablation and catalytic chemical vapor deposition are processes mainly used for synthesis of carbon nanotubes (CNTs). The advantages of CVD (chemical vapor deposition) are the relatively low temperature and the controlled and localized growth. Using modifications of the incoming CVD gas mixture by plasma (plasma-enhanced catalytic CVD or PE CCVD), with hot-filaments associated or not with plasma CVD (PE HF CCVD) could lower this temperature even more. [1]

Plasma-enhanced catalytic chemical vapor deposition techniques have been widely developed in the past years for carbon nanotubes or carbon nanofibers (CNFs) production. This method displayed great advantages over the classical thermally-activated CVD processes. PE CCVD provides high carbon selectivity, large rate of growth, growth on a flat surface, better control of the growth parameter, the possibility to growth localized and vertically aligned CNTs and more recently the possibility to achieve growth on important substrate like copper or stainless steel and the control of the CNTs size down to few or single wall carbon nanotubes (SWCNTs). [2]

OES (optical emission spectroscopy) was used for plasma diagnostic during CVD growth processes of carbon nanotubes. The gas mixture consisted on the precursor gas (C_2H_2), small addition of NH_3 and H_2 as vector gas. Two different activation modes of CVD, such as plasma enhanced (PE) and plasma enhanced hot filament (PE HF) CVD were examined and compared using Andor Mechelle ME 5000 optical emission spectrometer equipped with intensified CCD camera Andor iStar. Characteristic plasma temperatures (electron and gas) were evaluated from Balmer series and from H_2 molecular emission spectra.

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P-04

STUDY OF HYDROGEN-ARGON HELICAL RF DISCHARGE

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Helical discharge has been used to study of hydrogen-argon RF plasma generated at 27 MHz. Aim of this study was an investigation of this kind of plasma source as hydrogen emission vacuum UV (VUV) line radiation at 121.56 nm (Lyman-α). Discharge has been studied in two quartz discharge tubes with diameter 6 mm and 21 mm, respectively at pressure 160 mTorr. In the presented contribution integrated optical signal from the resonators axis was measured for argon admixture ranging from 0% to 80%. Gas temperature has been determined from emission of molecular hydrogen Fulcher-α band ($d^3\Pi_u^- – a^3\Sigma_g^+$). Density of atomic hydrogen has been investigated by optical emission actinometry using lines from Blamer series and compared with VUV hydrogen line emission of Lyman-α. Addition of argon to the mixture increased atomic hydrogen density and intensity of the Lyman-α line. Measurements were finally compared with kinetic model.

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P-05

A NEW CROSS-SHAPED GRAPHITE FURNACE FOR REDUCTION OF INTERFERENCES IN 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 sample was injected manually inside one part of the crossed furnace in a way perpendicular to light path. The analyzed sample then heated gradually under slow heating conditions with ramp time ranged from 5 to 8 seconds in the cross shaped furnace then pushed into the measuring zone using the original inner and additional purge gas. The sample is adsorbed strongly on porous graphite or ballast body, evaporated and transferred with different rates at different temperatures during the temperature program allowing the separation of analyte and matrix signals.

Analysis of some trace elements such as in standard urine sample (Seronorm 2525) showed complete to partial separation of analyte and background signals with good sensitivity and repeatability.

P-06

DETERMINATION OF TRACE AMOUNTS OF CADMIUM BY FLAME ATOMIC ABSORPTION SPECTROMETRY AFTER PRE-CONCENTRATION USING SILICA GEL COATED WITH SCHIFF'S BASES

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A method for preconcentration of cadmium ions is proposed by using minicolumns packed with silica gel modified by two different Schiff's bases [N,N'-Bis(salicylidene)-2,2-dimethyl-1,3-propylenediamine or (Bis- (2-Hydroxyaceto-phenone)-2,2-dimethyl-1,3-propanediimine)]. The retained analyte onto the sorbent was eluted with a small volume of nitric acid. The cadmium ions in the eluted solution were determined by flame atomic absorption spectrometer (FAAS). Two Schiff's bases different in structure have been used to compare the effect of the structure on the separation efficiency. Different interfering factors, like pH of the sample solution, sample volume, and amount of Schiff's base were studied to optimize the conditions for the pre-concentration of cadmium ions in aqueous solutions. Additionally, the matrix effect of some different compounds of the sample has been also investigated to attain the separation efficiency of the sorbents. One of the main benefits for the total analytical procedure is the fact that concentration factors of up to 100 could be achieved.

P-07

DIRECT DETERMINATION AND QUANTIFICATION OF SULPHUR SPECIES IN SOLID FUELS BY ETV-ICP OES - ECONOMICAL AND ENVIRONMENTALLY FRIENDLY

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The presence of sulphur in solid fuels like coal and biomass is highly relevant for the processing industry. Depending on the current bond form of sulphur species (sulphate minerals, sulfide minerals - predominantly pyrite - and the organic matrix) in energy resources, it forms heat transfer degrading deposits during the process or leads to deactivation of catalysts and high - temperature corrosion of materials which are used. In addition to the problems during processing the knowledge of the distribution of sulphur within the coal and its mineralogical impurities and separated conversion products (pyrolysis or ash) is required to determine the suitability of a particular coal treatment or cleaning strategy. There is a strong effect of the different major species of sulphur on the fouling behavior in the boiler and the desulphurisation efficiency, that's why the total sulphur content will not provide sufficient information to assess the suitability of a specific method.

Therefore the quantitative determination of the different sulphur species is imperative. The traditionally method is a multistage extraction process. This standardised procedure requires very complex equipment, preparative effort, is very time consuming and costly. That's why a rapid-process analysis is precluded. A further analysis technique is to combust the sample in oxygen and - depending on the combustion temperature - to determine the released SO_2 by infrared spectroscopy absorption measurement. The disadvantage of this principle is the impossibility of simultaneous detection of other elements.

For a better understanding of the element release during the thermo-chemical conversion, the Institute of Analytical Chemistry explores the applicability of element speciation in solids by ETV-ICP OES. This work is part of the BMBF funded project German Centre for Energy Resources (DER) in cooperation with Virtuhcon and the department Research and Development of RWE power. By ETV-ICP OES it is possible to analyse coal samples or its processing products within a few minutes. Apart from the determination of the total content it is possible to get information about the species of an element by the different release of elemental forms in relation to temperature. Especially sulphur, where a variety of peaks can be observed in timescan, gives rise to the assumption, that different species are released at different temperatures.

The presented research shows the possibility of qualitative and quantitative determination of sulphur species by the fast, economical and environmentally friendly solid sampling method – ETV-ICP OES.

P-08

SELENIUM CONTENT IN WHEAT AND ESTIMATION OF THE SELENIUM DAILY INTAKE IN DIFFERENT REGIONS OF ALGERIA

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In this work, we have measured the selenium content in wheat produced locally in eight different regions of Algeria from East to West, and we have established the annual consumption of selenium for five socioprofessional categories. Instrumental Neutron Activation Analysis is used. The selenium levels in wheat samples varied from 39 (Tiaret) to 92 µg/kg (Khroub), with a mean value about 56 µg/kg. The mean of selenium daily consumption per person in the eight regions varied from 39 to 52 µg/day which is close to the minimal FAO recommendation.

P-09

MOLECULAR ANALYSIS OF POSSIBLE LIGANDS AND RECEPTORS RESPONSIBLE FOR INTERACTION BETWEEN *Francisella* AND BRAIN MICROVASCULAR ENDOTHELIAL CELLS

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Francisella tularensis is able to adhere to various types of the cells, including macrophages, endothelial or epithelial cells etc. Adhesion of *Francisella* is the basic event in the crossing of bacteria across various biological barriers. Many pathogens adhere to the barrier cells, mediated through adhesion molecules, and evoke events required for their translocation across cell barriers. Molecular principles of invasion of blood-brain barrier (BBB) by *Francisella* are still unknown. Present study is aimed at investigation of the molecules responsible for adhesion of *Francisella* to the brain microvascular endothelial cells (BMEC). Series of experiments performed to search protein candidates involved in adhesion of *Francisella* to BMEC, showed that type IV pili subunits (PIlE4 and PilW) of *Francisella* and ICAM-1 of BMEC might be the potential candidates. Type IV pili are important virulence factors in numerous bacteria, such as *Neisseria* and *Pseudomonas*. Gil et al. [1] have shown that *pilE* subunits (PilE1-PilE5) are homologous to *pilA (P. aerigunosa)* and *pilE (N. meningitidis),* which are involved in adhesion processes. To confirm interaction between type IV pili subunits and ICAM-1, his-tagged form of PilE1, PilE3, PilE4, PilE5 and PilW were prepared and hybridized with recombinant ICAM-1 (reverse line blot hybridization assay), wherein only PilE4 protein, but not others, interacted with BMEC. PilE4:ICAM-1 interaction was then confirmed by pull down assay. His-tagged form of PilE4 was bound on nickel affinity beads and hybridized with ICAM-1. Complex was eluted and subjected directly for MALDI mass spectrometry. Mass spectrometry clearly showed presence of His-tagged PilE4 of *F. tularensis* (peak ~41.9 kDa) and its interacting partner ICAM-1 (peak ~57.4 kDa). Results of pull down assay coupled with MALDI mass spectrometry confirms that PilE4, but not PilE1, PilE3, PilE5 and PilW, might play potential role in adhesion of *F. tularensis* LVS to host cells and is crucial for pilus-facilitated adhesion to BMEC.

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P-10

DEVELOPMENT OF SIMPLE AND RAPID ELUTION METHODS FOR PROTEINS FROM VARIOUS AFFINITY BEADS FOR THEIR DIRECT MALDI-TOF DOWNSTREAM APPLICATION

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Commercially available desalting techniques, necessary for downstream MALDI-TOF analysis of proteins, are often costly or time consuming for large-scale analysis. Here, we present techniques to elute proteins from various affinity resins, free from salt and ready for MALDI mass spectrometry. We showed that 0.1% TFA in 50% acetonitrile or 40% ethanol can be used as salt-free eluents for His-tagged proteins from variety of polyhistidine-affinity resins, while washing of resin beads twice with double-distilled water prior to the elution effectively desalted and recovered wide-range-molecular size proteins than commercially available desalting devices. Modified desalting and elution techniques were also applied for Flag- and Myc-tag affinity resins. The technique was further applied in co-precipitation assay, where the maximum recovery of wide-range molecular size proteins is crucial. Further, results showed that simple washing of the beads with double distilled water followed by elution with acetonitrile effectively desalted and recovered 150 kDa factor H protein of the sheep and its binding partner ~30 kDa BbCRASP-1 in co-precipitation assay. In summary, simple modifications in the desalting and elution strategy save time, labor and cost of the protein preparation for MALDI mass spectrometry; and large-scale protein purifications or co-precipitations can be performed with ease.

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P-11

QUANTIFICATION OF BIOACCUMULATION AND BIOVOLATILIZATION PROCESSES USING ICP OES AND CV AAS

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The mobility of various substances in the natural environment can be affected by many factors, microorganisms also play an important role. The bioaccumulation and biovolatilization are important processes ongoing in the biogeochemical cycles of substances. In the process of biovolatilization the inorganic compounds of metals and metalloids are transformed into volatile organic forms in the presence of certain microorganisms. For bioaccumulation, a substance gets into the inside of living cells, where it binds and is stored in different structures or converted into another form.

In this experiment the species of filamentous fungus *Scopulariopsis brevicaulis* were used. Processes of bioaccumulation and biovolatilization of arsenic, antimony, selenium, tellurium, thallium, mercury and bismuth in various oxidation stages by the biomass of this fungus from aqueous solutions were performed in the laboratory conditions. The aim was to quantify the ability of *S. brevicaulis* to bioaccumulate and biovolatilizate these elements. Biovolatilization and bioaccumulation processes were conducted for 30 days in Erlenmeyer flasks with liquid culture medium, in which the fungus was cultivated, supplemented with the corresponding element. For quantification of the bioaccumulation and biovolatilization of As, Sb, Se, Te, Tl and Bi inductively coupled plasma optical emission spectrometry (ICP OES) and for Hg cold vapour atomic absorption spectrometry (CV AAS) was used. Bioaccumulation highest rate has been demonstrated for Bi (III) (87% of the initial amount or 2.23 mg of Bi (III), respectively). Highest percentage of biovolatilization was confirmed for the Hg (II) (50% or 1.07 mg of Hg (II), respectively). The total amount of the element removed from aqueous solutions was greatest in the case of Hg (II) (95% or 0.214 mg Hg (II), respectively) and in the case of Bi (III) (89.8% or 2.54 mg Bi (III), respectively).

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P-12

DETERMINATION OF TRACE ELEMENTS IN QUARTZ FILTERS BY LA-ICP-MS TECHNIQUE

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Assessment of occupational exposure to trace elements occurring in the workplace is based on the determination of metals concentrations in the air in the breathing zone of the employee. The introduction of the LA-ICP-MS (mass spectrometry with inductively coupled plasma combined with laser ablation) technique for determination of air samples offers great opportunities for eliminating pretreatment steps, like mineralization process. Reducing execution time and low cost saving necessary to conduct research of environmental work would be possible.

Aim of present study was to assess of the applicability of LA-ICP-MS technique (LXS-500, Cetac, USA, ELAN DRC-e, Perkin Elmer, SCIEX) for the determination of metals in air samples in the occupational settings and compare techniques: laser ablation LA-ICP-MS (quartz filters) and ICP-MS (by extraction from quartz filters and digestion membrane filters).

All analysis were conducted using two methods LA-ICP-MS in quartz filters and ICP-MS in quartz filters after extraction 10 ml 1% HNO_3. The study included 20 air quartz filters collected at work stations in Copper Smelter.

Methods for metals determination in quartz filters by LA-ICP-MS and ICP-MS were developed and optimized. Validation parameters: linearity, range, limit of detection, limit of quantification, precision, accuracy, repeatability and recovery for maximum admissible concentration (MAC) levels in Poland were evaluated. Comparison three techniques showed similar results of arsenic determination.

On the basis of its analysis and validation set of parameters can be considered that analytical methodologies are correct. Results indicate that, LA-ICP-MS can be used in the future to monitoring of work environment. Application of this technique can be possible after finished few technical problems, like: heterogeneity of dust covering the surface of the filter, lability of dust on the filter (e.g. filter placed under water surface), lack of appropriate reference materials (e.g. own prepared tablets). Method of determination of arsenic in the workplace through the use of modern analytical instrument LA-ICP-MS developed for the first time in Poland.

P-13

OPTIMIZATION OF MEAT SAMPLE PRETREATMENT BY FACTORIAL DESIGN FOR CADMIUM DETERMINATION FOR THE OFFICIAL FOOD CONTROL

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The monitoring of inorganic contaminants levels in food products is important because their exposure can affect humans and animals due to their toxic potential and cumulative effects. Cadmium is among the toxic substances controlled in muscle and entrails of bovine animals, porcine, poultry, horses, ovine and caprine, by Ministry of Agriculture, Livestock and Food Supply (MAPA) for food control at Brazil. Currently, in National Agricultural Laboratory (LANAGRO-SP), the meat sample treatment is carry out by calcination, a time consuming step limited by availability of equipment. Decreasing this time means an increase of operational capacity in routine analysis. In the proposed method, the sample was previously hydrated for 60 minutes and then solubilized with 25% (w/v) TMAH (5 ml/1 g sample), and the extraction procedure was carried out at room temperature for 45 minutes. The sample treatment optimization, was performed using a 2^{4-1} Fractionary Factorial Design, and the main factors studied were: moisture sample, e.g. dry or fresh, TMAH proportion added (2 or 5 ml per g), hydration time (30 or 60 minutes) and extraction time (20 or 45 minutes). In these experiments, the sample mass was fixed at 0.5000 and the recovery values were evaluated as answer variable. The cadmium quantification was carried out by GF AAS using external analytical curve in HNO_3 1% (v/v), pyrolysis and atomization temperatures were: 500 and 1500°C, respectively, in the presence of 5 μg of $Pd(NO_3)_2$ + 3 μg of $Mg(NO_3)_2$ as chemical modifier. Especially when there is not replicates, a normal probability plot can be used to separate the real effects from those which are noise and can behaving like they were from a normal distribution centered at zero. In these measured levels, there was no significant factor. However, in order to determine the best conditions for those factors that it is considered important for sample treatment, new levels were evaluated using a 2^3 Factorial Design with center point. For these experiments only fresh mass (utilized in routine analysis) was used for TMAH proportions of 1 to 2 ml g^{-1}, hydration time from 4 to 30 minutes and extraction time between 4 and 50 minutes. Again, no effect studied was significant considering Pareto chart for standardized effects. Thus, this study was important to determine the minimum amounts for each factor, resulting in a low cost and very fast sample treatment for cadmium determination in comparison with the current method.

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P-14

CHEMICAL AND BIOLOGICAL STUDIES OF THE DISTRIBUTION AND SPECIATION OF ZINC IN *Plantago lanceolata* L.

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Plantago lanceolata L. is a common perennial plant. It is known to accumulate heavy metals in its tissues, especially if populations from contaminated locations are considered. It suggests a development of specific tolerance mechanisms. The results of a survey of plants grown from seeds collected from a calamine spoil mound localized in southern Poland (Bolesław near Olkusz) reach in zinc, lead, cadmium and thallium, exceeding natural soil levels are presented. Plants from seeds collected from calamine spoil were grown on 50% Knopp nutrient medium on perlite: control medium and medium enriched with zinc to 50 mg/l Zn. After two months the leaves of plants were subjected to chemical analysis.

The aim of our study was to investigate the distribution of zinc in leaf tissues and its changes influenced by additional zinc fertilization. Speciation of zinc was also studied. Zinc was chosen because it is essential micronutrient, however after exceeding optimal concentrations it exerts a toxic effect on organisms. Simultaneously the distribution of biologically important elements was observed: sodium, magnesium, phosphorus, sulphur, potassium, calcium and manganese.

The distribution of zinc and other elements in *Plantago lanceolata* leaves was studied using LA ICP MS (laser ablation inductively coupled plasma mass spectrometry). After optimalization of LA ICP MS parameters and choosing an appropriate internal standard the semi-quantitative information on elements concentration and its changes in tissues was gathered. Then, distribution maps were constructed in order to facilitate the inspection of any changes of the concentration of elements, depending on tissue and zinc nutrition.

Additionally, to cross-check the results of LA ICP MS analysis, histochemical staining of zinc in plant tissues with dithizone (diphenylthiocarbazone) was performed. The cross-sections of leaves were examined by light microscopy.

The determination of zinc speciation was conducted using an inductively coupled plasma mass spectrometry (ICP MS) and high performance liquid chromatography (HPLC). The size exclusion chromatography (SEC) was used to evaluate the molecular weight of zinc-containing compounds. The ion-exchange was used to separate various zinc species. Preliminary speciation studies showed possible zinc compounds in *Plantago lanceolata* leaves. These results are very important in studies of *Plantago lanceolata* zinc tolerance mechanisms.

P-15

THE DETERMINATION OF MERCURY SPECIES USING THERMAL DESORPTION ANALYSIS IN AAS

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Thermal desorption of mercury from the solid phase is a useful method for the study of mercury behaviour in soil, sediments and tailings. The principle of this method consists of sample heating in a regulated flow of inert carrier gas with online detection by AAS, which is commonly used. The desorption of each mercury specie depends on its thermal stability and on the binding intensity in material. The obtained signal is thus the mercury release curve in the observed temperature range.

Thermal behaviour of the following six species was observed: Hg^0, $HgCl_2$, HgO, $HgSO_4$, HgS and Hg bound to humic acids. Thermal desorption curves were recorded in the temperature range of 50 – 450°C at various absorbances (A = 0.004 – 0.5). The following desorption intervals were observed: 60 – 120°C for Hg^0, 100 – 200°C for $HgCl_2$, 110 – 400°C for HgO, 160 – 380°C for $HgSO_4$, 270 – 350°C for humic bound mercury and 240 – 430°C for HgS.

Contaminated soils samples collected from two localities were also studied in this research. The first sampling site was a waste incineration plant in Hradec Králové, the second was an old hammer mill for ore processing near Příbram (Czech Republic). The curves of mercury release of real samples were measured from aliquots containing always 100 ng Hg. The contained mercury was released within the temperature range of 150 – 350°C for all the samples. Elemental mercury content was also determined in the studied soil samples. The content of Hg^0 was calculated from the difference between the total mercury content and the content after heating at 105°C for 48 hours.

The method of mercury desorption analysis is a suitable tool for the study of environmental samples. It is also a simple screening method for the assessment of mercury stability in material and is usable in the speciation analysis.

