SPEKTROSKOPICKÁ SPOLEČNOST JANA MARKA MARCI

16th Czech – Slovak Spectroscopic Conference

including

Microsymposium Challenges in Raman spectroscopy

Hotel Harmonie, Luhačovice, Czech Republic

May 27 - 31, 2018

BOOK OF ABSTRACTS

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Dear participant of the 16th Czech-Slovak Spectroscopic Conference,

I welcome you cordially on behalf of the Ioannes Marcus Marci Spectroscopic Society and also personally at a joint scientific meeting of Czech and Slovak spectroscopists. I am pleased that, despite a large number of more specialized conferences, which represent certainly a prestigious ambience for presenting the results of your research work, you have shown interest to continue the tradition of a scientific meeting across “the spectrum of spectroscopy”. The majority of contributions presented at this conference concern spectroscopy as a tool for chemical analysis. For a given analytical task, more methods are commonly used, which applies to various spectrochemical analysis methods, too. Multidisciplinary spectroscopic conference might be useful from this point of view. The conference is also intended for non-academic laboratory specialists, who are interested in a comprehensive solution of a given analytical task and may find inspiration there. With international participation and the awarding of Ioannes Marcus Marci Medal to the outstanding scientists in the field of spectroscopy, this conference is the most important event organized by the Ioannes Marcus Marci Spectroscopic Society and Slovak Spectroscopic Society.

The Czechoslovak Spectroscopic Society was founded in 1949, and in 1993 Ioannes Marcus Marci Spectroscopic Society became its successor in the Czech Republic. From the very beginning of the existence of the Czechoslovak Spectroscopic Society, the Czechoslovak Spectroscopic Conference was held every four years. Between 1993 and 2007, the spectroscopic societies of the Czech Republic and the Slovak Republic organized conferences separately. In 2007 Ioannes Marcus Marci Spectroscopic Society and Slovak Spectroscopic Society have agreed to jointly organize spectroscopic conference every two years. The numbering of conferences is based on the country in which the conference is held. In Slovakia, this joint conference continued the tradition of successful Slovak Atomic Spectroscopy Conference, and thus the first joint scientific event, which was held in 2008 in Častá-Papiernička, was XIXth Slovak-Czech Spectroscopic Conference. Then followed in 2010 the 14th Czech-Slovak Spectroscopic Conference in Litomyšl, in 2012 the XXth Slovak-Czech Spectroscopic Conference & European Symposium on Atomic Spectrometry (ESAS) in Tatranská Lomnica, in 2014 the 15th Czech-Slovak Spectrosopic Conference & ESAS in Prague, in 2016 the XXIst Slovak-Czech Spectroscopic Conference in Liptovský Ján.

This 16th Czech-Slovak Spectroscopic Conference takes place nearly in the center of former Czechoslovakia, in Eastern Moravia. Luhačovice, the small town with 5000 inhabitants, the spa with healing mineral water springs and unique buildings designed by Slovak architect Dušan Jurkovič, with functionalistic architecture of Emil Králík and Bohuslav Fuchs, represents a suitable venue for scientific meetings. Besides, the city is in a beautiful natural environment, which is suited for hiking trips.

With great pleasure I thank the organizing committee of the conference and scientific board for preparing interesting scientific and attractive social program. I wish you that you enjoy the conference, venue and beautiful Moravian countryside.

Viktor Kanicky

16th Czech – Slovak Spectroscopic Conference

PROGRAMME

Sunday 27 May

16:00-19:00	**REGISTRATION**
19:00-24:00	**WELCOME PARTY with barbecue**

Monday 28 May

8:30-9:00	**OPENING CEREMONY** (V. Kanický, M. Miglierini)		
Session 1 Atomic spectrometry *(AAS, GD-OES)* *Chair:* **Viktor Kanický**			
9:00-9:15	CP1	Metrohm	Metrohm Spektroskopie – Budiž světlo
9:15-10:00	PL1	A. D'Ulivo	Chemical vapor generation by aqueous boranes: from analytical applications to mechanistic investigation
10:00-10:30	IL1	Z. Weiss	Advances in glow discharge emission spectroscopy: selective excitation, transition rate diagrams and beyond
10:30-10:45	OL1	J. Kratzer	Trace determination of selenium by hydride generation in-atomizer trapping atomic absorption spectrometry
10:45-11:30	**COFFEE BREAK**		
Session 2 Atomic spectrometry *(Miniature plasma sources)* *Chair:* **Zdeněk Weiss**			
11:30-12:00	IL2	J. Franzke	Dielectric barrier discharges - plasma fundamentals and applications in analytical chemistry
12:00-12:15	OL2	A. Hrdlička	Plasma pencil in analytical spectrochemistry - achievements and prospects
12:15-12:30	OL3	M. Dvořáková	Matrix effects in plasma pencil and analysis of real samples
12:30-14:00			**LUNCH**
Session 3 Sample preparation/Sample introduction *Chair:* **Alessandro D'Ulivo**			
14:00-14:30	IL3	M. Aghaei	Particle journey through an ICP torch: what modeling reveals?
14:30-14:45	OL4	F. Polák	Aluminium and antimony bioextraction from aluminosilicates and ferric oxohydroxides in presence of filamentous fungus Aspergillus Niger