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P-16

SORPTION STUDY OF P(V), As(V) AND Sb(V) ON Fe (OXY)HYDROXIDES DURING THE THERMAL TRANSFORMATION AND CHANGE OF THEIR SURFACE PROPERTIES

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Sorption study of arsenic, antimony and phosphorus on iron (oxy)hydroxides is important for the control of the mobility, toxicity, and availability of these elements in natural environments. Iron (oxy)hydroxides have a high specific surface area. This makes them effective sorbents for a large range of dissolved ions, molecules and gases [1]. Under the appropriate conditions, almost every iron oxide can be converted into at least two others. In the environments, they often modify the availability and environmental impact of adsorbed elements, for example, heavy metals [2]. The study of adsorption isoterms revealed that antimony has higher affinity for all studied sorbents. Amounts of immobilized ions reached their maxima on sorbent prepared at 250°C. Thermal treatment of sorbent at higher temperatures (250-450ºC) leads to the decrease of sorption capacity to the original values. The surface properties of goethite and products of its thermal modification at different temperatures have been studied by BET method, FT-IR, XRD and DTA-TGA. The maximum of surface area (82.3 $m^2.g^{-1}$) was reached at 250°C. The further increase of temperature leads to the reduction of a specific surface area to the original value. Further analysis confirmed the complete transformation of goethite to hematite at temperatures 200-250°C accompanied with the disappearance of hydroxyl absorption bands at ~800 and ~900 cm^{-1} in FT-IR spectrum and significant loss of weight observed on TGA curve. The powder X-ray difraction analysis confirmed identity of the solids as well-crystallized goethite at 150-200°C and as well-crystallized hematite at 250-350°C.

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P-17

DETERMINATION OF METHYLMERCURY IN SOIL SAMPLES BY GC-AFS

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The toxicity of mercury in the natural environment depends not only on its total concentration, but also on its chemical form. Methylmercury is the most toxic form of mercury. Therefore, it is important to estimate not only the total mercury concentration, but also that of this species. The determination of total mercury content was carried out with atomic absorption spectrometry (AAS). The pyrolysis AAS approach with gold amalgamation using the AMA-254 analyzer was used. The advantageous coupling of gas chromatography and atomic fluorescence spectrometry detection (GC-AFS) was used for the determination of methylmercury.

The determination of methylmercury in soil involves several analytical steps, including extraction, derivatization, preconcentration into the organic solvent or into the solid phase, separation by GC, pyrolysis of mercury species and detection by AFS. The procedure for extraction of mercury species from solid samples is based on acidic leaching. For increasing extraction efficiency, ultrasound assisted extraction was used. The extraction efficiency of the total mercury was determined using the AMA 254 mercury analyzer, extraction yields of methylmercury by GC-AFS.

For GC analysis, mercury compounds need to be converted to peralkylated volatile compounds. Aqueous alkylation with sodium tetraethylborate is one of the commonly used derivatization methods. The sample was adjusted to pH 5 by sodium acetate buffer. The pH of the sample is an important factor influencing derivatization. The preconcentration of derivates using solid phase microextraction (SPME) in head-space variant and liquid-liquid extraction were used. Certified Reference Material CC580 and real samples of soil were analyzed.

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P-18

DETERMINATION OF SULPHUR DIOXIDE AND ANTIOXIDANTS IN WINE BY SPECTROSCOPIC METHODS

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As fruits, vegetables and beverages contain different varieties of antioxidant compounds such as vitamins (especially vitamins C and E), flavonoids and carotenoids; a diet rich in these is assumed to offer protection against cardiovascular diseases, cancer and age-related degenerative transformations. In recent years there has been much publicity given to consumer concerns about the addition of chemicals to food. One area of concern is the interaction between additives and the possible health risks or joint effects of the cocktail of additives that is consumed each day. Sulphur dioxide, in its various forms, is added to food to inhibit and control the growth of microorganisms, to inhibit enzyme-catalysed reactions, to inhibit non-enzymic browning, and to act as an antioxidant and reducing agent. By providing stabilizing and conditioning functions, it improves the appearance and maintains the quality of foods and wines. However, it has drawn much attention recently because of its allergenic effect on those individuals who are hypersensitive. Nowadays, many countries have set strict limits on the residual amount of sulphur dioxide in different types of food. Therefore, sulphur dioxide content of wine should be precisely determined along with their total antioxidant content. The aim of this work was to measure the CERAC antioxidant capacity and sulphur dioxide amount of wine samples. There are interference effects of sulphur dioxide on the CERAC method. Therefore, sulphur dioxide in wine samples was established with molecular atomic absorption method. For this purpose, several hollow cathode lamps (As, Se, Sb, Mg) were used and as a result of in this study, Se, which was used hollow cathode lamp at a wavelength of 204 nm, was choosen for the analysis of sulfur dioxide. Molecular atomic absorption methods were used to determination of sulphur dioxide in the sulphited wine samples and antioxidant capacities of the same samples were analysised by CERAC and CUPRAC. Real antioxidant capasity of wine samples were found substracting the quantity of interferent sulphur dioxide. CERAC (Ceric ion reducing antioxidant capacity) assay, is based on the room temperature - oxidation of antioxidant compounds with Ce(IV) sulfate in dilute sulfuric acid solution, and measuring the absorbance of unreacted Ce(IV) at 320 nm. CUPRAC method was used for determining the sulphite levels of sulphited wine samples by prior separation of monohydrogensulphite at pH 3 on an anion exchanger followed by spectrophotometry. The desulphited wine solutions were analysed for their antioxidant content by CUPRAC. The CERAC method results were highly reproducible, and correlated well with those of CUPRAC. Turkish wines generally showed higher antioxidant capacity than those reported in the literature from other varieties of different geographical origin.

P-19

APPLICATION OF ICP-MS AND CHEMOMETRICS FOR DETERMINATION OF THE WINE ORIGIN

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The aim of this work was to evaluate the possibility of determining the origin of the wine on the basis of its elemental composition. For this purpose an analysis of major and minor elements was accomplished in selected varieties of wines. In total, 48 parameters for six wine subregions in Bohemia and Moravia was determined and used. The sum of 35 parameters represented the concentration of selected elements and other 13 parameters were created from the measured values. The concentration of elements was determined by inductively coupled plasma mass spectrometry (ICP-MS). For the purpose of classification of samples into the groups multivariate statistical methods were used. The measured data set was firstly separated using analysis of variance (ANOVA) and discriminant analysis (DA). It has been proved that the selected variables influence the distribution of wines into categories according to their geographic location. Canonical discriminant analysis, principal component analysis (PCA) and cluster analysis has been used for graphical projection. Simultaneously the model based on our analysis was created to enable classification of an unknown wine sample according to the origin of wine.

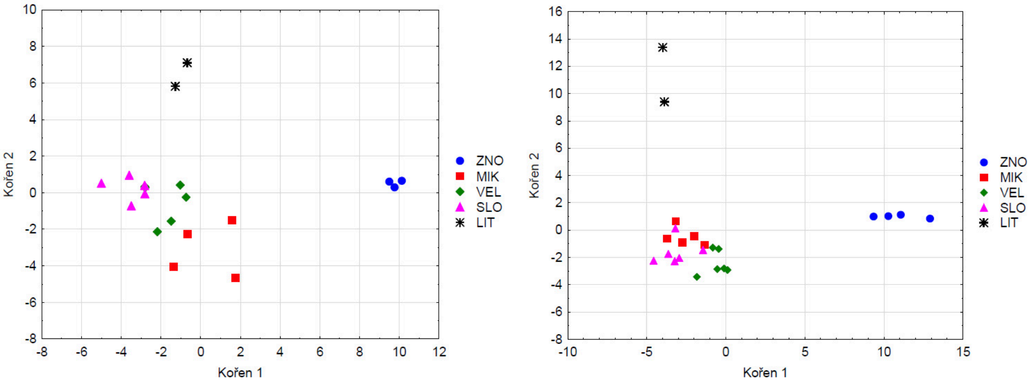

Fig. 1.: Graphical view of results from canonical discrimination analysis – white wines (left), red wines (right)

P-20

STUDY OF PLATINUM ADSORPTION ONTO MODIFIED SBA-15 WITH RESPECT TO ANALYTICAL APPLICATION

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Platinum is one of the most relevant metals present in the biosphere, particularly in the atmosphere. The main sources of platinum in environment are converters applied in motor vehicles to reduce the pollutants [1]. During the use the catalysts are slowly destroying what results in the reduction of efficiency and releasing of platinum group metals from supporting material [2] what leads to the platinum concentration increase in environment.

Determination of the content of platinum in industrial, medical, geological and environmental samples is also of great importance, so new analytical procedures enabling the platinum determination on trace levels in complicated matrices are still needed to be elaborated. Among most sensitive and selective analytical techniques, inductively coupled plasma atomic emission spectrometry (ICP OES), inductively coupled plasma mass spectrometry (ICP MS), and electrothermal atomic absorption spectrometry (GF AAS) seems to be the most appropriate. However, in the case of very low concentration of platinum or complicated matrices containing interfering substances, the analyte preconcentration step is usually required. This stage, through the separation of analyte from the matrix, often minimizes interferences and improves the detection limit. Ordered mesoporous silica materials with organic groups incorporated onto the mesopore channels surface guarantee high adsorption capacities for noble metals Among this sorbents SBA-15 seems to be the most promising due to high thermal stability, large mesopores, thick pore walls and presence of interchannels micropores [3].

In this work SBA-15 modified with 3-mercaptopropyltrimethoxysilane as a thiol groups source were synthesized by sol-gel method and applied for Pt(IV) ions adsorption. In order to check the possibility of the application of synthesized sorbents for separation and enrichment of Pt(IV) ions from environmental samples solutions the parameters affecting on loading capacity were studied in detail. Additionally, the removing of platinum species from loaded sorbents was studied using inorganic acids and thiourea in respect to their concentrations. Modified SBA-15 was applied as adsorbent for Pt(IV) preconcentration, before its determination in digested geological samples, by using of silica slurry sampling atomic absorption spectrometry with electrothermal atomization.

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P-21

DETERMINATION OF BISMUTH IN SOILS AND SEDIMENTS BY SLURRY SAMPLING GFAAS USING CHEMICAL MODIFIERS

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The content of bismuth in soils ranges from 0.2 to 1.5 mg/kg. Bismuth can be accumulated in soils rich in iron oxides and organic matter. The growing use of bismuth in medicine and industry causes its spreads into environment, and therefore, the probability of its exposure to human organism increases rapidly. Because of the mobility and accumulation of bismuth in the environment, its concentration must be monitored. It is necessary to use sensitive and accurate method of its determination. The most commonly used analytical methods for the determination of trace metals in soils are: atomic absorption spectrometry (AAS), atomic emission spectrometry with inductively coupled plasma (ICP-OES), X-ray fluorescence (XRF) and mass spectrometry with inductively coupled plasma (ICP-MS).

Very attractive technique for rapid determination of bismuth in soil and sediments seems to be slurry sampling graphite furnace atomic absorption spectrometry (GF AAS). In comparison with classical GF AAS, which includes acid digestion step, the slurry sampling GF AAS technique shortens analytical procedure and oversimplifies the sample pretreatment. In addition, it reduces possibility of contamination and the risk of analyte losses during the sample preparation. During the bismuth determination by the above mentioned technique the loss of the bismuth in drying and pyrolysis step is very disadvantages. It worth noting that the introduction of solid sample into the graphite tube may cause strong interferences, which can be reduced by the use of pyrolytic graphite tubes and chemical modifiers stabilizing bismuth at high temperatures. These modifiers can be divided into two groups. One of them are classical modifiers, which are introduced into the atomizer with every dosing cycle. The second group are permanent modifiers which, contrary to classical modifiers, are introduced into the atomizer only once just after first use of the atomizer. The use of permanent modifiers provides lowering of modifier blanks, better detection limits, improvement of the signal term stability. Both, noble metals and those forming high-melting carbides may be applied as permanent modifiers.

In this paper the procedure of bismuth determination in soil and sediment samples using slurry sampling graphite furnace atomic absorption spectrometry with classical and permanent modifiers is presented. The effect of the amount of added titanium, zirconium, tungsten, and niobium, as permanent modifiers, on the analytical signal was compared. On the basis of preliminary study, the favorable modifier was chosen for bismuth determination in soil samples paying attention to optimization of time temperature programme.

P-22

DIRECT DETERMINATION OF TRACE METALS IN SUSPENSION FERTILIZERS BY SLURRY INTRODUCTION INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY

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The utilization of suspension fertilizers constitutes a modern and effective method for providing plants with essential micro- and macronutrients. Comparing to solid fertilizers they have beneficial impact on the environment. The accurate matching of nutrients to the needs of crops guarantees a large increase in the yield. The widespread use of fertilizers in agriculture and horticulture must also take into account the environmental requirements, particularly regarding the content of harmful elements in fertilizers, which are introduced into the soil or supplied directly to the plants by foliar feeding. Determination of micro- and macronutrients in suspension fertilizers is usually carried out using procedure involving a digestion step. In that time-consuming procedure expensive reagents of high purity are needed. Direct determination by slurries introduction into argon plasma seems to be an attractive analytical approach to eliminate those limitations. It is worth mentioning that the optimal particle size distribution for foliar feeding fertilizers should not exceed 10μm because of nutrients availability by plants and its stability in time. Those specific properties of suspension fertilizers creates the opportunity to its for direct introduction into the argon plasma for the determination of trace metals.

The purpose of this study was the develop of a method for direct determination of selected trace metals in suspension fertilizers. The preliminary studies included: slurry transport efficiency, as well as optimization of plasma parameters and slurries preparation. Additionally optional pneumatic nebulizers and spray chambers were tested for slurry introduction into the argon plasma. The particle size distribution of the prepared slurries were examined by application of a laser analyzer. In this study the torch with an additional stream of gas in the inner aerosol spray tube was used. Taking into account chemical composition and specific properties, adequate samples of fertilizers were selected. The influence of nitric acid addition to the commercially available suspension fertilizer on signal intensity and stability were studied thoroughly. Glycerol or a detergent-nonionic surfactant were applied for slurries stability. Possible interferences, and methods of their elimination were studied in details. In addition the samples were acid digested using a closed microwave system to compare the results obtained by proposed and classical methods.

P-23

OPTIMIZATION OF SPECTROCHEMICAL ANALYSIS OF “WHITE” MULTICOMPONENT MIXTURES USING DIRECT CALIBRATION

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Analysis of the complex absorption spectra of the multicomponent mixtures of known qualitative composition ("white" mixture), for example, pharmaceutical formulations, is one of the most common problems in analytical chemistry. To solve this problem *a priory* given matrix of calibration spectra is used. Concentrations of the components in the standard mixtures for calibration reflect all possible systematic changes in physical-chemical and instrumental factors.

It is obvious that the relative components’ optical densities can impact on the obtained figures of merit. However, until now the estimation of this effect was not performed. In this work the first stage to solve the problem is to use conventional assumptions about the noise of the spectrum: homoscedastic (constant variance) and uncorrelated. It was shown that the standard deviation of the vector of the relative concentrations obtained in the quantitative spectrochemical analysis of "white" multicomponent mixtures using direct calibration depends on the relative optical densities of the component spectra of the calibration matrix and reaches a minimum in a certain range of the relative intensities. The choice of the calibration matrix corresponding to this range of values allows optimizing analysis.

Further investigation was made taking into account heteroscedastic and correlated noise. The source of such noise, in particular, is a randomly varying baseline, due to both instrumental and physical-chemical factors, which total compensation, is practically impossible.

A new computer modeling method for calculation of the covariance matrix of the heteroscedastic correlated noise in spectra has been developed. This method is based on the baseline simulation by polynomial with random parameters. A simple way to calculate the errors of the concentration vector due to the errors of the calibration matrix in direct calibration has been proposed. The impact of the heteroscedastic correlated noise and of the calibration errors on the choice of the optimal scheme of direct calibration has been evaluated. The proposed approach is used to evaluate the effectiveness of the standard (according to the regulations) calibration set for Excedrin tablets analysis. It is shown that the recommended ratio of the components’ concentrations is not optimal.

P-24

ESTIMATION OF THE MINIMUM UNCERTAINTY OF QUANTITATIVE SPECTROSCOPIC ANALYSIS

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Much attention has been paid lately to estimating the measurement uncertainty in analytical spectroscopy [1] and, in particular, its impact on the limiting properties of the mathematical methods used to improve spectral resolution [2] as well as on the precision of quantitative analysis. These studies lead to the development of new techniques that allow obtaining more spectrochemical information and of new data processing mathematical algorithms that decrease the uncertainty of analytical results. However, it may well happen that the concentration errors inherent in computer-aided quantitative measurements are close to the minimum achievable level. In this case improving the employed mathematical procedures would be useless. In view of the above, we have developed the method of evaluating the lower error limit of quantitative determinations in analytical spectrometry. The method is based on our previous finding that the relative mean squared error (RMSE) of the concentration vector depends on the relative intensities of the pure-component spectra (matrix **W**) of the calibration matrix (**S**) [3]. In this work, the following calibration methods were employed and compared: the Principal Components Regression (PCR), the Partial Least Squares (PLS) regression, and the Classical Least Squares (CLS) method in direct and inverse forms with and without Tikhonov regularization (TR). The minimal relative standard errors of prediction (RSEP) were obtained for a given mixture and for a mixture from a large set of mixtures. The calculations were performed using computer-generated noisy spectra of multicomponent mixtures in the cases of well and poorly separated constituent spectra. UV-VIS spectra of Excedrin tablets were also studied. The effect of concentration matrices was checked using closure and non-closure training set matrices. It has been shown that the hypothetical optimal matrix **S** does actually exist. For the CLS method, in general case, and for the CLS-TR method, for Gaussian doublets, this fact is proved theoretically, while in all other cases, the proof is based on numerical analysis. We have found that for the PLS and PCR methods, in a wide range of matrices **W**, RMSE values are close to optimal, whereas, for the regularized CLS method, the optimal matrix S depends mainly on the concentration vector of the mixture being analysed. The effect of the concentration vector on RSEP values is small for all these methods.

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P-25

HEAVY METAL REMOVAL FROM AQUEOUS SOLUTION USING LIBYAN NATURAL ZEOLITE AND ACTIVATED CARBON

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Various techniques have been applied to treat heavy metal-contaminated water such as phytoremediation technologies. In this study the abilities of Libyan natural zeolite and activated carbon to remove Zn, Cu, Cd and Pb from aqueous solution were studied in batch system. The effect adsorption dose, metal ion concentrations and the agitation time on removal efficiency were studied; the measurements of target elements were carried out by flame atomic absorption spectrometer. It was observed that the highest removal level of Zn, Cu, Cd and Pb ions for powdered Libyan natural zeolite was achieved at adsorbent dose of 0.75 g, initial metal concentration of 25 mg/l, and at contact time of 60 minutes. Under these optimum conditions, the removal efficiency was 83.4%, 97.78%, 94.97% and 97.33% of Zn, Cu, Cd, and Pb ions, respectively. In case of powdered activated carbon, the highest removal level for Zn, Cu, Cd, and Pb ions was achieved at adsorbent dose of 0.25 g, initial metal concentration of 25 mg/l and contact time of 60 minutes. The removal efficiency was 97.38%, 99.5%, 98.18% and 96.11% of Zn, Cu, Cd, and Pb ions respectively. In general, the results showed that the removal level was considerably high for both the zeolite and activated carbon, however, the efficiency of heavy metal was as a function of adsorbent dose values and less adsorbent dose in case of activated carbon was required to achieve the same efficiency removal obtained with Zeolite.

P-26

DETERMINATION THE ELEMENTAL UPTAKE OF BARRAMUNDI (*Lates calcarifer*) LARVAE FED BY Co, Zn AND Mn ENRICHED *Artemia nauplii* USING ATOMIC ABSORPTION SPECTROMETRY

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Barramundi *(Lates calcarifer)* is a predatory fish species native in Southeast Asia. Based on the geothermal potentiality of Hungary the high market potential warm-water fish barramundi can be produced economically. Living nourishment organisms such as *Artemia nauplii* play an essential role in the larval rearing of barrramundi. However, zooplanktons in natural aquatic enviroments contain minerals in a higher concentration than the usually fed newly hatched *Artemia*. Therefore the goal of recent study was to investigate the uptake of cobalt on the larval growth of barramundi when fed individually and combined with Zn and Mn supplemented *Artemia*.

In our experiment newly hatched *Artemia nauplii* was enriched with cobalt chloride, zinc sulphate and manganese chloride. Concentrations were 50 and 100 mg l^{-1} for $CoCl_2$ (Co-1 and Co-2) and for $MnCl_2$ (Mn-1 and Mn-2) individually, as well as for $CoCl_2$ along with $ZnSO_4$ (Co-Zn-1 and Co-Zn-2) and for $CoCl_2$ along with $MnCl_2$ (Co-Mn-1 and Co-Mn-2) in combination. A total of 1900 barramundi larvae from 15-30 day post hatching were fed supplemented *Artemia* in 9 groups of treatments in duplicate. *Artemia* was sampled, washed by ultrapure water then centrifuged. Moisture content was determined by gravimetric method. Samples were digested on a hot plate with the mixture of 65% (m/m) HNO_3 and 30% (m/m) H_2O_2 prior to analysis. The Co, Zn and Mn concentration of *Artemia* and 40 larvae from each treatments were determined by FAAS and GFAAS method. Blank samples were set to verify the purity of applied reagents.

All treatments had significant effect ($p<0.05$) on the Co, Mn and Zn level of *Artemia* – the concentrations increased in paralell with the dose of supplementations. No interactions in the uptake occured between the elements. Co and Mn supplementation had no significant effect on the Zn uptake of the larvae. In case of Co-Zn-1 and Co-Zn-2 treatments significantly higher Zn concentration was measured than in the others ($p<0.05$). Cobalt had a significant negative effect on the Mn uptake of the larvae - significantly higher Mn accumulation compared to the control group was only observed when Mn was fed in itself ($p<0.05$). The highest Co concentration was measured in the Co-2 group however Co level in Co-Mn-1 and Co-Mn-2 groups were significantly higher than in the control ($p<0.05$). Statistically no difference was found in the Mn concentration of Co-1 and Co-2 groups compared to the control whilst the Co concentration was determined to be significantly lower in Mn-1 and Mn-2 groups than in control ($p<0.05$). Therefore a competitive antagonism between the Co and Mn uptake of barramundi larvae can be assumed.

P-27

DETERMINATION AND SPECIATION OF ARSENIC COMPOUNDS IN FISHES

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Arsenic is well known as a toxic element that can occur in foodstuffs in several forms. These forms have for humans different toxicity, therefore is total amount of arsenic in the foodstuffs insufficient information. For humans is dangerous accumulation of arsenic in food chains.

In the framework of this work was created a procedure for the determination and speciation of arsenic compounds in food samples like fishes, which has been optimized. The procedure involved the use of high performance liquid chromatography (HPLC) method and detection by atomic fluorescence spectrometry with hydride generation technique (HG-AFS). As comparison method was used mass spectrometry method with inductive coupled plasma (ICP-MS) for determination of total arsenic content. Conditions of measurement have been optimized for the separation and detection part of the connection separately. The procedure has been used for the determination of arsenic forms in samples of fishes.

Optimization of separation part included the selection of the suitable chromatographic column, the mobile phase and the appropriate testing the pH of mobile phase. For the speciation of arsenic compounds has been selected the column Hamilton-PRP X 100. The mobile phase for separating compounds of arsenic is composed of a mixture of potassium hydrogen phosphate and potassium dihydrogen phosphate. The pH of mobile phase was tested in the range of 5-7. Results have shown that arsenic compounds have been distributed optimally at pH of mobile phase 6.1.

Optimization for the detection part included testing of appropriate concentration of hydrochloric acid and sodium tetrahydroborate. Conditions were optimized for the involvement of the apparatus for the analysis of reducible forms of arsenic and for the analysis of not reducible forms of arsenic. The results of the measurements have shown that for the analysis of reducible forms of arsenic is the appropriate combination of 1.5 mol/l HCl and 1.2% of $NaBH_4$ and for the analysis of not reducible forms of arsenic 6 mol/l HCl and 1.4% $NaBH_4$.

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P-28

SELENIUM DETERMINATION IN TWO/THREE-COMPONENT CULTIVATION SYSTEM (FUNGUS/HUMIC ACID/MINERAL PHASE) BY ICP OES

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To assess the transfer of selenite into living microbial biomass in presence of organic matter and solid phases, the two or three component cultivation systems were prepared, which included growing fungus, mineral phase (ferric oxyhydroxide or bentonite) and/or humic acids. This two/three-component cultivation systems were enriched with selenium in form of selenite (0.209 mmol/l) and inoculated with filamentous fungus *Aspergillus niger*. The fungus was cultivated under laboratory conditions until the stationary growth phase was reached. After 18 day cultivation, the non-dissolved components (biomass, mineral phase and precipitated humic acids) were separated from the remaining solution and after digestion the selenium concentration was determined in each sample using ICP OES (λ = 196.090 nm). Expect for bentonite, each component reduced bioavailability of selenium significantly (Fig.1), indicating relative strong binding of selenium to non-dissolved phases. The most efficient component restricting selenium uptake was complex of FeOx and humic acids, which reduced absolute selenium content in biomass by 75%.

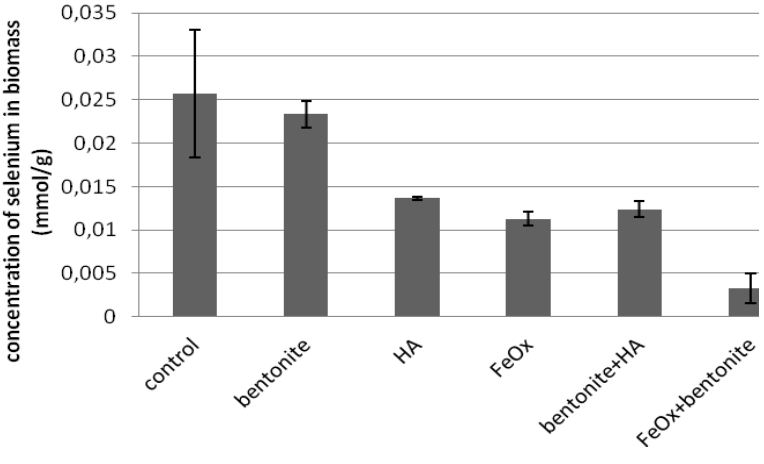

Fig.1 Concentration of selenium in biomass after 18 day cultivation in the presence of various solid phases (HA, humic acid; FeOx, ferric oxyhydroxide)

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P-29

ULTRASOUND ASSISTED SEQUENTIAL EXTRACTION FOR DETERMINATION OF BIOAVAILABLE FRACTION OF CADMIUM AND LEAD IN SOIL BY ETAAS - GREEN SAMPLE PRETREATMENT

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In order to evaluate the bioavailability of metals present in soil various approaches based on one step extraction or sequential extraction can be used. The most popular is BCR or modified BCR procedure, which aims to fractionate heavy metals in soils. The content of metals in acid-extractable fraction (extracted with 0.11 mol l^{-1} CH_3COOH) can be used to assess the potential harm of the metal to human and animal health considering its transfer in soil - vegetable - human/animal. Although the content of heavy metals in reducible and oxidizable fractions is less than in acid-extractable fraction, the metals from these two fractions can be released into soil solution and re-absorbed by plants when the soil environment is changed to oxidizable or reducible conditions. Therefore, the sum of heavy metals in the first three fractions (acid-extractable, reducible and oxidizable fractions) of BCR procedures is considered as bioavailable form.

In this work the conditions for ultrasound assisted extraction of bioavailable forms of cadmium and lead in soil according to modified BCR procedure were developed. Solutions of 0.11 mol l^{-1} CH_3COOH, 0.5 mol l^{-1} $NH_2OH{\cdot}HCl$ and 1 mol l^{-1} CH_3COONH_4 were used for extraction of metals. The working parameters of ultrasound probe: a power and a time of sonication were optimized. The developed procedure with electrothermal atomic absorption spectrometric determination of metals was validated. The accuracy was checked by analysis of certified reference material BCR 701. The bioavailable fractions of Cd and Pb in soil from Podlaskie region were determined according to developed ultrasound assisted procedure.

Considering the fact, that application of ultrasound probe allows for shortening of the time of analysis from about 50 h to 25 min (in comparison to traditional BCR procedure), the developed procedure can be classified as a green sample pretreatment method.

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P-30

NEW MODIFICATION OF DIFFUSIVE GRADIENT IN THIN FILM TECHNIQUE (DGT) FOR DETERMINATION OF METALS IN SEDIMENTS

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The diffusive gradient in thin film (DGT) technique has been used for measuring fluxes and concentrations of labile metal species in waters, soils and sediments. The DGT probes offer a number of advantages over other conventional monitoring techniques as grab sampling, by reducing the errors of sample storage and transportation. When DGT probes are exposed to aqueous systems over a certain time, metal species diffuse into the binding gel through the diffusion layer and thus provide time averaged concentrations of metal species in situ.

The work demonstrates the performance of a new modified constrained probe packed with Spheron-Oxin® based resin gel for in situ sediment characterization by DGT technique. High resolution of the modified probe and pre-concentration capability can provide direct information on spatial distribution of metals in sediments. The depth profiles of manganese and iron monitor redox processes that control uranium remobilization in the sediment core. Combination of DGT technique with ICP MS analysis can characterize abundance of uranium isotopes, and thus provide information on the sources and the fate of uranium in sediments and related environmental systems.

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P-31

STABLE ISOTOPE RATIO MASS SPECTROMETRY OF WATER SAMPLES FROM DUNAJ AND MORAVA RIVERS IN BRATISLAVA, SLOVAKIA

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Knowledge about isotopic composition of H and O in natural waters are more and more widely applied in study of climatic, hydrological and hydrogeological problems. This kind of data represents one of the few tools that allows us to track water molecule in the hydrological cycle. Isotope composition of natural waters of meteoric origin depends mainly on temperature, amount and composition of atmospheric vapor, altitude, latitude and other factors.

This study demonstrates the application of continuous flow isotope ratio mass spectrometry (IRMS) especially the equilibration method for the analyses of $\delta^{18}O$ and $\delta^{2}H$ in water samples of Danube and Morava rivers in Bratislava (Slovakia). We performed the monitoring on random monthly samples from May 2010 to January 2012. Aim of this study was to help to distinguish origin of groundwater present in Quaternary fluvial sediments in wider area of Danube and Morava river confluence. As a potential source of groundwater in studied area is considered groundwater originating in local precipitation, then groundwater from Danube bank infiltration and finally Morava bank infiltration. IRMS works on the principle of original compounds conversion into simple gases. For this purpose the GasBench II was used, which performed automatic sampling and transferring the sample gas into the universal interface ConFlo IV. This interface ensured continual flow of the sample and reference gases in the mass spectrometer Delta V Advantage. The results of the project documented the characteristic distribution of isotopes in water from each river. Isotope composition of Danube river water in Bratislava is in range $\delta^{18}O$ = -10.34‰ to -11.90‰ with average -11.15‰, and $\delta^{2}H$ ranges from -75.0‰ to -84.9‰, with average value -79.2‰. In late spring (May, June), the presence of isotopic “light” (depleted) water from snow thawing in Alps is typical. Distribution of O and H isotopes in Morava river water is different. The value of $\delta^{18}O$ ranges from -8.48 ‰ to -10.69 ‰ with average -9.52‰, $\delta^{2}H$ ranges from -63.86‰ to -72.6‰, with average value -68.3‰.

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COACERVATIVE EXTRACTION OF LEAD FROM NATURAL WATERS PRIOR TO ITS DETERMINATION BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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In this work, a simple and sensitive method for separation/preconcentration of ultratrace lead from natural waters prior to its determination by electrothermal atomic absorption spectrometry (ETAAS) has been proposed. The method is based on the extraction of Pb-dithizone complex with coacervates made up of lauric acid in the presence of a water-miscible cosurfactant (methanol). Several important factors affecting extraction efficiency such as pH, concentrations of lauric acid and dithizone, ionic strenght, extraction and centrifugation time were investigated and optimized (see schematic description below). After separation of aqueous bulk solution from surfactant rich phase, the final extract was redissolved using 0.2 M HNO_3 in methanol. Under the optimized conditions (using 10 ml sample), preconcentration factor 18.5, limit of detection 0.24 μg/l, limit of quantification 0.80 μg/l, relative standard deviation 3.5% (for 2 μg/l of Pb), linearity of the calibration graph in the range 0.8-4.0 μg/l (with correlation coefficient better than 0.998) were achieved. The method was validated by the analysis of certified reference material (TMDA-61). Finally, the method was applied for separation/preconcentration and determination of lead in natural waters.

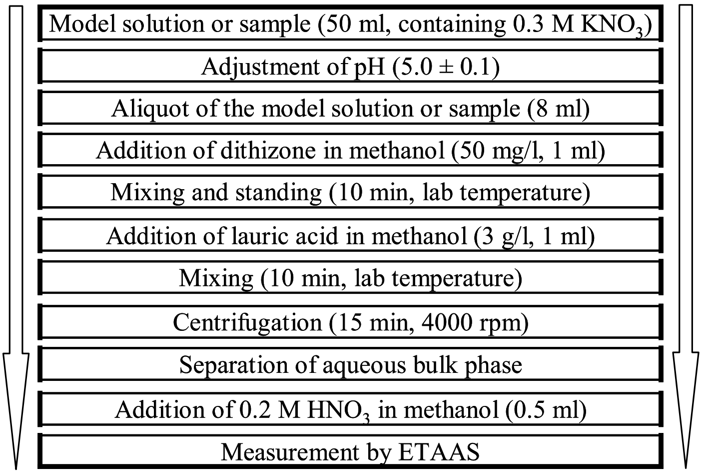

Figure 1. Schematic description of the optimized procedure for coacervative extraction of lead prior to its determination by ETAAS.

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SPECTROELECTROCHEMICAL STUDY OF 4-AMINOBENZENETHIOL ON COPPER, SILVER AND GOLD: WHAT IS THE ROLE OF THE METAL ON THE REACTIVITY OF THE ADSORBED SPECIES?

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The aromatic mercapto derivative 4-aminobenzenethiol (4-ABT) is a substance that can be easily adsorbed on Au, Ag and Cu surfaces. We have used 4-ABT to evaluate effectiveness of surface-enhanced Raman scattering (SERS) on different Cu substrates [1] at 1064-nm excitation. No formation of 4,4'-dimercaptoazobenzene (4,4'-DMAB) indicated by bands around 1440, 1395 and 1150 cm^{-1} was observed in contrast to results published by Wu et al. [2-3] and Canpean et al. [4] for Ag and Au substrates at excitation in the visible range. Thus, we decide to study 4-ABT on all three metals in a spectroelectrochemical cell aiming at the role of the metal and electrode potential on formation of 4,4'-dimercaptoazobenzene at 785-nm excitation. In the case of Au, the bands of 4,4'-DMAB are observed in a broad range of potentials from 0.2 to -0.8 V. Only at very negative potentials (below -1.0 V), these bands disappear practically and only spectral features of 4-ABT are observed. In the case of Ag, the bands of 4,4'-DMAB are observed in a comparable range, that means from 0.1 to -0.7 V, but their intensities are weaker than on gold surface. Thus, the extent of reaction is smaller on Ag surface compared to Au one. In the case of Cu, there is no evidence of 4,4'-DMAB at any potential value. Only characteristic bands of 4-ABT are observed in the whole potential range; the highest band intensities are related to potentials around -0.7 V.

We can conclude that the crucial aspect of surface photocatalytic formation of 4,4'-DMAB from 4-ABT is the metal. The reaction is very effective on Au and it is inhibited on Cu. The tentative explanation is related to the strength of bond of sulfur to the individual metal; the strongest bond is proposed on Au, the weakest on Cu.

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DC ARC SPECTROSCOPIC STUDIES OF EVAPORATION PROCESSES OF IMPORTANT ELEMENTS IN VARIOUS Pd BASED CATALYSTS

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Solid sampling DC-arc-OES, “green chemistry” based analytical approach, forms a suitable method for impurities monitoring in carbon or silica supported catalysts. Such types of catalysts are used in hydrogenation processes. Impurities within them can strongly affect the process of hydrogenation.

The optimization of evaporation and subsequent excitation process is necessary condition for successful application of DC-arc-OES method. Method of evaporation correlation curves [1, 2] was used for monitoring of accompanying elements evaporation in above mentioned supports with constant addition of PdO.

The effect of used carrier spectral electrode materials (high-resistance amorphous carbon – SW and graphite – SU, respectively), as well as their type that defines the available quantity of the sample (type 380: 7 mg of sample, type 304: up to 20 mg of sample) was studied.

Except of evaporation process optimization, another task of study was to obtain the maximum intensities of spectral lines. It was found that the evaporation from graphite electrodes with a large volume (SU-304) is insufficient and incomplete. Moreover, intensities of evaluated elements were mostly low which also affect the values of limits like LOD and LOQ, respectively.

In contrast, evaporation from high-resistance electrodes with a small volume (SW-380) was accomplished, even in the case of such elements like titanium. Intensities of spectral lines, in this case, were significantly higher and also promising in terms of limit criteria. Specific details and results will be presented.

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SPECTROMETRIC ASSESSMENT OF PHYTOAVAILABILITY AND ECOTOXICOLOGICAL EFFECTS OF MERCURY IN THE SOIL-PLANT SYSTEM (*Hordeum vulgare* L.) UNDER LABORATORY CONDITIONS

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Determination and methods used to predict the phytoavailability of risk metals in soil-plant system in various conditions belong to current issues of serious concern. In our work we studied transfer, bioaccumulation and ecotoxicological effects of soluble form of mercury in *Hordeum vulgare* L. grown in calcareous, „non-contaminated“ soil from Slovakia to which we applied water solution of soluble mercury with various concentrations. Experiment was held under laboratory conditions. To obtain phytoavailable mercury in soil, the first – acid extractable step of optimised BCR SEP (Community Bureau of Reference three-step sequential extraction procedure) was applied. Concentrations of mercury both in soil and plant material (both in solid material and extracts) were measured directly by CV AAS (AMA-254). To assess ecotoxicological effects of mercury, VIS spectrophotometry was used. Bioconcentration factor and extraction yields from first BCR SEP acid extractable step were calculated and correlated and so used to assess the phytoavailability of mercury.

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MONO-STANDARD CALIBRATION FOR ANALYSIS OF SOLID ENVIRONMENTAL SAMPLES USING SS-DCA-OES METHOD

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A comprehensive optimization and validation is an important process, which is necessary to carry out in case of comparing of methods, the exchange of the measuring equipment, development of new methods as well as in case of control or improvement of the used method. This contribution presents a continuation of our extensive experimental work focused on the optimization and validation of the SS-DCA-OES method, using modern instrumentation of the spectrometer Atomcomp 2000 (partially programmable DC arc discharge, Echelle optical system and CID detection, working range 175 - 900 nm), which was originally used for the analysis of ceramic powders. After optimization of basic experimental parameters and evaluation of their impact on the efficiency of evaporation (model samples and samples of sediments were used), determination of the performance characteristics of the method, under already optimized conditions (work without Ar atmosphere, using AgCl as spectrochemical addition, setting the parameters of arc - 6S, 6A, 18A-19s, 40s-12A), was done. The paper is specifically focused on mono-standard calibration with using of CRM of sediments GBW 07312 and BCR 277 with graduated weight (2-12 mg). Obtained results for selected elements Cd, Cr, Ni, Pb were computed using a statistical software QC Expert 2.5™. Analytical calibration was evaluated in terms 3s-criterion) and correlation coefficient. Successful validation of the objective method of (basic figures of merit as an absolute member, standard deviation, sensitivity, limit of detection means an extension of instrument applications in the field of environmental analysis.

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DETERMINATION OF Si/Al MOLAR RATIO IN MICROPOROUS ZEOLITES USING CALIBRATION FREE LASER INDUCED BREAKDOWN SPECTROSCOPY (CF- LIBS)

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The laser induced breakdown spectroscopy (LIBS) has been used for analyses of different materials types for several decades. LIBS is suitable for rapid analysis of alloys [1], powder samples [2], biological tissues [3], geological samples [4] and ancient artifacts [5]. Calibration free approach of LIBS was applied to the analysis of three different types of microporous zeolites. For more accurate determination of Si/Al molar ratio, some parameters, i.e. transition probability (Einstein coefficient), population density of lower level, energy of upper level and ratio between neutral and singly ionized particles in laser induced plasma, were taken into account. Determination of Si/Al molar ratio using CF- LIBS is in good agreement with results achieved by classical wet chemical analyses. But in comparing with classical chemical analysis and other spectroscopic methods, CF- LIBS can provide fast and multielemental analysis, which not require sample pre- treatment or manipulation with strong chemicals and without using standard samples for calibration curve constructing.

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FOURIER TRANSFORM INFRARED MICROSPECTROSCOPY (FTIR-M) AS AN EFFECTIVE TOOL FOR IDENTIFICATION OF VIRALLY INFECTED CELLS AND CELLS CONTAMINATED WITH BACTERIA OR FUNGI

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Fourier transform infrared micro-spectroscopy (FTIR-M) can detect small molecular changes in cells and therefore was previously applied for the identification of different biological samples. In the present study, FTIR spectroscopy was used for the identification and discrimination of Vero cells infected with herpes viruses or contaminated with bacteria or fungi in cell culture. Vero cells in culture were infected herpes simplex virus type 1 (HSV-1) or contaminated with E. coli bacteria or fungi and analyzed by FTIR microscopy at 24 h post-infection/contamination. Specific different spectral changes were observed according to the infecting or contaminating agent.

For instance, both pure fungi and cell culture contaminated with this fungi showed specific peaks at 1030 cm^{-1} (Fig. 1B) and at 1373 cm^{-1} regions, while pure *E. coli* and cell culture contaminated with this bacteria showed a specific and unique peak at 1657 cm^{-1}.

These results support the potential of developing FTIR microspectroscopy as a simple, reagent free method for identification and discrimination between different tissue infection or contamination with various pathogens.

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PROVENANCE STUDY OF ARCHEOLOGICAL RAW MATERIAL USING LA-ICP-MS

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With the increasing interest of archaeologists and geologists in ancient raw materials and their provenance there was a need to develop nondestructive analytical methods with low limits of detection. Such a method with a low level of destructivity can be LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry).

One of the major benefits of LA-ICP-MS method is a relatively simple sample preparation or even no preparation of the analyzed sample. On the other hand simple sample preparation is disadvantaged by relatively difficult process of optimization of the measuring parameters such as pulse frequency, diameter of a laser beam and its energy. Also the process of data calibration and quantification is quite complicated and requires the use of standard reference material.

This work presents preliminary results of LA-ICP-MS analysis of samples made from porcellanite, which was commonly used as a raw material for manufacturing stone tools in the past. Set of analyzed samples included both source material and artifacts mainly from Czech Republic. One sample came also from Poland. NIST SRM 610 was used as a calibration material for quantification purposes. The resulting data were than subjected to multivariate statistics including Principal component analysis (PCA), which represents an essential part of multivariate data analysis. Our results indicate that LA-ICP-MS is a suitable method for provenance determination of the porcellanite material.

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THERMODYNAMIC MODEL AND PRINCIPAL COMPONENT ANALYSIS OF RAMAN SPECTRA OF 15(Na_2O,K_2O).10(CaO,ZnO).75(ZrO_2,SiO_2) GLASSES

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Thermodynamic model of Shakhmatkin and Vedishcheva was constructed for 15(Na_2O,K_2O).10(CaO,ZnO).75(ZrO_2,SiO_2) glasses. Within this model, the studied glass is considered as an ideal solution of system components defined by the stoichiometry of stale crystalline phases of particular system. From 26 considered model components only 13 were identified as significant, i.e. with relative abundance exceeding 1 mol.%, on the basis of equilibrium molar amounts. Principal component analysis of background subtracted Raman spectra resulted in 8 independent components. The correlation analysis of equilibrium molar amounts obtained from TD model is presented for explanation of the PCA result.

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NEW METAL TAG REAGENT FOR HIGHLY SELECTIVE AND SENSITIVE ANALYSES OF AMINO ACIDS AND DIPEPTIDES BY LC-ICP-MS

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Inductively coupled plasma mass spectrometry (ICP-MS) is not only useful as a powerful inorganic analytical tool but also as the newest ultra-trace organic analytical technique: metal-tagged analysis. We formerly developed the new analytical method of the metal-tagged amino acids by LC-ICP-MS. In this study, we have designed and synthesized a ruthenium complex, as an excellent metal tag reagent for amino acid and dipeptide analyses. The new reagent's flame is smaller than that of the existent reagent. Ten different amino acids and dipeptides derivatized with the reagent were successfully separated from each other simultaneously by high performance liquid chromatography (HPLC). The ruthenium in the derivative was detected by on-line quadrupole ICP-MS, and the detection limits of the amino acids and the dipeptides (signal-to-noise ratio of 3) were 100 amol per injection.

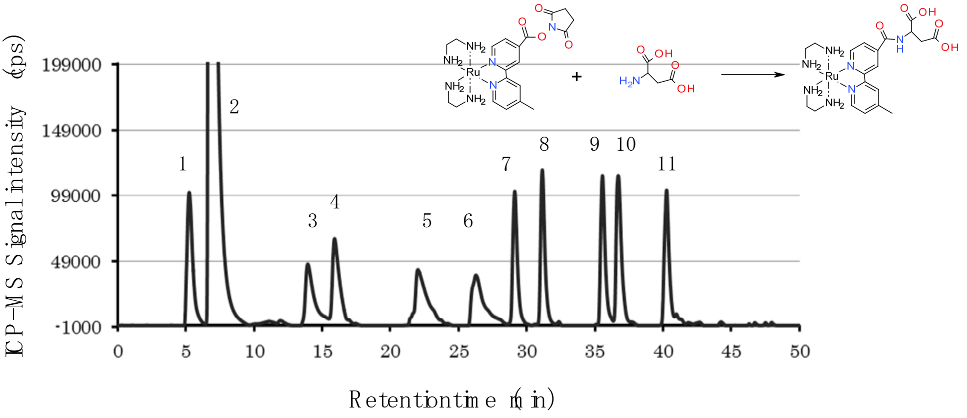

Figure: This figure was the chromatogram of 8 amino acids and 2 dipeptides derivatized with the new metal tag reagent (with ICP-MS, m/z=102).

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RTG FLUORESCENCE SPECTROSCOPY STUDY OF GLASS MELTING FILTER DUST COMPOSITION

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The filter dust (FD) from glass batch melting is one of the hazardous waste in glass production. Depending on composition, the filter dust is recycled in the glass manufacturing in the batch or exported to a landfill. Objective of this work was to investigate the quantitative composition of filter dust by means of X-ray fluorescence spectrometry on a Bruker S8 TIGER fluorescence spectrometer. QUANT EXPRESS semi-quantitative method was used. The samples of the filter dust were collected from two cloth filters and one electrostatic separating filter during one year on a weekly basis. Samples for analysis were prepared by pressing with the addition of wax. After optimization of sample preparation, precision and accuracy of QUANT EXPRESS semi-quantitative method was evaluated by monitoring of filter dust composition depending on time. Subsequently, the selected samples of filter dust were monitored for reproducibility of used method.

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ARSENIC SPECIATION IN URINE OF SUBJECT WITH OCCUPATIONAL EXPOSURE

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Arsenic(As) is a human toxin and carcinogen. The toxicity and bioavailability of arsenic species is highly depending on form or species, therefore determination of total inorganic arsenic metabolites (excluded of organic As from dietary intake) is insufficient for a complete toxicological evaluation and risk assessment.

A speciation technique for arsenic has been applied using high performance liquid chromatography connected to inductively coupled plasma mass spectrometry (HPLC-ICP-MS). Five As-species (arsenite, arsenate, dimethylarsinic acid, mono-methylarsonic acid, arsenobetaine) have been separated with isocratic elution within less than 10 minutes. Arsenic speciation has been analyzed on urine samples of occupational exposure workers.

ELAN DRC-e ICP-MS with Dynamic Reaction Cell (Perkin Elmer, SCIEX, USA) was used for arsenic determination. A cyclonic spray chamber, a Mainhard nebulizer and peristaltic four-channel pump were used. The instrument Series 200 HPLC (Perkin Elmer, SCIEX, USA) was used to separate arsenic chemical forms. An Anion Exchange, Hamilton PRP-X100 column (5µm x 15cm) was used under the following conditions: 5 mM (NH_4NO_3) Ammonium Nitrate/ 5 mM ($NH_4H_2PO_4$) (dibasic), flow rate 1.5ml/min, injection volume 100µl.

The mean value for total urinary arsenic (n=27) was 67.4 µg/l (58.2 µg/g creat.) with a range of 4.7 to 201.1 µg/l (12.6-173.3 µg/g creat). In 15 causes the concentrations of As_{tot}. in urine were under to the values of biological exposure index valid currently in Poland (35 µg/g creat). The mean values of urinary arsenic species were as follows: sodium arsenite (As(III) 10.6 µg/l (8.9 µg/g creat.): sodium arsenate (As(V) 5.4 µg/l (5.1 µg/g creat.); monomethylarsenic acid (MMA) 7.1 µg/l (5.6 µg/g creat.); dimethylarsinic acid (DMA) 22.5 µg/l (18.2 µg/g creat.); arsenobetaina (AsB) 19.5 µg/l (18.2 µg/g creat.).

This arsenic speciation method using HPLC-ICP-MS technology coupled with dynamic reaction cell (DRC) was developed in our laboratory primarily for determination arsenic species in urine samples obtained from subject with occupational exposure. This technique described here allows a more reproducible, sensitive and quick analysis of arsenic species in urine samples.

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DETERMINATION OF Cr(III), Cr (VI), AND Cr (ACAC)$_3$ IN WATER BY ION-EXCHANGE DISKS/METAL FURNACE ATOMIC ABSORPTION SPECTROMETRY

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A new method for the simultaneous determination of Cr(III), Cr(VI), and Cr(acac)$_3$ in water was developed using a cation-exchange extraction disk (CED) placed on an anion-exchange extraction disk (AED) and combined with metal furnace atomic absorption spectrometry (MFAAS). A 100 ml water sample was adjusted to pH 5.6 and was passed through the CED placed on the AED. Chromium(III) acetylacetonate and Cr(III) were adsorbed on a CED while Cr(VI) was adsorbed on an AED. The adsorbed Cr(acac)$_3$ was eluted with 50 ml carbon tetrachloride, followed by the elution of Cr(III) using 50 ml of 3 mol l^{-1} nitric acid. Chromium(VI) was eluted with 50 ml of 3 mol l^{-1} nitric acid. The eluate of Cr(acac)$_3$ was diluted to 100 ml with carbon tetrachloride and those of Cr(III) and Cr(VI) were diluted with deionized water. These species were analyzed with MFAAS. The calibration curve drown with Cr(acac)$_3$ aqueous solution showed good linearity in the range of 0.1–1 ng. The detection limit corresponding to three times the standard deviation (n = 5) of blank values was 22 pg. The recovery test for Cr(III), Cr(VI), and Cr(acac)$_3$ showed desirable results (96.0%–107%) when 5 μg of each was added to three 100 ml (50 μg l^{-1}) water samples i.e., tap water, rainwater, and mineral water (Table 1). In order to confirm whether the recovered organic Cr was indeed Cr(acac)$_3$, fourier transform infrared spectroscopy was used. In humic acid solution, Cr(acac)$_3$ was recovered quantitatively (103%), whereas Cr(III) and Cr(VI) showed poor recoveries of 84.8% and 78.4%, respectively.

Table 1 Analytical results of Cr(III), Cr(VI), and Cr(acac)$_3$ in water samples

Samples	Added/μg L^{-1}			Found/μg L^{-1}			Recovery, %		
	Cr(III)	Cr(VI)	Cr(acac)$_3$	Cr(III)	Cr(VI)	Cr(acac)$_3$	Cr(III)	Cr(VI)	Cr(acac)$_3$
Tap water	0	0	0	N.d.	N.d.	N.d.			
	50.0	50.0	50.0	53.7 (4.8)[a]	52.8 (2.6)[a]	50.7 (4.7)[a]	107	106	101
Rain water	0	0	0	N.d.	N.d.	N.d.			
	50.0	50.0	50.0	51.0 (2.3)[a]	49.2 (6.4)[a]	50.0 (6.2)[a]	102	98.4	100
Mineral water	0	0	0	N.d.	N.d.	N.d.			
	50.0	50.0	50.0	51.4 (7.6)[a]	48.9 (4.6)[a]	48.0 (1.0)[a]	103	97.9	96.0

Sample volume: 100 mL. a. Relative satandard deviation, % (n = 5). N.d. Not detected.

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SOFTWARE SOLUTION FOR POST-COLUMN ISOTOPE DILUTION HPLC-ICP-MS

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Isotope dilution (ID) is a powerful technique allowing accurate measurements which are traceable to the SI system. By the combination of isotope dilution with high performance liquid chromatography and inductively coupled plasma mass spectrometry (HPLC-ICP-MS) is thus possible to obtain an analytical tool for the accurate speciation analysis. The problem is the evaluation of data obtained in this way. For post-column species-unspecific ID, which is isotopically enriched solution mixed with effluent from the column, is necessary to evaluate chromatogram point by point which is very difficult to do manually. At present, there is no software solution for processing of referred data type. The subject of this work was the development and validation of software for processing of data obtained by referred method. The software development was done in the programming language Object Pascal through the program Delphi 7 Personal. Software includes basic and advanced features like automatic detection of input data format, choice of isotopes for ID including also their sums, data filters, export to MS Excel, calculations of the mass discrimination correction, detector dead time correction or automatic modification of the input parameters based on detection of selected isotopes. The software validation was proved by static and dynamic software testing and by analysis of certified reference material and real samples of plants. Software also allows evaluation of chromatograms by calibration curve method with or without internal standard.

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ON THE USE OF CHROMATOGRAPHY FOLLOWED BY MASS SPECTROMETRY FOR SPECIATION OF ZINC IN PLANTS

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The aim of this work was to optimize the analytical procedure enables the investigation of zinc speciation in plants exposed to the industrial contamination. For this purpose the HPLC ICP MS was used and the experimental conditions for various chromatography separation were optimized. The analytical scenario for speciation studies was developed toward the evaluation of the bio-mechanism which enables plants to adapt for unfavorable environmental conditions.

Plants of *Plantago lanceolata*, well adapted to unfavorable environmental conditions of mining dump were used in this study. Important features of these plants are the ability to accumulate metals, e.g zinc and the mechanisms protecting plants from harmful environmental influence. Therefore mining dump plants are attractive objects of research related to remediation processes.

In this work zinc speciation both in roots and over ground parts of *Plantago lanceolata* was evaluated. Plants were grown under hydroponic conditions in a Knapp medium enriched with zinc inorganic compounds. Than a part of floral material was exposed to liquid nitrogen and used in speciation investigation. Zinc-containing species were extracted using a set of extractants solutions at various pH, from 4 to 10. Therefore the effect of pH of extractant medium on the speciation of zinc was examined.

The determination of zinc speciation was conducted using an inductively coupled plasma mass spectrometry (ICP MS) and high performance liquid chromatography (HPLC). The size exclusion chromatography (SEC) was used to evaluate the molecular weight of zinc-containing compounds. The ion-exchange chromatography was used to separate various ionic zinc species. Selected fractions of eluent were collected and analyzed using electrospray ionization mass spectrometry (ESI MS) in order to examine the structure of zinc compounds.

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DFT, FT-IR AND RAMAN INVESTIGATIONS OF 1-PYRROLIDINO-1-CYCLOPENTENE

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FT-IR and Raman spectra of 1-pyrrolidino-1-cyclopentene (1py1cp) have been experimentally reported in the region of 4000-10 cm^{-1} and 4000-100 cm^{-1}, respectively. The optimized geometric parameters, normal mode frequencies and corresponding vibrational assignments of 1py1cp ($C_9H_{15}N$) are theoretically examined by means of the B3LYP hybrid density functional theory (DFT) method together with the 6-31++G(d,p) basis set. Furthermore, reliable vibrational assignments have made on the basis of the potential energy distribution (PED) and the thermodynamics functions, highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of 1py1cp have been predicted. Calculations are employed for three different conformations of 1py1cp in gas phase. Comparison between the experimental and theoretical results indicates that density functional B3LYP method is able to provide satisfactory results for predicting vibrational wavenumbers and envelope conformer is predicted to be the most stable form of 1py1cp.

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DEVELOPMENT OF ULTRASOUND-ASSISTED EMULSIFICATION SOLIDIFIED FLOATING ORGANIC DROP MICROEXTRACTION FOR DETERMINATION OF TRACE AMOUNT OF IRON AND COPPER IN WATER, FOOD AND ROCK SAMPLES

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Trace metals play an important role in human metabolism and either excess or deficiency of them in the living organism can lead to biological disorder [1, 2]. Diary ingestion of copper is indispensable for good health. However, high amounts of copper can be harmful, causing irritation of nose and throat, nausea, vomiting, and diarrhea [3]. Iron is mainly distributed in hemachrome, which occupied 60–70% of total iron in a body. A lack of iron can lead to iron deficiency anemia. Iron is stored in the body and large amounts can be toxic [4]. In the present study a simple and efficient liquid-phase microextraction technique was developed using ultrasound-assisted emulsification solidified floating organic drop microextraction (USAE-SFODME) combined with flame atomic absorption spectrometry, for the extraction and determination of trace amounts of iron and cooper in real samples. 2-mercaptopyridine n- oxide was used as chelating agent and 1- dodecanol was selected as extraction solvent. The factors influencing the complex formation and extraction were optimized. Under optimum conditions, an enrichment factor of 13.1 and 13 is obtained for iron and copper respectively from only 6.7 ml of aqueous phase. The analytical curves were linear between 40- 800 μg l^{-1} and 20- 1200 μg l^{-1} for iron and copper respectively. Based on three standard deviation of the blank, the detection limits were 8.6 μg $l^{-1}$and 4.1 μg l^{-1} for iron and copper respectively. The relative standard deviations (R.S.D) for ten replicate measurements of 500 μg l^{-1} of metal ions were 2.9 and 1.2 for iron and copper respectively. The proposed method was successfully applied for determination of iron and copper in environmental waters and some food samples including chess, rice, honey, powdered milk and black tea. Finally, method validation was made using rock certified reference material.

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DIRECTLY SUSPENDED DROPLET MICROEXTRACTION AND DETERMINATION OF TRACE AMOUNT OF IRON AND COPPER IN WATER, FRUIT, VEGETABLE AND ROCK SAMPLES

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Heavy metal composition of foods is of interest because of their essential or toxic nature. For example, iron, zinc, copper, chromium, cobalt and manganese are essential, while lead, cadmium, nickel and mercury are toxic at certain levels. Iron and copper are essential for human life at low concentrations, but they can also be toxic at high concentrations [1]. However due to matrix effect and low concentration of metal ions, efficient separation and preconcentration steps are essential prior to analytical measurements. In recent years there has been a growing interest in the development of miniaturized preconcentration methods based on liquid–liquid or solid phase extraction [2, 3]. In the present study a miniaturized liquid-phase extraction procedure based on directly suspended droplet microextraction combining with flam atomic absorption spectrometry for determination of trace amount of iron and copper was developed. The method is based on the extraction of the iron and copper complexes with 2-mercaptopyridine n- oxide onto a microdrop of methyl isobutyl keton (MIBK) as extractant solvent and subsequent flame atomic spectrometric determination. The factors influencing the complex formation and extraction were optimized. Under optimum conditions, enrichment factors of 25.7 and 25.4 were obtained from only 6.5 mL of aqueous phase for iron and copper respectively. The calibration graphs were linear between 40- 800 $\mu g\ l^{-1}$and 40- 1200 $\mu g\ l^{-1}$ for iron and copper respectively. Based on three standard deviation of the blank, the detection limits were 3.76 $\mu g\ l^{-1}$ and 1.84 $\mu g\ l^{-1}$ for iron and copper respectively. The proposed technique has been successfully applied for the determination of iron and copper ions in water samples, food samples and also rock certified reference materials with high efficiency.

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ELEMENTAL ANALYSIS OF BENTONITES USING CF-LIBS

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Geological samples, more precisely bentonites, have been analyzed by laser-induced breakdown spectroscopy (LIBS). The samples are named after the respective dominant element, so calcium bentonites. These issue from region of France. In LIBS, a pulsed laser light is focused on the sample to create the breakdown and spark of material and light emitted in the spark is analyzed by spectrometer. For determination the concentrations of the elements in the samples, calibration free laser-induced breakdown spectroscopy (CF-LIBS) was used.

In this work, we have recorded the LIBS spectra of three different samples to show the difference in the elemental composition. The aim of this work was to evaluate the performance of LIBS for the determination of trace elements, like barium and strontium, present in samples. The element analysis with LIBS have also compared with the measurement with ICP-MS.

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SURFACE-MODIFIED LUMINESCENCE OF Ru(II) POLYPYRIDINE COMPLEXES

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Ru (II) polypyridine complexes have been in focus of interest of coordination chemists as well as molecular spectroscopists in numerous studies, e.g. those devoted to elucidation of the localized/delocalized character of their metal to ligand charge transfer (MLCT) transition. Owing to their relatively long phosphorescence lifetimes, these complexes are frequently employed as luminescence probes [1]. In this study, we compare surface-modified phosphorescence from ^{3}MLCT excited state of Ru(bpy)$_3$ / Ru(II) tris(2,2'-bipyridine) complex/ and of Ru(bpy)$_2$(dcbpy) / Ru(II) bis(2,2'-bipyridine)(4,4'-dicarboxy-2,2'-bipyridine) complex/ adsorbed on Ag nanoparticle (NP) surfaces in Ag NP/complex hydrosol systems. Each of the two complexes is attached to Ag NP surface in a different manner: while dicationic Ru(bpy)$_3$ is attached electrostatically to the negatively charged outer part of the electric double layer enveloping the NPs [2], Ru(bpy)$_2$(dcbpy) is chemisorbed on Ag NP surface via the COO$^-$ group(s) of the (dcbpy) ligand. For the electrostatically bonded Ru(bpy)$_3$, the existence of two apparent short phosphorescence lifetimes indicates that there is heterogeneity of adsorbed Ru(bpy)$_3$ dication localizations within the system, which differ either by the strength and spacial distribution of the optical fields (isolated NPs versus aggregates), or by the distance of the chromophore from Ag NP surface. Furthermore, the phosphorescence lifetime of the chemisorbed Ru(bpy)$_2$(dcbpy) is almost 30 times shorter than that of Ru(bpy)$_3$ which indicates the strong effect of the direct interaction of the luminophore with the Ag NP surface on the efficiency of the non-radiative energy transfer from the adsorbed luminophore to the plasmonic metal NP.

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DETERMINATION OF TRACE METALS IN PHTHALOCYANINE-CONTAINING MATERIALS BY ATOMIC ABSORPTION SPECTROMETRY

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Phthalocyanine derivates (PTC), macrocyclic compounds with basic structure consisting of four pyrrole units with metal atom (Cu, Ag, Zn) coordinated in the centre of the molecule, could be utilized in various environmental technologies due to inhibitory effect on different microorganisms including pathogens. The advantageous possibility is application of PTCs added to the filtration system for wastewater treatment. The defined amount of PTC (maximum 1%) is mixed with polyurethane and electrospinning process is used for preparation of polymer nanofibres. Electrospun polyurethane nanofibers incorporating with PTC on the spunbond layer form nanotextile which is used in experimental filtration device. This arrangement provides elimination or complete removal of present microorganisms.

The aim of this work was observation of various metals and their concentration level before and after the filtration tests. The permeability of the filtration nanotextile membrane was also studied by using model metals solutions. Different samples of nanotextiles prepared for the experiment were analysed and after decomposition or extraction the metal occurs in PTC was determined. For the determination of metals high-resolution continuum source atomic absorption spectrometry was used.

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EFFECT OF CHEMICAL FORM OF MERCURY ON THE QUALITY OF RESULTS OF MERCURY CONTENT IN NATURAL WATER BY ICP-QMS

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The impact of chemical form of mercury on the quality of the results obtained by inductively coupled plasma quadruple mass spectrometry (ICP-QMS) was studied. The investigations were carried with the use of model samples containg an example inorganic species: mercury(II) nitrate and an example organic species: phenylmercury(I) acetate. The optimization of following experimental conditions e.g. the nebulizer gas (argon) flow rate, the lens voltage and the RF power was performed towards best analytical performance for individual chemical form of mercury. It was found that the sensitivity was significantly higher in the case of Hg(II) in comparison with the measurements, when mercury was present in form of PhHg(I). Thus, the measured total concentration of mercury in natural samples may not reflect the real content if the calibration has been made with the use of standard solutions containing single mercury species. This hypothesis was confirmed by the recovery studies, which were performed for the determination of mercury species in various water samples - it was not possible to obtain accurate results for Hg(II) with the use of calibration curve made for PhHg(I), and vice versa. Although the respond of ICP-QMS detector is sensitive in respect of the chemical form present in a sample, we intend to find-out conditions assuring the uniform response of measurement system. Three different strategies were investigated: 1) calibration of ICP-Q MS with a single-compound mercury standard solutions under compromised conditions; 2) microwave digestion of natural water samples applied before measurements; 3) the use isotope dilution mass spectrometry.

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INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY USED IN SORPTION STUDY OF PLATINUM AND PALLADIUM ONTO NANOMETER-SIZED TITANIUM DIOXIDE

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In this work, removal of Pt(IV) and Pd(II) from aqueous solutions was investigated. Hexachloroplatinate and tetrachloropalladate ions were used as model ions for the studied metals. Batch adsorption experiments using nanometer sized titanium dioxide (nano-TiO_2) as a sorbent were performed for this purpose. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used for the determination of the metals in model solutions. The optimal pH for the maximal adsorption of Pt(IV) was found to be pH 4.0; for Pd(II) it was 5.5. The kinetic data were analyzed on the basis of pseudo-first-order and pseudo-second-order kinetic models. The correlation results suggested that the adsorption processes followed pseudo-second-order kinetic model (see Table 1 below). The results obtained from equilibrium adsorption studies were fitted to Langmuir and Freundlich adsorption isotherm models. The adsorption isotherms were better fitted by the Langmuir isotherm equation and the maximal adsorption capacity of the sorbent was 8.75 mg/g for Pt(IV) and 11.7 mg/g for Pd(II) according to this isotherm (see Table 2 below). The study indicated that nano-TiO_2 is an effective adsorbent for the adsorption of Pt(IV) and Pd(II) from aqueous solutions.

Table 1. Coefficients of pseudo-first-order and pseudo-second-order kinetic models for Pt(IV) and Pd(II).

	Pseudo-first-order-kinetics			Pseudo-second-order-kinetics		
	q_e(cal) ($mg.g^{-1}$)	k_1 (min^{-1})	R^2	q_e(cal) ($mg.g^{-1}$)	k_2 ($g.mg^{-1}.min^{-1}$)	R^2
Pt(IV)	1.59	0.120	0.9785	3.03	0.183	0.9996
Pd(II)	5.53	0.102	0.9928	6.04	0.043	0.9985

cal – calculated; k_1 and k_2 – rate constants; R – regression coefficient

Table 2. Coefficients of Langmuir and Freundlich isotherms for Pt(IV) and Pd(II).

	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	q_{max} ($mg.g^{-1}$)	b_L ($l.mg^{-1}$)	R^2	k_F ($mg.g^{-1}$)	n ($l.mg^{-1}$)	R^2
Pt(IV)	8.75	4.95	0.9993	6.90	8.58	0.9053
Pd(II)	11.7	1.15	0.9988	8.52	4.02	0.8984

q_{max} and b_L – Langmuir constants; k_F and n – Freundlich constants; R – regression coefficient

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ON THE USE OF MASS SPECTROMETRY FOR THE INVESTIGATION OF BIOTRANSFORMATION OF SELENIUM 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 the investigation of the biotransformation is of great importance, especially in supporting investigation towards designing functional food. Mass spectrometry plays an important role in this field being used either for the elemental analysis (e.g. ICP MS) or for the investigation of the structure of various molecules (e.g. ESI MS).

The aim of the study was to assess the biotransformation of selenium in various foodstuff. Therefore the main goal was to study the speciation of selenium as well as its total content in different strains of *Lactobacillus* bacteria grown on medium supplemented with selenate (IV), various tissues from animals feed with probiotic bacteria enriched with selenium or plants grown in medium with the addition of selenates.

In order to estimate the effectiveness of selenium uptake by chosen organism, the total content of selenium was determined by using the microwave digestion followed by ICP MS measurements. Then, the biotransformation pathway as well as final compounds produced by the particular organisms from the inorganic precursor were investigated. For this purpose several extractants were used and the extraction conditions were optimized for each type of the organisms.

Selenium speciation was then evaluated after chromatographic separation, namely by HPLC followed by ICP MS inspection of the presence of selenium in chromatographic fractions or by ESI MS used for the evaluation of the structure of compounds being present. The main attention was focused on the identification of organic selenium species, mainly Se-methionine, Se-Met-selenocysteine and their derivatives. All results confirm that plant, microbial and animal organisms performed biotransformation of inorganic selenium precursors to its organic species. Thus their could be a good candidate for their use as a source of selenium in functional food products with pro-health effects on human body.

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PROFICIENCY TESTING IN WINE ANALYSIS

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The quality variety wines which are produced in specified regions of Slovakia are mostly watched category of wine in European Union. Quality control have to begin from soil analysis in the wineyard, throught the sampling during winemaking process to the final wine analysis. Protocol of analysis has to have an uncertainty of measurement and should be made in accredited laboratory.

In Slovakia there are 6 wine growing regions (Tokaj, East Slovakia region, South Slovakia region, Middle Slovakia region, Nitriansky region and Small-Carpathian region) where the quality wines with protected designation of origin are produced. Central Controlling and Testing Institute in Agriculture in Bratislava has an accredited laboratory for testing wine products before introduction into the market.

The article presents the results of our measurements in Proficiency testing FAPAS which were organized by Central Science Laboratory in York (England) in 2010 and 2011. Also results from proficiency testing between Slovak and Czech laboratories in 2009 and 2010 are added. Quality control in the wine sector presents very important feature in the market, therefore using certified reference materials and checking the accredited laboratories is very helpful [1]. Testing of wine in our laboratory is performed by EN ISO/IEC: 17025. This system needs validation of methods, reliability, precision, accuracy, qualified personal, rapidity and also taking parts in the international proficiency tests. The results shows, that z-score lies not outside the range ±2 and this is a chance that our results are actually acceptable.

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ON-LINE SPE-FAAS METHOD FOR DETERMINATION OF CHROMIUM IN WATER SAMPLES

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Chromium in the environment may be present at two common oxidation states, as compounds of Cr(III) and Cr(VI), which have different toxicological and biological properties. Cr(III) is an essential component of living organisms, having an important role in the metabolism of glucose, lipids and proteins, whereas Cr(VI) is a potentially carcinogenic agent. The wide industrial application of chromium (in metallurgy, metal smelting, electroplating, tanning, pigment manufacturing) has led to the contamination of soil, sediments, surface and ground water, that can cause serious health problems for humans and animals.

Therefore, the development of simple and reliable analytical procedures for chromium speciation in aqueous environmental samples is still required. Such method should combine the step of selective and efficient separation of chromium species with their sensitive determination. For that purpose the most popular is coupling of solid-phase extraction (SPE) with atomic absorption spectrometry. The implementation of automated on-line sample separation system allows for removal of matrix components and pre-concentration of analyte prior its direct transfer to the atomizer, what help to solve various analytical problems. The new sorbents, ion-imprinted polymers (IIP) have been introduced as selective materials for the separation of metal ions by SPE technique, recently.

In this work the method based on on-line coupling the separation of Cr(III) ions on microcolumn with analyte determination by flame atomic absorption spectrometry (SPE-FAAS) was developed. The microcolumn was filled with a new polymer prepared by imprinting of Cr(III) ions in the form of its complex with 8-hydroxyquinolinum (8HQ) into polystyrene-divinylbenzene matrix. The conditions for retention and elution of the analyte were optimized. It was found that effective retention of Cr(III) on the column containing 100 mg of the Cr-8HQ-VP polymer occurred from the solutions of pH 8-9. For quantitative elution of analyte the solution of 0.1 mol/L nitric acid was used. The application of computer-operated solenoid valves in the designed system allows for introducing the appropriate portion of eluate directly to the nebulizer of FAAS spectrometer. The proposed on-line SPE-FAAS method was applied for determination of analyte in real water and waste samples.

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REMOVAL OF HEAVY METALS FROM THE AQUEOUS SOLUTIONS AND ACID MINE DRAINAGE AT THE SMOLNIK LOCALITY BY *Aspergillus niger* WILD TYPE STRAINS

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Heavy metal pollution represents a significant environmental problem today arising from its toxic effects and accumulation throughout the food chain. Therefore the decontamination of the environmental pollution by toxic metals is a very important in the improvement of the quality of the environment. Conventional physico-chemical processes in use for heavy metal removal from aqueous solutions include precipitation, coagulation, ion exchange, extraction methods, adsorption etc. The application of biological technologies represents a new direction of solving the environmental burden by toxic metals. This attractive alternative techniques utilize the ability of microorganisms to bind heavy metals in aqueous solutions. The uptake of heavy metals by biomass can take place by an active mode known as bioaccumulation or by a passive mode termed as biosorption.

The present work involves an investigation of the ability of various *Aspergillus niger* (*A. niger*) wild type strains for removal of some heavy metals from experimental aqueous solutions of individual elements and the mixture of the elements and from acid mine drainage (AMD) at the Smolník locality (historical mine region). Heavy metals such as cadmium, copper, chromium, manganese and zinc were selected from the elements in order to study accumulation properties of the four strains of the *A. niger* species isolated from different environments (from weak alkaline pH = 7.7 to ultra acid pH = 3.0). Metal concentrations in live biomass were determined by flame atomic absorption spectrometry. According to the results, the bioaccumulation of the metals by studied strains of the *A. niger* from the AMD was in the order Cu (19 - 31%) > Zn (10 - 18%) > Mn (5 - 7%). The results have confirmed that using the *A. niger* as biosorbent for removal of the metals from water environment could be a strategy for its remediation.

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ELECTROCHEMICAL HYDRIDE GENERATION ATOMIC ABSORPTION SPECTROMETRY FOR THE DETERMINATION OF SOME INORGANIC ELEMENTS

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A flow-injection system with electrochemical hydride generation and atomic absorption detection for the determination of arsenic and selenium is described. This technique has been developed in order to avoid the use sodium tetrahydroborate, which is capable of introducing contamination. The sodium tetrahydroborate ($NaBH_4$) - acid reduction technique has been widely used for hydride generation (HG) in atomic spectrometric analyses. However, this technique has certain disadvantages. The $NaBH_4$ is capable of introducing contamination, is expensive and the aqueous solution is unstable and has to be prepared freshly each working day. In addition, the process is sensitive to interferences from coexisting ions.

A simple electrochemical flow-through cell with powder carbon as cathodic material was used and optimized. The influence of the generation current, concentration of the catholyte, carrier stream, flow rate of the sample and interferences by other metals on the generation of hydrogen arsenide and hydrogen selenide were studied. This system requires only a small sample volume and is very easily automatized. The electrochemical HG technique combined with AAS is a well-established method for achieving the required high sensitivity and low detection limits.

A Perkin-Elmer 5000 AAS was used, with an electrically heated quartz tube atomizer. The electrolyte is continuously conveyed by peristaltic pump. The sample solution is introduced into the loop and transported to the electrochemical cell. A constant current is applied to the electrolytic cell. The gaseous reaction products, hydrides and hydrogen, formed at the cathode, are flowed out of the cell with the carrier stream of argon and separated from the solution in a gas-liquid separator. The hydrides are transported to an electrically heated quartz tube with argon and determined under operating conditions for hydride forming elements by AAS.

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ELEMENTAL ANALYSIS OF SYSTEMS BASED ON GOLD NANOPARTICLES USING OF X-RAY FLUORESCENCE AND INDUCTIVELY COUPLED PLASMA - OPTICAL EMISSION SPECTROSCOPY

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Systems based on modified gold nanoparticles has been prepared and studied recently for various scientific and practical applications, e.g. in optical spectroscopy, plasmonics, electronics and separation science [1, 2]. Both the final nano-particulate systems and various precursors (intermediate systems) have to be characterized by various physico-chemical methods. The information on elemental composition is crucial for the estimation of the content of nanoparticles in the systems and for calculation of their coverage by modifying (mostly organic) ligands. X-ray fluorescence spectroscopy methodologies have been developed for characterization of gold nano-particulate systems aiming at determination of several elements, predominantly gold and sulfur, because thiol group is ordinarily used for fixation of organic substances on gold surfaces. Unusual ratios of L and M lines of gold have been observed with relative enhancement of M lines for nano-particulate systems. Nevertheless, the detection limits are insufficient for characterization of several (quite dilute) nano-particulate systems. Thus, the determination of gold content based on inductively coupled plasma – optical emission spectroscopy (ICP-OES) is developed for characterization of systems prepared in both aqueous and various non-aqueous media. Reliable data can be obtained to check the individual preparation steps of quite complex systems based on modified gold nanoparticles.

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INVESTIGATION OF DISSOLVED CATIONIC ALUMINIUM SPECIES SORPTION ON SOME NANO-SIZED METAL OXIDES FOR ANALYTICAL PURPOSES USING ATOMIC SPECTROMETRY METHODS

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Sorption of dissolved cationic Al (III) cations on nanometer-sized TiO_2 (anatase), ZrO_2 (zirconia) and α-FeOOH (goethite) was investigated with aim to separate and preconcentrate trace amounts of Al in water solutions by solid phase extraction (SPE) prior to its determination by slurry electrothermal atomic absorption spectrometry (ET AAS) and inductively coupled plasma optical emission spectrometry (ICP OES). The measured sorption data follows the Langmuir isotherm using a monolayer adsorption model. Maximum sorption capacity of studied metal oxides was determined to be 27.7 mg Al g^{-1} TiO_2, 20.1 mg Al g^{-1} ZrO_2 and 37.9 mg Al g^{-1} α-FeOOH at pH 5.0-6.0. Adsorption of Al(III) on the all oxides is relatively fast with similar kinetics using a pseudo-second order model. Finally, the batch & slurry mode of SPE procedure with the direct TiO_2 or ZrO_2 phase-slurry sampling followed by ET AAS detection and quantification was used. α-FeOOH was not possible to use by this way because of strong spectral interferences of iron from goethite for slurry ET AAS. Furthermore, the desorption and elution of Al from all three metal oxides using nitric and hydrochloric acid with various concentrations (0.1-5.0 M) was not sufficient. The method accuracy was checked by the analysis of lake water CRM TMDA-61 and by the technique of analyte addition (sample spiking). Under the optimal conditions, the calibration curve for batch & slurry TiO_2 or ZrO_2 SPE with a 10-fold preconcentration was linear up to 40 μg L^{-1} Al. The limit of detection (LOD) and the limit of quantification (LOQ) was 0.1 μg L^{-1} Al and 0.32 μg L^{-1} Al, respectively, with a preconcentration factor of 20 and a relative standard deviation (RSD) lower than 5%.

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DISTRIBUTION OF MANGANESE IN THE SOIL-WATER-PLANT IN THE ZONE OF BURSHTYN THERMAL POWER STATION

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In the surface layers of the lithosphere manganese's behavior is very complicated and depends on several factors, most important of which are the pH value and redox potential. The conditions that promote oxidation of manganese, sharply reduce the availability of this metal to plants and vice versa. Biochemical functions of manganese are concentrated mainly in redox processes.Systematic study of content and forms of manganese in the biosphere, depending on season, the distance from environmental contaminant and features of morphological structure of plants that grow in areas of pollutant's influence are not conducted. The work is conducted in the northeastern part of Ivano-Frankivsk region, where the Burshtynska thermal power plant (BuTPP) is located which is on the list of top 100 environmental contaminates among the industrial establishments of Ukraine and represents the largest environmental contaminat of Precarpathian mountains and neighboring countries. This work presents the results of gross distribution and exchange (movable) forms of manganese in soils, water and celandine (*Chelidonium Majus* L.) zone location area of BuTPP and area of active influence of it at a distance of 8 and 16 km. Quantitative analysis of gross and soluble manganese was conducted by atomic absorption spectrometry method with inductively bound argon plasma on Plasmaquant-110. Mineralization of the studied materials was carried out by conventional "wet " ashing method. Analysis of manganese gross content in soils where BuTPP is placed and zone of active influence of thermal power plant on different seasons of the year gives the reasons to state that the gross content of manganese in areas of active influence of thermal power plant is significantly higher, has season dependence with the minimum values in autumn and shows a pronounced tendency to decrease which is connected with distance degree from environmental contaminates. The content of movable manganese in spring in the TPP area and 8 km distance is significantly higher than metal content in the control area. A similar dependence of the movable manganese's content is established in the autumn season. The content of gross and movable manganese in water of TPP location area and zone of its' active influence is significantly higher than similar rates of control areas and has seasonal dependence only in summer. The results of manganese content research in organs of celandine, which sprouts in area of technological influence of BuTPP gives reasons to state that changes in metal content in celandine have a complicated specificity which depends on season, distance of the industrial facility and morphological structure of plants.

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THE AAS ANALYSIS OF SELECTED TOXIC METALS IN NATURAL WATERS AND SOILS FROM AN AREA AFFECTED BY MINING ACTIVITIES (ŠPANIA DOLINA, SLOVAKIA)

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Heavy metal contamination affects some areas in Slovakia where for long historical periods took place heavy metals mining and processing activities. Špania Dolina is located in Central Slovakia close to the town of Banská Bystrica, in the southern part of Low Tatra Mountains. This region was world-famous for intense mining activity, especially for mining and processing of copper.

This study is focused on the AAS analysis of selected metal elements in the soil, surface and groundwater from the locality of the Špania Dolina. The sampling sites were selected on the basis of their position relative to the dump field Maximilian in order to assess its potential impact on environmental contamination. Soil samples (0–15 cm depth) and water samples were collected during the year 2011. The samples were analyzed for metals by the atomic absorption spectrometry method with electrothermal atomization - ETAAS (As, Sb, Ni, Pb, Cd, Co, Ag, Se, Cr) and flame atomization - FAAS (Cu, Zn, Fe, Mn).

Determinations were performed using the atomic absorption spectrometer AAS Spectra DUO 240 FS, Varian (FAAS) and using the atomic absorption spectrometer Avanta Σ, GBC (ETAAS) equipped with deuterium background corrector and GF 3000 graphite furnace. For both techniques were optimized measurement conditions for a various types of samples. These techniques were validated and quantification of uncertainty was performed. The measured results are presented.

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DETERMINATION OF WATER CONTENT IN OIL WITH THE APPLICATION OF FTIR SPECTROMETRY

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In order to determine water content in oil, the volumetric Karl Fischer method is usually used in tribotechnical diagnostics. In the case presented in the paper, a validated potentiometric titration was used, which is commonly applied to determine water content in crude oil substances within the range from 0.01% to 10% of water with an expanded uncertainty U = 8%. The measurements were performed with a semi-automatic potentiometric titrator 702 SM Titrino using a polarisable double platinum electrode with a constant electric current Ipol = 25 μA. It is a time consuming method that requires a good skill of a laboratory technician and involves harmful chemicals application. Therefore, based on this method, the FTIR (Fourier Transform Infra-Red Spectrometry) method for the quantitative determination of water in oil was. The method was developed to determine water in aircraft engine oil ASTO-555 (Aero Shell Turbine Oil 555). It is synthetic polyester oil with a good bearing capacity of a lubrication film containing additives which increase its thermal and oxidative stability. Since the presence of water is manifested in different regions of the infrared spectrum depending on the type of base oil in the range of wavenumber approx. 3100 to 3700 cm^{-1}, it is necessary to measure water content for each lubricant separately according to a mutual reactivity of water and a specific lubricant. Oil spectra were measured with the SPECTRUM 1000 spectrometer in the central region of the infrared spectrum in the range of wavenumber from 700 cm^{-1} to 4000 cm^{-1} in BaF_2 measuring cell with the thickness of 0.1 mm and a resolution of 4 cm^{-1}. As the source of radiation, the spectrometer makes use of a globar (silicon carbide), the Michelson interferometer for a spectrum signal processing and the DTGS bolometric detector (deuterated triglycine sulphate). The FTIR method was developed by the calibration curve method based on the volumetric measuring of water content of the prepared samples of oil ASTO-555 with accurately weighed quantity of water within the range approx. 0.2 to 2% of water and an absorption band area of water in the range of wave number 3110 cm^{-1} to 3745 cm^{-1}. The method accuracy was verified by the measuring of the actual oil samples with the known water content.

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ANALYTICAL SCENARIO FOR THE INVESTIGATION OF BIOTRANSFORMATIONS OF SELENIUM IN PLANTS

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Selenium is an essential element for the proper functioning of humans and animals. This is due to its incorporation in proteins important for cell metabolism, known as selenoproteins. Selenium, if present in a biologically active chemical form, affects the elimination and inhibition of the formation of oxygen free radicals, thus protecting cells from damage, aging and metabolic disorders.

Its recognized antitumor properties seem to be particularly important. A direct correlation between increasing number of cancer occurrences and selenium deficiency in the diet has been observed. Population living on selenium-poor areas more often suffer from cancer than those living in areas rich in this element. Therefore, all researches towards development of dietary supplementation of selenium, which could compensate a natural deficiency of selenium, are considered to be important. It is known that consumption of vegetables which have the ability of biotransformation of inorganic forms of selenium taken up from the soil into the most favorable to humans, antitumor, organic forms - selenoaminoacids, may play a significant role in the prevention of cancer.

The aim of this study was to evaluate the biotransformation of different selenium inorganic precursors by onions (*Allium cepa* L.) grown hydroponically or in soil. In particular, identification of selenium organic compounds in plants was of a great interest as this allows understanding of the processes of biotransformation as well as distribution of selenium. The special attention was focused on the comparison of the influence of the support used for the cultivation of plants on the biotransformation of selenium.

Both biological and chemical methods were used in order to collect complementary information about the response of the plants to the presence of selenium inorganic compound either in Knopp solution (used as a support for the hydroponic cultivation) or in soil. In order to evaluate the growth of onion roots and the mitotic activity in apical meristem of roots, Allium Test was used. Also the cell ultrastructure of root tips of plants was analyzed using transmission electron microscopy (TEM).

Total content of selenium in various plant organs was determined after microwave-assisted digestion in closed vessels followed by inductively coupled plasma mass spectrometry (ICP-MS). High-performance liquid chromatography (HPLC), coupled to ICP-MS was used for the selenium speciation. The specific difference in the behavior of the selenium in plant's organ will be highlighted.

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ON THE SPECTRAL BEHAVIOR OF RIFAMPICIN MOLECULES IN SOLUTIONS AND FERROFLUIDS

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Rifampicin, a well known and widely used antitubercular agent, was investigated in the frame of this study by spectral and theoretical means, focusing on the intermolecular interactions occurring between this antibiotic and various non-polar and polar solvents, as well as between this drug and iron oxides (such as magnetite nanoparticles). Using quantum mechanical molecular modeling (PM3 semi-empirical method, HyperChem package), the changes in the rifampicin structural and physico-chemical features (dipole moment, polarizability, frontier energies, atomic charges and bond lengths etc.) were revealed when passing from gas phase to solution. All calculations were performed on the fully optimized geometries of the rifampicin molecule. Electronic and vibrational spectra were simulated as well, the results being further compared with the ones recorded experimentally. The solvent effect upon rifampicin absorption spectra was emphasized mainly in polar solvents by a blue shift of 1160 cm^{-1} in the UV range and respectively, of 460 cm^{-1} in the visible range. By correlating the obtained spectral data with Bakhshiev's mathematical model, it was found that the orientation-induction interactions were dominant in the binary solutions of rifampicin with polar solvents, while the dispersion forces were the main ones manifesting in rifampicin solutions with non-polar solvents. The solvent influence upon rifampicin binary solutions was also evidenced by Raman measurements comparatively with the Raman spectrum of rifampicin powder. The computational plotting of rifampicin 3D mapped electrostatic potential also revealed four interaction sites (with high electronegativity), which may explain the strong interaction between rifampicin and iron oxides. Following the synthesis of iron oxide nanoparticles (Fe_3O_4) with subsequent dispersion in aqueous solution with rifampicin, characterization of the resulted ferrofluid was carried out through various methods (UV-Vis electronic spectra and diffuse reflectance spectra recordings; X-Ray diffraction and Vibrating Sample Magnetometry measurements etc.) confirming that, based on the direct coupling of rifampicin to magnetic nanoparticles, it was possible to obtain magnetic carriers with wide biomedical applications.

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MOLECULAR MODELING AND SPECTRAL INVESTIGATION ON SOME TRIPHENYLTETRAZOLIUM CHLORIDE DERIVATIVES

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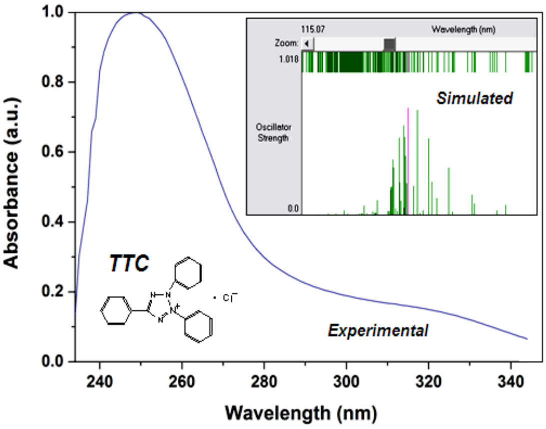
TTC (2,3,5-triphenyltetrazolium chloride) is a redox indicator - spectrally active in the ultraviolet range, that is enzymatically reduced in living tissues by various dehydrogenases up to TPF (1,3,5-triphenylformazan) - spectrally active in ultraviolet and visible range.



The theoretical UV-Vis (Figure to the right) and IR spectra of TTC and three TPF derivatives were generated (following geometry optimization) using HyperChem program based on semi-empirical method PM3. Also the values of several structural features (such as dipole moments, energy of the highest (E_{HUMO}) and lowest (E_{LUMO}) electronic states, etc.) were calculated. The results showed significantly increased values of the two frontier energy levels as well as of the dipole moments in the TPF2 and TPF3 molecules (that differ from TPF1 and TTC by the nitro or carboxyl functional group substituted in the para- or ortho- position of the second phenyl ring). Solvent box model was applied to the studied compounds to evidence solvent influence on the solute molecular parameters mentioned above. Spectral measurements were carried out in the UV-Vis range using a solvent array with various physico-chemical properties – with focus on the intermolecular interactions in diluted solutions. Solvent shift effect was discussed based on the Bakshiev's theory [1] considering mainly the dipole-dipole and dispersive interactions between solute and solvent. The recorded infrared spectra revealed some vibrational modes between 1500 and 1600 cm^{-1} for TTC (but not the TPF derivatives) that can be assigned to the presence of the tetrazole ring, while the strong vibration at 1220 cm^{-1} was evidenced in the TPF1 to TPF3 IR spectra (but not in TTC one) possibly due mainly to the C-N stretch loosened up after the breakage of the -N-N= bond from the tetrazole ring of TTC in the reducing process to TPF [2]. The differences in the IR spectra of the three TPF were also discussed based on the influence of the substituents in each triphenylformazan derivative.

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oaTOF-ICP-MS ANALYSIS OF GADOLINIUM IN ALGAE, SURFACE AND WASTE WATER

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Contrast mediums based on gadolinium compounds have been utilized for an imaging of any anatomical sections by magnetic resonance since 1988. These Gd-complexes show great stability and inertness inside human body and therefore are excreted in an unchanged form. Excreted Gd follows a regular way of waste water disposal and even despite this process, Gd persists and continues to surface waters (Hennenbrüder *et al.*, 2004). An increased concentration of anthropogenic Gd in surface waters have been studied since 1996 and this phenomenon received name "the positive gadolinium anomaly". Anthropogenic gadolinium enters water ecosystems and can accumulate in river plants, organisms and sediments. Natural food chain could be the way of possible health risk for humans. With regards to widespread utilizing of gadolinium based contrast mediums for magnetic resonance, a monitoring and elimination of anthropogenic gadolinium in natural ecosystems appears to be necessary (Kulaksiz *et al.*, 2011).

In our study, we investigated a possible use of oaTOF – ICP – MS for determination of lanthanides especially Gd in waste water. Examined waste waters were provided by two easts–Czech hospitals (College hospital in Hradec Králové and Regional hospital of Pardubice). Obtained data proved the positive gadolinium anomaly. Second part of this study was dedicated to the bioaccumulation experiment. Algae of family Chlorella was cultivated in Gd mediums. Bioaccumulation factors were assessed after one months of cultivation. We faced a contamination problem during the bioaccumulation experiment as well as problems connected with a small sample preparation.

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MULTIELEMENTAL ANALYSIS OF HORSE HAIR BY oaTOF-ICP-MS

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An analysis of hair is plentifully utilized to asses an impact of the environment, or diet habits on the state of health of organism (biomonitoring of pollutant´s exposition and bioaccumulation). Hair tissue presents a very specific tool to consider an intoxication of organism by various elements (As, Cd, etc.) or by organic compounds such as PCDD, PCDF, PCB, PAH, THC, barbiturates and so on. Trace elements, minerals, drugs, toxins and their metabolites are incorporated to the structure of hair during life where can be determined even after long time. Usually a hair stem presents information about exposition of drugs or other chemicals several months or years retrospectively and a hair root reveals an actual exposition (Dunnett *et al.*, 2003). An analysis of horse hair is connected with horse riding where it can be useful for horse health assessment or as a proof of banned compounds. Elemental composition of horse hair can be investigated from many aspects such as dependence on the state of health, age, colour, stabling, feeding, etc. (Anielski *et al.*, 2005).

We collected one hundred samples of horse hair from horse stables through Czech Republic. 32 testing horses came from Siglavy (České Budějovice) stable, 23 came from Jeníkov (near Giant Mountains) and 45 horses originated from private horse breeders in a vicinity of Pardubice. Samples were washed, to eliminate exogenic contamination, by optimized procedure prior to digestion and following analysis. A multielemental analysis of horse hair by oaTOF-ICP-MS was optimized and obtained huge pack of data was submitted to multi-dimensional statistical analysis. Statistical evaluation was focused on different groups of horses according to different types of stabling, stabling places, colour and gender. No significant differences between individual groups were found.

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ICP-MS FOR ANALYSIS OF FISH SCALES AND OTOLITHS OF PERCH (*Perca fluviatilis*) AND BREAM (*Abramis brama*)

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Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was utilized for the analysis of the fish scales and the otoliths collected from two species of fish perch (*Perca fluviatilis*) and bream (*Abramis brama*). Perch ranks among freshwater predatory fish and bream is omnivorous fish. The fish scale has characteristic structure similar to bones or teeth, all these materials are composed of following parts: organic section forms collagen type I, inorganic part consists of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) with presence of a significant amount of foreign ions and water [1, 2]. The otolith is calcified biomineral which is comprised of mainly mineral phase calcium carbonate ($CaCO_3$) and organic matrix. The organic phase only accounts for 0.01 - 10% of the total mass [3].

Samples of calcified tissues were analyzed by inductively coupled plasma mass spectrometry. We gained the average amount of selected elements in the scales by decomposition in the mineralization equipment and following ICP-MS analyses. Laser Ablation (LA) in conjunction with inductively coupled plasma mass spectrometry (LA-ICP-MS) was used for the direct analysis of the solid samples of fish scales and otoliths. These direct analyses allow obtaining the elemental distribution in the tissue. We were able to observe differences between storage of elements in an anterior and posterior part and focus of scales. The obtained results reflect the dietary habits and status of individuals in the food chain.

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APPLICATION OF 5-PHENYL-3-AMINO-2,4-DICYANOBENZOATES AS SPECTROSCOPIC PROBES FOR MONITORING IN REAL TIME PHOTOPOLYMERIZATION PROCESSES

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Molacular spectroscopic probes found a variety of use as fluorescent probes and labels in many applications. For example fluorescent probes are the most powerful tools that can be used to measure solvent polarity and viscosity [1,2], in biochemical applications and in material science. Molecular fluorescent probes are used in order to understand the physical and chemical processes that occur at the molecular level. This is possible because their fluorescence is sensitive to the mobility and/or microviscosity of the molecular environment in which the fluorescence probe molecules are located. One of the most important applications of fluorescence probes is a monitoring of the polymerization processes especially photopolymerization processes.

The photocurable compositions were prepared by dissolution of the photoinitiator and each probe in monomer (TEGDVE for cationic photopolymerization and PEGDA for free radical photopolymerization), so as to obtain the concentrations 5.0 10^{-3} mol/dm^3 of the probe and 1 wt% of the photoinitiator. The cure monitoring system used in this study was described previously [2].

In this communication the performance of a series of 5-phenyl-3-amino-2,4-dicyanobenzoates derivatives as fluorescent probes for monitoring of cationic photopolymerization of monomers by Fluorescence Probe Technology (FPT) has been studied in comparison to the performance of 7-diethylamino-4-methylcoumarin (Coumarin 1) probe. It was found that the phthalimide probes are much more stable than Coumarin 1 under cationic polymerization conditions. Moreover, the 5-phenyl-3-amino-2,4-dicyanobenzoates probes turned out to be long-wavelength sensitizers for the diaryliodonium photoinitiators used to initiate the polymerization process. The sensitizing effect of the probes compensates in excess the inhibiting effect of their amino groups on the cationic polymerization kinetics.

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DEVELOPING OF FLUORESCENCE PROBES BASED ON ACENAPHTHENE FOR MONITORING OF PHOTOPOLYMERIZATION PROCESSES BY FLUORESCENCE SPECTROSCOPY

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Fluorescence Probe Technology (FPT) is a new method, which offers the possibility of on-line applications for monitoring of polymerization processes by means of specially designed fluorescent molecular probes that change their fluorescence characteristics upon changes occurring in their environment.

During the past few years monitoring of polymerization processes using fluorescent probes has been the most popular and powerful tools that can be used in order to understand the physical and chemical processes that occur at the molecular level [1, 2]. This is possible because their fluorescence is sensitive to the polarity and/or microviscosity of the molecular environment in which the probe molecules are located. One of the most important applications of fluorescent probes in polymer chemistry is monitoring of a photopolymerization process. Theoretically, every process that causes change of the system polarity or microviscosity should be able to be monitored by using fluorescent probes. However, depending on the type of the process and the monitoring parameters, appropriate structure and characteristics of the probe are required. Therefore, there are no completely versatile probes.

Search for new probes for monitoring polymerization resulted in the discovery of probes that are derivatives acenaphthalene which were used to study the kinetics of cationic and free radical photopolymerization.

The photocurable compositions were prepared by dissolution of the photoinitiator and each probe in monomer, so as to obtain the concentrations $5.0.10^{-3}$ mol/dm^3 of the probe and 1 wt% of the photoinitiator. The cure monitoring system used in this study was described previously [2].

In this communication new fluorescent probes containing acenaphthalene ring were characterized and their principal applications are presented. It was found that 5-(2-phenylethenyl) acenaphthene and 5-(phenylamino) acenaphthene are well adaptable for the monitoring of cationic and free radical photopolymerization processes with good sensitivity.

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QUANTITATIVE ANALYSIS OF B_2O_3 CONTENT IN GLASSES BY X-RAY FLUORESCENCE SPECTROSCOPY

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The presence of B_2O_3 in glasses causes many of their interesting properties, such as high resistance against the temperature shocks, outstanding dielectric properties and also the preparation of glasses which melt down at low temperature and are used for vitrification of nuclear waste. It is necessary to know the exact amount of B_2O_3 in glasses in order to optimize their properties. We focused on elaboration of B_2O_3 quantitative determination method using the XRF analysis. The samples for analysis were prepared by pressing with the addition of wax. To detect the corectness of the analytical method, there were observed the influence of used spectral line for each chemical element, the method used for determination of the intensity of analytical line, matrix effects and also the influence of conditions during the preparation of samples. The significance of listed influences was evaluated by the analysis of variance. Calibration curves were made by using the standards. After selection of appropriate conditions for analytical lines intensity measurement and optimalization of conditions for samples preparation by pressing we specified the reliability interval for B_2O_3.

P-74

VIBRATIONAL SPECTROSCOPIC ANALYSIS OF SOME HOFMANN TYPE COMPLEXES

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Some new Hofmann type complexes with chemical formula of $M(4pypp)_2Ni(CN)_4$ (where 4pypp = 4-(1-pyrrolidinyl)piperidine and M = Ni or Co) have been prepared and their FT-IR and Raman spectra are reported in the region of 4000-200 cm^{-1} and 4000-100 cm^{-1}, respectively. The ligand molecule, polymeric sheet and metal – ligand bands of the compounds are assigned in detail. Vibrational spectra together with assignments of 4pypp ($C_9H_{18}N_2$) are experimentally and theoretically studied in the region of 400-100 cm^{-1}. Normal mode frequencies and corresponding vibrational assignments of $Ni(CN)_4^{2-}$ are theoretically examined by standard quantum chemical technique. The results suggest that these compounds are similar in structure to the Hofmann type complexes and the 4phpy ligand molecule bonds to the metal (M) atom of $|M\text{-}Ni(CN)_4|_\infty$ polymeric layers.

P-75

BIOANALYTICAL ICP-MS METHOD FOR QUANTIFICATION OF POTASSIUM CHANGES IN THE CELLS AND SUPERNATANTS AFTER ACTION OF CYAA TOXIN

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Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is becoming commonly used technique for quantification of a concentration of elements in biosamples to support the studies in the field of microbiology. The biggest advantage of this method is sensitivity and accuracy of the analysis.

The purpose of this poster is to present a bioanalytical ICP-MS method procedure applied to the quantification of changes of intracellular potassium concentration after action of pore-forming adenylate cyclase toxin (CyaA) from bacterium *Bordetella pertussis*. Several lines of cells were treated with CyaA toxin causing different degree of potassium release due to its interaction with target plasma membrane. The ICP-MS was employed to carry out kinetic studies monitoring the changes of the potassium and sodium concentration inside the cells and in the cell supernatants in different time-points. The quantification was realized using external calibration with potassium standards in the range 0-2 ppm prepared in water for cells samples and in the reaction buffer for supernatants. Scandium was used as an internal standard. In result the ICP-MS procedure provided a reliable and straightforward analytical approach enabling kinetic studies in the microsamples for biological studies.

Acknowledgement: This project was supported by Grant project P302/11/0580 and with institutional support RVO:68081715

P-76

INFLUENCE OF THE DIFFERENT FARMING SYSTEMS ON ELEMENTAL CONTENT OF *Vitis vinifera* AND ON ANTIOXIDANT PROPERTIES OF WINE

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The aim of this study was to evaluate the influence of two fastest growing viticulture farming systems in the Czech Republic and Europe (Integrated and Organic farming system) on elemental content of *Vitis vinifera* and wine and the effect of different farming systems on total antioxidant activity of wine.

Two cultivars of *Vitis vinifera* (Sauvignon blanc and Pinot noir) and samples of 2010 Pinot noir claret wine from both farming systems have been chosen for analysis. Due to comparative nature of this work, all plants were grown under well defined organic and integrated farming system conditions (Czech regulations 242/2004, IFOAM standards 2005, EU regulations 2092/91) by the same farmer and producer, so we have excluded the influence of different methods of treating and winemaking.

The determination of 22 elements (Li, Be, Na, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Sn, Ba, Tl, Pb – selected by essentiality and possible toxicity) in extracts of soil, leaves, grapes and wine samples collected from vineyards of Ivaň (belongs to wine region Mikulov, bigest wine region in Czech republic) was performed. For this purpose, inductively coupled plasma-mass spectrometry has been used. For the determination of elements influenced by polyatomic interferences, collision cell technology on He/H mode has been used.

Antioxidant properties of Pinot noir cleret samples from ecological and integrated production were investigated by Electron paramagnetic resonance spectroscopy, using stable radicals 1,1-diphenyl-2-picrylhydrazyl (DPPH). For evaluation EPR spectra, Origin and MicromathScientist software were used. As reference technique UV-VIS spectroscopy (734 nm) using ABTS system was chosen.

For the evaluation of data multivariate statistical methods were used (ANOVA, DA, PCA).

Results revealed differences in elemental composition of *Vitis vinifera* leaves, berries and also the wine related to farming practice. Concentrations of Cu and Zn were significantly different and link between the farming practice and the content of these elements was found. It was found that farming systems had almost no influence on radical scavenging activity of wine.

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P-77

ELEMENTAL ANALYSES OF TEXTILE STRUCTURES BY LIBS

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An analysis of textiles is a specific part of elemental analyses. Structures based on fibres (structural units of textile structure) have large surface area, high porosity and specific optical properties. In the case of Laser Induced Breakdown Spectroscopy (LIBS) is connected the analyses of textile with specific problems such as high variability of result and selection of sample holders.

In this study are described in details the textile structures as a matrix of elements, which should be analysed. The overview of elemental analyses aims is described according personal experiences of authors and literature research.

Experimentally is in this study described the elemental analyses if polyamide by LIBS. Polyamide is analysed in different form: foil, standard textile and nanofibres. Of forms of polyamide were modified by different concentration of chromium, which was in the samples measured by LIBS.

Real concentration of chromium in polyamide was exactly estimated by standard inductively coupled plasma optical emission spectrometry (ICP-OES).

The typical problems of elemental analyses of fibre structures were described and comment in this study. Some solutions are proposed and discussed.

P-78

COMPARISON OF SOLID-SAMPLING SPECTROGRAPHIC AND SPECTROMETRIC METHOD AT THEIR UTILIZATION FOR DETERMINATION OF IMPURITY ELEMENTS IN PD-C CATALYSTS

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The kinetic of catalytic processes can be influenced by impurities or by accompanying elements present in the catalysts or their supports respectively. Therefore, it is effective, within the application of catalysts, to monitor these components, mostly present at accompanying or trace concentrations.

Pd catalysts supported on carbon or SiO_2 are widely used for hydrogenation processes. Both of these combinations are an appropriate medium for the application of direct (solid-sampling) methods of atomic spectroscopy, which are in accordance with the principles of the so-called “green chemistry” (no chemicals, almost no waste). For this purpose, efficiency of classical spectrographic and modern spectrometric method of DC-arc-OES was compared.

From the obtained results it can be stated, that classical spectrographic method (PGS-2 spectrograph, free-burning DC-arc discharge) with photographic registration of spectra but with a modern semi-automatic densitometry and suitable evaluation software is also applicable for purposes of rapid informative analysis.

Spectrometric method, using CID-Echelle spectrometer Atomcomp-2000 with an integrated, computer-controlled DC arc excitation, enables optimization of the process via a choice of a large number of spectral lines of different orders of the spectrum.

Results of validation of both methods, including control analysis and analysis of several real samples, will be presented.

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P-79

SELF-ABSORPTION EFFECT USED IN MULTI LAYER PLASMA MODELING FOR ELEMENT DENSITY DETERMINATION IN LIBS ANALYSIS

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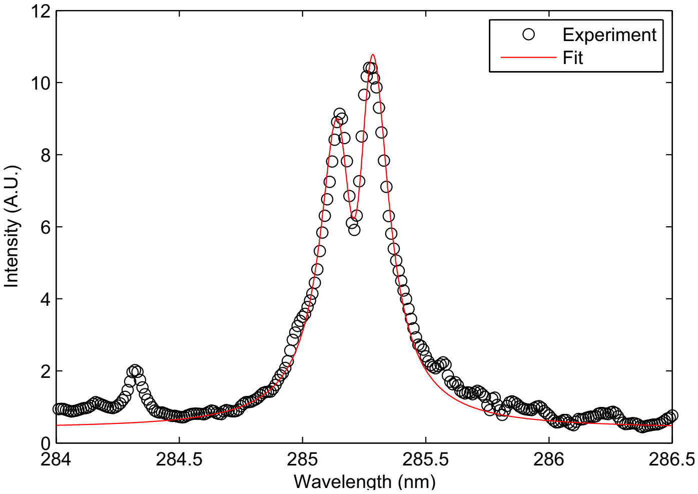
Laser-induced breakdown spectroscopy (LIBS) is the method which is mainly used for sample composition determination. This method is attractive as sample preparation is not needed and the experimental apparatus is simple, however it has some drawbacks. One of them is consequence of self-absorption which is considered to be a negative phenomenon influencing analyzed emission spectra. This effect decreases spectral lines intensities which are not longer proportional to density number of related element contained in the sample and so causing the error in the results. Recently some publications comment influence of self-absorption in LIBS analysis and its correction. This contribution presents possibility of usage of the self-absorption phenomena in positive way for determination of density number of magnesium in the laser induced plasma of aluminum alloys. For this purpose, many layers plasma model have been used for simulation of the profiles for two resonance magnesium transitions (Mg I 285.213 nm and Mg II 280.271 nm). The emission lines are strongly affected by self-absorption and their shape is self-reversed. The simulation is fitted to the experimental profiles obtained for different composition of magnesium in aluminum alloys (see figure) and results are compared with the nominal values.



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P-80

POSSIBILITIES OF MODERN SPECTROMETRIC METHOD (SS-DCA-OES) FOR THE CATALYSTS TRACE ANALYSIS: 2. OPTIMIZATION OF CALIBRATION

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To speed up chemical reactions, in which molecular hydrogen acts, are recently used not only mono-metal but many times two- or multi-metal supported catalysts. Catalytic properties are closely related to the nature and contents of metals present in the catalyst. Combining two or more transition metals is possible to achieve a synergistic effect, which causes increase of activity and selectivity of this catalyst compared with mono-metal catalyst, using identical reaction conditions. Spectral identification methods have of course different ability to identify trace amounts of accompanying elements in the catalysts. The aim of the analysts is to apply time-saving and inexpensive method with good detectability and sensitivity. The development of any new method, respectively, improvement of already used method requires optimization of both, the basic experimental parameters (see above) as well as comprehensive validation, determination of performance characteristics of methods, thus verifying its suitability for its intended purpose. Accomplished evaporation of the metals is an important assumption of good detectability and provides reliable results of that method. After optimization of basic experimental parameters and evaluation of their impact on the efficiency of evaporation, the optimization of the calibration process already under optimized conditions (without Ar atmosphere, using spectrochemical additives) of the mentioned method SS-DCA-OES was the next step. The mono-standard calibration using model samples with graduated weight (2 - 12 mg) was applied. A statistical program QC Expert 2.5™ was used for computing of selected parameters of the calibration line as the absolute member, standard deviation, sensitivity, limit of detection (3s-criterion) and correlation coefficient.

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P-81

RELIABILITY OF DETERMINATION OF SOME ANALYTES IN OIL BY RD OES

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The principle of optical emission spectrometry with a rotating disk electrode (RD OES) is very suitable for a routine analysis of a large number of samples. The determination reliability has been investigated in oil samples whose analysis is performed in order to diagnose aircraft engines condition. A great advantage of this method is that it does not require a sample treatment prior to the analysis and enables a simultaneous concentration determination up to 21 chemical elements within 30 seconds. The disadvantage is that it refers to the so called black box in which the individual results of the determination cannot be affected by an operator in the sense that only the resulting value of the concentration can be seen, which an averaged value of three successive measurements is. The measurement is carried out during 30 seconds, of which the first 6 seconds are spent on pre-burn, while during the remaining 24 seconds, the background signal as well as the sample signal are measured in turn; the measurements are repeated three times. The way in which the sample is brought into the spark discharge affects the atomization and excitation of chemical elements that are a part of wear particles. These are the particles generated by wear of friction pairs of devices that are lubricated with the oil concerned. It is known that the particles larger than 5 – 8 μm are not brought into a spark discharge by a rotating disk electrode or they do not manage to evaporate. Thus, the measured value is lower than the actual concentration. A relative standard deviation of a determination repeatability given by a spectrometer manufacturer is within the range 1 to 13%. The absolute values of standard deviations are determined for different groups of elements while measuring oil reference materials with the elements concentration (10, 30 and 50) $\mu g.g^{-1}$ as it is shown in Table 1. The paper compares the measurements reliability of reference materials that are used for the calibration of the spectrometer and actual oil samples with the indications given by a device manufacturer, who provides procedures and acceptable limits ensuring the measurement precision and accuracy.

Table 1. Standard deviations of the repeatability of elements concentration determination given by the device manufacturer

Concentration ($\mu g.g^{-1}$)	Fe, Cr, Al, Cu, Mg, Ni, Si	Ti, B	Ag, Na, Mo	Pb	Sn	Zn
10	0.71	0.78	0.94	1.08	1.17	1.36
30	1.58	1.87	2.45	2.01	2.06	3.61
50	2.55	3.04	4.03	3.13	3.16	6.02

P-82

POSSIBILITIES OF DIRECT SPECTROMETRIC METHOD (SS-DCA-OES) FOR THE CATALYSTS TRACE ANALYSIS:
1. OPTIMIZATION OF EVAPORATION

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In the process of hydrogenation of aromatic compounds carrying nitro- group in the liquid phase is necessary to use a suitable catalyst. Non-supported or supported catalysts of noble metals are most frequently used. Commonly used supports are porous materials such as oxides of Al, Fe, Si, or carbonates of earth metals alkaline. In a commercial scale is available a wide range of supported catalysts, but their financial costingness may pose some limitations. In the process of obtaining alternative supported catalyst from one's own resources may come to the contamination of trace quantities of other metals depending on the purity of chemicals and sterility of reaction medium. Accompanying metals can affect the efficiency of the catalyst in the negative as well as positive way. Determination of impurity metals contents in the catalysts, in relation to their effectiveness in the reaction, can provide information on the impact of these metals on the activity of the active component of the catalyst. The spectral methods (FAAS, ETAAS, ICP-OES, XRF) are commonly used for determination of metals in catalysts. However, these techniques require time-consuming sample preparation, which is often a source of contamination. Applying direct spectral method SS-DCA-OES can avoid this problem. The work presents results of the first part of extensive experimental work aimed at optimization and validation of the given method for purposes of elements trace analysis in the catalysts. Specifically, this is the study of evaporation of selected metals (Cd, Cr, Ni, Pb) in model samples prepared by mixing of matrix (SiO_2, Al_2O_3, Fe_2O_3) and gradually diluted basic sample consisting of corresponding metal oxides. Evaporation was studied in terms of nett intensities of elements obtained during 60 s exposure time under different experimental conditions (lower and higher flow of Ar, without Ar, with/without spectrochemical addition of $AgCl/Li_2CO_3$). Signal intensity was evaluated as the integrated intensity in the time interval from 4 to 45 s and reproduced in the form of standard evaporation curves.

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P-83

DETERMINATION OF SELENIUM USING PHOTOCHEMICAL VOLATILE COMPOUNDS GENERATION COUPLED WITH ATOMIC ABSORPTION SPECTROMETER

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Presented work is focused on the determination of selenium in aqueous samples using UV-photochemical generation of its volatile compounds coupled with atomic absorption spectrometry detection. This way of sample introduction is an alternative to conventional chemical or electrochemical volatile compounds generation. The method is based on the fact, that in the presence of a low molecular weight organic acid (formic, acetic, propionic or malonic), nonvolatile precursors (inorganic selenium(IV)) are converted by the effect of UV irradiation from the condensed phase to volatile species (selenium hydride, selenium carbonyl, dimethyl selenide, diethyl selenide, respectively). The resulting gaseous products are then rapidly transported to the externally heated quartz tube for detection by atomic absorption spectrometry (AAS) [1]. Two designs of flow-through photoreactor were first constructed. In both arrangements, the photoreactor was realized by low-pressure Hg vapor UV lamp (20 W, 254 nm). In the first case, PTFE tubing was wrapped around UV lamp; in the second case, the quartz tube was attached to the surface of UV lamp. Then optimum experimental conditions for UV-photochemical volatile compounds generation using formic acid were found. Formic acid was chosen for the study as a representative of the simplest organic acids. The conditions for optimal time of irradiation of the analyte, which is dependent on the sample flow rate and the length of PTFE tubing or the quartz tube, were studied. Further key parameters were also optimized: the carrier gas flow rate as well as the auxiliary hydrogen flow, concentration of formic acid or concentration of additives. Analyte response was significantly increased by adding H_2O_2, $NaNO_2$, $NaNO_3$ or HNO_3 [1]. The signal increased approximately five times when nitrate anion was added. A detection limit of 58.0 ng l^{-1} Se(IV) with a repeatability of 2.1% (RSD, n = 10) was obtained with proposed method. Consequently, the generation efficiency was investigated. It was determined by comparing of slope of calibration curves of UV-photochemical and reference chemical generation.

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P-84

INVESTIGATION OF MICROWAVE PLASMOID AT ATMOSPHERIC PRESSURE BY OPTICAL EMISSION SPECTROSCOPY

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In this work we generated and investigated a microwave plasma at atmospheric pressure. We used resonant absorption with a metallic antenna. This lead to the gas ionization forming a plasmoid. The effect of flowing argon gas and air on the plasmoid characteristics was investigated using optical emission spectroscopy(OES) from 200 to 1100 nm. The temperature of the microwave plasma was evaluated using the Boltzmann plot method and the electron density was determined by using the Saha-Boltzmann equation. A magnetron whose output power ranging from 90 to 900 watts was used. The electromagnetic wave at 2.45 GHz enters the chamber with stainless steel lining through a rectangular waveguide. The resonant absorption by the metallic antenna produced corona at the tip of the antenna which initiates the plasmoid. The characterization of the produced plasma was carried out by OES regarding different materials for antenna. Fore example, tungsten, cupper, aluminum, nickel, graphite and iron were used to study the emission from plasmoid as well as plasma temperature. It was revealed that the antenna material could change the initiation deposited power. The lower work function, the lower initiation magnetron power. The plasma temperature and electron density were evaluated using OES measurements as indicated in Table 1.

Table 1. Plasma temperature and electron density

Antenna	Temperature Air (eV)	Temperature Argon (eV)	Density Air (cm^{-3})	Density Argon (cm^{-3})
Tungsten	1.58	0.83	3.6×10^{13}	2.5×10^{11}
Graphite	1.3	0.99	5.9×10^{12}	1.3×10^{10}
Copper	1.66	1.25	8.3×10^{13}	9.9×10^{11}
Nickel- iron	1.03	0.52	3.1×10^{13}	4.2×10^{12}
Nickel-chromium	1.26	0.78	1.1×10^{13}	6.1×10^{11}

The brightness and the size of the plasmoid were increased by increasing the output power of the magnetron. At highs values of the feeding power to say at 900 watts, sprinkle on the tip of the antenna can be seen. It can be concluded that the created plasma with argon is cooler because of low voltage breakdown. In addition the volume of the created plasma with argon gas compared with that of the air was smaller.

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P-85

INVESTIGATION OF ADDITIVE GASES TO THE ARGON GAS ON THE PLASMA JET LENGTH IN DIELECTRIC BARRIER DISCHARGE APPARATUS

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Atmospheric pressure cold plasma jets are playing an important role in various plasma processing applications such as surface treatment [1, 2]. Because the plasma jet length is an important parameter in the surface processing, in this paper, we considered cold plasma jet length dependencies on the applied voltage at 18.56 KHz frequency, gas flow rate and additive gases (oxygen and nitrogen) to the main gas argon. We used the Optical Emission Spectroscopy (OES) apparatus to compare the emission spectra of the plasma jet in wavelength range from 200 to 1000 nm for different gas compositions. The plasma jet was generated in a glass tube. The system consists of two electrodes, in which one electrode is insulated from another by dielectric material. The voltage waveform was recorded by Tektronix-DPO-2012 oscilloscope with a high voltage probe P6015A. The current was measured by a current amplifier TCPA-300 with a current probe TCP-312. The produced plasma jet by Ar/N_2 and Ar/O_2 and their emission spectrum are shown in figure 1 and 2, respectively.

Figure 1. Right: Ar/N_2 cold plasma at 5.48 KV and 4:0.2 (lit/min) gas flow rate and left: Ar/O_2 cold plasma at 5.76 KV and 4:0.2 (lit/min) gas flow rate.

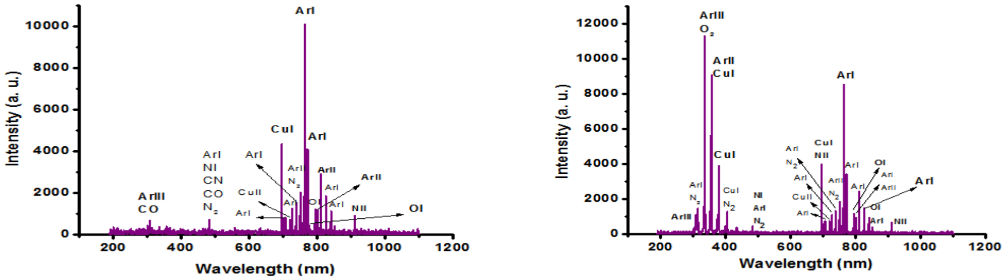

Figure 2. Emission spectrum of plasma from right: Ar/N_2 (4:1 lit/min) and left: Ar/O_2 (12:1 lit/min).

It was seen that the additive nitrogen gas at flow rate greater than 0.5 lit/min, has more influence on the plasma jet length than that of oxygen gas. It was also proved that by increasing the input voltage leads to prolongation of the jet length scaling as $\sqrt{V}$.

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P-86

DETERMINATION OF CHROMIUM SPECIES IN THE WORKPLACE AIR USING HPLC-ICP-MS TECHNIQUE

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Chromium is frequently present in the environment and the workplace. Occupational exposure to welding fumes is a known health hazard. There is substantial evidence that some chromium (Cr) containing substances are toxic for humans; furthermore hexavalent chromium is known to be carcinogenic (1group - IARC). Exposure to Cr(VI) has been known to be responsible for the damage airways, irritating skin disease, asthma, bronchopulmonary cancer. According to the welding process, stainless steel welders may be exposed to all chemical species of chromium (metallic chromium, chromium III and chromium VI compounds). The toxicity depends on the chemical forms in which the chromium is present. It is necessary to quantify the individual oxidation states of chromium for an accurate assessment of their impact.

The objective of this work was to application of high performance liquid chromatography (HPLC) coupled to inductively plasma mass spectrometry (ICP-MS) to measure the chromium species in the workplace air.

Personal air samples were collected in the welders breathing zone over a period of about 6-7 hours, dust was collected on a membrane and glass filters. Concentration of the total chromium was determined by ICP-MS (ELAN DRC-e, Perkin Elmer, SCIEX, USA). The total hexavalent chromium and the water-soluble chromium species were analyzed by HPLC-ICP-MS. The separation of soluble chromium and total hexavalent chromium forms was used reversed – phased ion – pairing liquid chromatography. The soluble chromium compounds separation is accomplished by interaction of the chromium species with the different components of the mobile phase. The Cr(III) forms a complex with the EDTA, it is this complex that is retained on the column, Cr(VI) exists in solutions as dichromate. The total hexavalent chromium were extracted from the glass filters using (KOH and Na_2CO_3 solution). The anion exchange column was used for separation of Cr(VI) species. In order to eliminate spectral interference dynamic reaction cell (DRC) was used, making use of methane as a reaction gas.

The results from this work demonstrated that HPLC-ICP-DRC-MS technique can serve as a rapid, sensitive, precision system to determined chromium species in the workplace air samples.

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SIZE-DISTRIBUTION AND MOBILITY ASSESSMENT OF HG AND OTHER RISK ELEMENTS IN URBAN PARTICULATE MATTER AND AMENDED SOILS

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Urban particulate matter (PM) was collected in the most exposed area of Prague, close to highway, from filters of the air conditioning system in one large building. Finally four grain-size fractions: 0.507-0.119 mm, 0.119-0.063 mm, <0.063 mm and sub-fraction <0.025 mm were prepared after drying at the laboratory temperature. Several methods of destructive and non-destructive analysis were used to get elemental size-distributions: the Hg analyser AMA-254 (CV AAS), inductively coupled plasma - mass spectrometry (ICP-MS), electrothermal atomic absorption spectrometry (ET AAS), instrumental neutron activation analysis (INAA), proton-induced X-ray emission (PIXE). Labile forms of toxicologically important analytes (Hg, As, Cd, Cr, Mn, Ni, Pb, Zn) were measured by AMA-254 and ICP-AES in 2M HNO_3 extracted solutions.

The effect of soil amendment by one physical PM fraction (< 0.063 mm) on the risk element (As, Cd, Mn, Pb, Zn) mobility was investigated in a pot experiment. Two soils were selected as follows: i) uncontaminated Chernozem with cation exchange capacity (CEC) 255 mmol.kg^{-1} and pH level 7.2, and ii) slightly contaminated Fluvisol with CEC 201 mmol.kg^{-1} and pH level 6.8.

Results of Hg-distribution in PM fractions showed increasing contents towards smaller particles (<0.063 mm), in comparison with elements like Zn, Pb, (Cr) showing significantly higher contents in the 0.507-0.119 mm size fraction. Other analytes seemed to be independent of particle sizes, and they were enriched proportionally in all investigated PM fractions.

The leaching process by 2M HNO_3 proved a similar pattern for all analytes (Cd>Zn~Pb~Mn>As>Ni>Cr>Hg) in individual PM fractions. Mobility differences were seen in the coarse PM fraction (0.119-0.507 mm) for Pb, As, and Hg.

Nitric acid extractable portions were predominantly affected by soil type whereas the effect of PM physical fraction was negligible. Therefore, lower element extractability was observed for Chernozem characterized by higher sorption capacity compared to Fluvisol. Among the elements investigated, the relatively high mobility of Cd, Zn, and Mn was reported and opposite pattern was found for Cr and Pb.

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VARIABILITY OF TOTAL AND MOBILE ELEMENT CONTENTS IN THE ASH AFTER BIOMASS COMBUSTION

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Biomass such as wood chips or bark belong to the world wide increasing alternative to fossil fuels. Simultaneously, possible recycling of the ash produced after biomass combustion as a source of macro - and micronutrients for forests or agricultural land is widely discussed. Because of high variability of plant materials used for combustion nutrient contents and their plant-availability need to be described as affected by the combusted material and combusting conditions. Moreover, the levels of risk elements in the ash must be taken into account. In our experiments, seven samples of the ash representing both fly and bottom ash were analyzed for wide spectrum total and mobile contents of nutrient and potentially risk elements. Non-destructive X-ray fluorescence (XRF) spectrometry was compared with the inductively coupled plasma - atomic emission spectrometry (ICP-OES) and flame atomic absorption spectrometry (F-AAS) where microwave-assisted pressurized sample decomposition in a mixture of HNO_3, HCl, and HF was applied. As the reference methods, the instrumental neutron activation analysis (INAA), and the proton induced X-ray emission (PIXE) were used.

The results showed fairly good agreement between XRF and INAA (PIXE) results where correlation coefficients (r) varied between 0.96 and 0.98. Significant differences between element contents in the fly and bottom ash as well as among the ash of different origin were confirmed. Lower results documenting insufficient dissolution of the ash samples in the applied acid mixture were observed for both ICP-OES and AAS. In this case, weaker correlation with the INAA (PIXE) results not exceeding $r = 0.7$ were determined. Therefore, the sample decomposition step is a bottleneck of the accurate analysis of this type of material. Additionally, serious interferences limiting the determination of Ca, Mg, and K contents occurred in the case of F-AAS. For assessment of plant-available portions of the elements in the ash samples Mehlich 3 extraction procedure (Mehlich A. (1984), Commun. Soil Sci. Plant Anal. 15, 1409) and extraction with 0.11 mol.l^{-1} solution of CH_3COOH were applied. The results showed relatively low mobility of elements (especially micronutrients) in the ash samples regardless of their source and composition suggesting limiting the immediate effect of direct ash application as the fertilizer.

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AFFINITY OF SELECTED ELEMENTS TO INDIVIDUAL FRACTIONS OF SOIL ORGANIC MATTER

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The distribution of selected elements in individual fractions of organic matter from antropogenically contaminated soils was investigated. The attention was paid especially at Hg; furthermore, contents of S, Mg, Mn, Fe, Cu, Zn, and Pb were also measured. The decomposition of organic matter to particular fractions was carried out by the resin DAX-8. The sorption, as well as the desorption, of individual organic fractions on the resin were observed. HCl, KOH, and NaOH, at various concentrations, were used as extraction agents. The concentration of C was measured in each extract. Consequently, amounts of humic acids, fulvic acids, and total content of organic matter were calculated in all soil samples. The elements of interest were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) except mercury content where inductively coupled plasma mass spectroscopy (ICP-MS) was applied. Element affinity to organic matter and relations among concentrations of investigated elements were evaluated.

Ten soil samples were collected and the Advanced Mercury Analyzer (AMA-254) was used for the determination of the total Hg content. The values of Hg exceeded the maximum permissible limits (0.8 mg.kg^{-1} Hg) in several samples. The two highest Hg values reached up to the concentration 10.5 mg.kg^{-1} and in the highest one it was almost 29 mg.kg^{-1}. Results of the analysis showed that the Hg content bound to the humic acids is inversely proportional to the content of Mg, Mn, Fe and Zn. However, this dependence was not confirmed in the samples with the above limit content of mercury. In the case of fulvic acids, the relationship between Hg and S with Mg was observed. The relation showed again an inverse character; albeit, it was not found in the case of the three samples with the lowest Hg content in this particular fraction. Considering the correlations among remaining elements, they are represented mainly by the close relation of Mg, Mn, Fe, and Zn in humic acids. Focusing on fulvic acids, relation between Pb and Cu might be observed. Moreover, the connection between Pb and Zn was observed in the case of the total organic matter where positive significant correlations between these were observed.

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ELEMENTAL ANALYSIS OF IDENTIFICATION TAGGANTS BY F-AAS USING SLURRY SAMPLING TECHNIQUE

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New type of identification taggants (ITs) used for pre- and post blast explosives marking is being developed at the University of Pardubice in collaboration with Explosia Inc., Czech Republic[1]. These ITs consist of a polymeric carrier, ferromagnetic compound, UV component and combination of oxides. Powdered Fe and the UV component serve for traceability. The identification particle must endure extreme conditions occurring during a detonation, thus, high demands are put on the durability of the polymer matrix, which serves as a carrier for the coded information made by combination of metal oxides. Since the concentration of used oxides is in a percentage range, flame atomic absorption spectrometry (F-AAS) suggests itself as it is a widely used, robust method offering a high sample throughput. Moreover, F-AAS is a suitable technique for analyzing extremely small sample amounts, which can be typically found at the explosion site. Currently, a well established method for transferring the ITs into a liquid state is microwave digestion[1]. This approach is however time-consuming, therefore, in this work a new direct method using slurry sampling was developed. The influence of glycerol concentration, as the stabilizing agent, and the concentration of HNO_3 and HCl, as the analyte extractants, on the measurement sensitivity was investigated. The effect of sample mass or grinding time onto the determination of Mg, Pb, Zn, Cu, and Co was studied by means of analysis of variance. The accuracy of the method was verified by comparison of the data obtained by the proposed method with those obtained after microwave digestion by applying a paired *t*-test. Precision, detection power and matrix effects were also evaluated.

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P-91

FTIR METHOD AS A GUIDELINE TO STUDY DEGRADATION OF COMPOSITE BUILDING MATERIALS

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Today the most widely used method in most building research laboratories is Fourier transform infrared spectroscopy (FTIR). It is extremely cost-effective, and it has directly contributed to the current enhanced interest in organic materials in the analytical identification of fibre materials, woods, organic colorants and dyes, plastics as well as progressive composite building materials. Many benefits from FTIR analysis consists in area of studies degradation products as results of corrosive processes, as well as to examine materials during different phases of degradation.

Article will be present the results of a study of degradation processes occurring in lightweight-based composites made of hemp shives as organic fillers. Fourier transform infrared spectroscopy (FTIR) with ATR unit and RTG fluorescence spectrometry were used for identification of changes in the chemical properties of filler respectively inorganic matrix of composites. Alpha Brucker Platinum - ATR spectrometer, was used to identify the natural filler by measuring the transmitted radiation in a spectral range of 4000–360 cm^{-1} with a resolution of 4 cm^{-1}. A total of 24 scans were taken for each measuring sample. The results of the study of these processes are important not only in terms of durability of the composites and thus their suitability for building purposes, but also from a hygienic point of view.

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THE IMPORTANCE OF MULTIDISCIPLINARY ANALYTICAL APPROACH TO SOLVING PROBLEMS OF BIOCORROSION IN CIVIL BUILDINGS

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Microscopic fungi (moulds) are a serious problem on the surface structure of buildings. The internal environment of buildings is contaminated by various micromycetes, which are considered to be unsatisfactory hygienic conditions. Micromycetes produce mycotoxins and play an important role in the problem called "Sick Building Syndrome" (SBS). The side effect of the presence of microscopic fungi is degradation of surface and inner structure of building materials.

The work concerns about specific multidisciplinary analytical assessment of the interaction between fungi (moulds) and biocorrosion of plasters and masonry of cultural historical heritage in town Kosice.

The material for microbiological examination was collected using two independent methods, 1. “sedimentation method 2. “scrub away method”. The cultivation was performed at room temperature (22 ± 2.5°C) 10 days using special nutrient media:

- Sabouraud dextrose agar with added chloramphenicol (Hi-Media Laboratories Pvt.Ltd., Mumbai, India)
- Potato-dextrose agar (HIMEDIA Laboratories Pvt.Ltd., Mumbai, India.

Identification of micromycetes was based on evaluation of macro-and microscopic characteristics, and we detect about 10 genera of moulds in samples (Asp. flavus, Asp. Parasiticus, Clad. Herbarum, Penicillium verrucosum,. Fusarium etc..

Chemical Assessment of degradation processes was done on the individual obtained samples (depth up to 50 mm). The determination of chlorides, nitrates concentrations was used to classify the degree of salinity samples follow to WTA rules. Changes of alkaline reactions (pH values) were determined by potentiometric method (determination of the degree of carbonation).

Fourier transform infrared spectroscopy (FTIR) with ATR unit was used for identification of other corrosion products in samples. Alpha Brucker Platinum - ATR spectrometer was used to measuring the transmitted radiation in a spectral range of 4000–360 cm^{-1} with a resolution of 4 cm^{-1} .

The results obtained by all analytical methods confirm the need and the suitability a complex approach to solving of practical assessment of heterogeneous systems which they are actually embedded in building materials.

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ARSENIC COMPOUNDS IN LESS COMMON SPECIES OF VEGETABLE DETERMINED WITH HPLC-ICPMS

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In general arsenic is an element less available to plants. Its mobility in soil increases with increasing soil and soil solution pH. Some plant species that are grown in the soil with high arsenic concentrations are able to accumulate significant amounts. Plants have a number of mechanisms to detoxify the arsenic. Transformation of inorganic arsenic, the dominating arsenic compound in soil, to organic compounds with lower toxicity for plants is one of them. In plant arsenite As(III), arsenate As(V), dimethylarsinic acid (DMA) and methyl arsonic acid (MA) are usually detectable. We determined the arsenic species in edible parts of several vegetable species to assess wheather they are suitable for planting in the private gardens in the vicinity of former gold and silver mining and smelting activity with high soil arsenic concentrations.

In model pot experiments we grew less known vegetable species, namely turnip (*Brassica napus var. napobrassica*, L.), savoy cabbage (*Brassica oleracea convar. Acephela*, L.), black radish (*Raphanus sativus* var. *nigra*, L.), Spanish salsify (*Scorzonera hispanica*, L.), parsnips (*Pastinaca sativa*, L.). As a reference crop lettuce (*Lactuca sativa*, L.), which is among the most commonly grown vegetable was used. The experimental soils originated from two mining and smelting sites in Czech Republic - Příbram and Kutná Hora, in which the average total contents of arsenic reached 36 mg kg^{-1} and 473 mg kg^{-1}, respectively. These two soils are different in their physico-chemical properties. Arsenic compounds were extracted with 0.02 mol l^{-1} $NH_4H_2PO_4$ (pH 6) and detected by HPLC coupled with ICPMS. The arsenic species in the plants decreased in the order as follows: As(V) ~ As(III) >> DMA ~ MA. The distribution of arsenic compounds differed predominantly according to individual plant species whereas the effects of soil properties were negligible.

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DIRECT DETERMINATION OF BORON IN SILICON-MATERIALS BY ETV-ICP OES - AN EASY WAY?

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The direct solid sampling spectroscopic methods based on electrothermal vaporization of powdered samples proved to be a good alternative to methods using wet digestion in sample preparation because of the fast and simple sample pretreatment, lower contamination risks, and lower detection limits. Electrothermal vaporization combined with inductively coupled plasma optical emission spectrometry (ETV-ICP OES) is a multielement technique, which is suitable for trace element determination in different matrices. On the other hand difficulties in determination of Boron are well known for more or less all established analytical methods, wet chemical as well as different spectroscopic methods.

In the present work the ETV-ICP OES method was investigated to apply it for the determination of Boron in different Silicon-materials. Calibration possibilities of the method were studied, using several types of calibration standards - different certified reference materials, graphite-based home-made standards as well as dried aqueous standard solutions.

A comparison was made between two different spectrometers, obtained in two laboratories (Freiberg/Kempten). The use of different modifiers (CCl_2F_2, CF_4, CCl_4, and CHF_3) was also compared. The instrumental equipment was a Thermo Electron iCAP 6500 Duo (Freiberg) and a Spectro Arcos SOP (Kempten) coupled with a Spectral Systems ETV 4000c with 50-fold autosampler.

It is shown that the ETV-ICP OES is an interesting and realizable technique for Boron determination in Silicon. The metrological characteristics of the method were shown and discussed.

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SONO-EXTRACTIVE ISOLATION OF METALS FROM THE SOLID SAMPLE MATRIX

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Sonochemistry includes traditional applications such as synthesis [1], catalysis [2], fundamental studies of cavitation [3], electrochemistry, biotechnology [4] and material science [5]. The ultrasound applications in analytical chemistry are associated with the improvement of the sample preparation [6,7] and analytical detection [8]. The ultrasound-assisted heterogeneous sample preparation includes many complex processes and it can lead to the total or partial dissolution of the samples [9].

Spent batteries have been taken into consideration due to their hazardous material content and also as secondary source of metals. Recycling of the run-down portable batteries prefers pyro-metallurgical, hydro-metallurgical and bio-metallurgical processing [10]. All these processes need the quality control of the metal recovery development, and it offers suitably chosen analytical method. Therefore, the spent battery is technologically, environmentally and analytico-chemically important solid sample matrix.

This work presents part of optimization experiments of isolation and determination of the selected elements from the spent battery samples. For the isolation of the elements from the matrix the ultrasound assisted leaching into ethylenediaminetetraacetic acid was used (Sonopuls HD 2070 type of probe ultrasound disintegrator - equipped with probe made of high grade titanium alloy Ti-Al6-V4). Atomic absorption spectrometry (Analytik Jena ZEEnit 700 AAS) for the element analysis of extracts was used.

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P-96

GRAPHITE “FILTER-FURNACE” APPLICATION AT ELECTROTHERMAL ATOMIC ABSORPTION ANALYSIS OF SOME FOOD AND ENVIRONMENTALS

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To eliminate or reduce interferences that take place at the direct electrothermal atomic absorption spectrophotometry (ET AAS) determination of Pb, As, Cd and Ni in materials with complex chemical composition such as foods and environmental one of the most simple and effective tools are using the graphite "furnace-filter" atomizer as well as various matrix modifiers [1-3].

This article present the results of investigation on substantiation and optimization of operation parameters of graphite "furnace-filter" atomizer and Pd-Mg-matrix modifier (MM) at the direct ET AAS determination of Pb, As, Cd and Ni in mineral water, nonalcoholic beverage, wines, vegetable fats, olive and sunflower oils, river and marine waters.

The contribution to formation of analytical signal meanes of elements the furnace temperature values during pretreatment and atomization steps and some of mineral and organic components of analytes, including at its evaporation from furnace wall, L’vov platform and graphite "furnace-filter" atomizer with MM were studied.

It was shown that use of graphite 'furnace-filter "atomizer and Pd-Mg-matrix modifier allows ~ 2-2.5 times to increase sensitivity of Pb, As, Cd and Ni determination, completely eliminate or significantly reduce the interferences as a result of presence in analyte main components of materials to be analyzed as well as non-atomic absorption of light.

The procedures of direct ET AAS determination ≥ 0.02 $mg\cdot kg^{-1}$ of Ni in vegetable fats and oils; ≥ 0.005 $mg\cdot kg^{-1}$ Pb and 0.0002 $mg\cdot kg^{-1}$ Cd in nonalcoholic beverages, wines and ≥ 0.005 $mg\cdot kg^{-1}$ As in soft drinks and mineral waters have been proposed.

Accuracy of corresponding analysis results where confirmed by its comparison with other analytical chemistry methods and participation laboratory in “Professional testing and intercalibration programme”. The relative standard deviation (S_r) does not exceed 0.11.

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DETERMINATION OF RUTHENIUM IN ENVIRONMENTAL SAMPLES BY ETAAS AFTER ITS SEPARATION ON A NEW ION IMPRINTED POLYMERS

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Ruthenium, which belongs to platinum group metals, is typically present in common terrestrial rocks at ng g^{-1} level. Due to its unique physical and chemical properties, such as high melting temperature, inertness towards many chemical reagents, hardness, good conductivity, and versatile catalytic effect, growing use of ruthenium in different fields has been observed. The total ruthenium demand in 2011 year reached 25,2 tons. The metal was mainly used in the electronic (62%), electrochemical (16%) and chemical industries (13.5%), with smaller amounts being used in other applications. Extensive use of ruthenium based catalysts in industrial processes and more common generation of e-wastes as well as its use in medicine result in raising of ruthenium content in the environment. The widespread use of ruthenium and the fact that its compounds belong to a group of toxic substances, cause the need to develop analytical procedures enabling determination of ruthenium in real samples.

The ruthenium concentration in environmental samples is most often determined by electrothermal atomic absorption spectrometry (ETAAS). However, it was found that the presence of many transition metals, e.g. Ni, Co, and Fe, causes many spectral interferences during determination of ruthenium by ETAAS technique. The elimination of interferences is possible by the separation of analyte from matrix elements.

In this work a new ion imprinted polymers (IIP) for ruthenium recognition/pre-concentration were prepared and studied. The ruthenium ions were imprinted in polymeric network in the form of complexes with 2- thiobarbituric acid. The imprinted polymers were prepared via bulk polymerization using acrylamide and methacrylic acid as the functional monomers and ethylene glycol dimethacrylate as the cross-linking agent in the presence of methanol as porogen and 2,2-azobisisobutyronitrile as initiator. The synthesized IIP was used as a new support for solid phase extraction (SPE) of ruthenium from environmental samples before ETAAS determination.

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