14:45-15:00	OL5	M. Matulová (SK)	Sorption studies of selenium and iodine from aqueous solutions on natural and synthetic materials
15:00-15:30	CP2	Pragolab	Nexsa - small spot XPS and multi-technique analysis with Raman
15:30-16:15	**COFFEE BREAK**		
Session 4 Speciation analysis			***Chair:* Maryam Aghaei**
16:15-16:45	IL4	M. Urík	Experimental separation of mobile elements' fraction using extraction with extracellular fungal metabolites
16:45-17:00	OL6	P. Matúš (SK)	Determination of iodine fractions in soils using ICP MS after application of single and sequential extraction techniques
17:00-17:15	OL7	J. Švehla (CZ)	Method development for speciation analysis of volatile mercury forms in ambient air flue gases from incineration plants
17:15-17:30	OL8	M. Šebesta	Influence of zinc initial speciation on its distribution in aqueous media in presence of filamentous fungus or soils
17:30-17:45	OL9	J. Tóth (SK)	Using of immersion probe for kinetic spectrophotometric determination of dissolved chromium species in water samples
17:45-18:15	CP3	Anton Paar	Anton Paar Multiwave 7000 – microwave digestion at its best
18:15-19:15	**POSTER SESSION 1**		
19:30	**Buffet**		

Tuesday 29 May

Session 5 Special spectroscopic methods *(Mössbauer spectroscopy)* ***Chair:*****Joachim Franzke**			
8:00-8:45	PL2	M. Miglierini	Synchrotron radiation aided Mössbauer spectrometry
8:45-9:00	OL10	D. Holková	Properties of nanocrystalline alloy after irradiation of amorphous precursors
9:00-9:15	OL11	I. Bonková (SK)	Iron in biological tissues
9:15-9:30	OL12	L. Pašteka (SK)	Influence of external treatment on microstructure of selected steels
Session 6 Molecular spectroscopy *(Molecular luminescence)* ***Chair:*** **Renato Zenobi**			
9:30-10:00	IL5	M. Hof	Lipid driven nanodomains are fluid
10:00-10:15	OL13	J. Valenta	Determination of absolute emission efficiency of up- and down-converted luminescence and some other advanced optical characterization of fluorides doped with various lanthanides
10:15-10:30	OL14	P. Lubal	Time-resolved luminescence spectroscopy as a tool for study of chemical reactions of Eu(III) complexes
10:30-11:15	**COFFEE BREAK**		
Session 7 Molecular spectroscopy *(NMR)* ***Chair:*** **Marcel Miglierini**			
11:15-11:45	IL6	R. Fiala	NMR spectroscopy methods for the studies of biomolecular structure and dynamics
11:45-12:15	IL7	V. Sklenář	Disentangling puzzles - atomic resolution studies of protein disorder
12:15-12:30	OL15	H.Štěpánková	Local structure of garnets studied by NMR
12:30-14:00	**LUNCH**		
14:00-19:00	**EXCURSIONS**		
19:00-20:00	**POSTER SESSION 2**		
20:00	**Buffet**		

Wednesday 30 May

8:30-8:45	**To the memory of Assoc. Prof. B. Strauch** (B. Vlčková, I. Němec)		
Session 8 Molecular spectroscopy *(Raman, SERS, TERS)* *Chair:* **Blanka Vlčková**			
8:45-9:30	PL3	J. Popp	Clinical Raman spectroscopy - diagnosis before therapy
9:30-10:15	PL4	R. Zenobi	Tip-enhanced Raman spectroscopy - principles and applications
10:15-10:45	CP4	Nicolet CZ	Nicolet CZ company presentation
10:45-11:30	**COFFEE BREAK**		
Microsymposium Challenges in Raman spectroscopy starts as a paralell session see pages 14 -15 for its programme			
Session 9 LIBS *Chair:* **Norbert Jakubowski**			
11:30-12:00	IL8	J. Kaiser	3D chemical imaging through a combination of laser-induced breakdown spectroscopy and computed tomography
12:00-12:15	OL16	P. Pořízka	Dimensionality reduction of multi-variate laser spectroscopy data
12:15-13:45	**LUNCH**		
Session 10 LA-ICP-MS *Chair:* **Margaretha T. C. de Loos-Vollebregt**			
13:45-14:30	PL5	N.Jakubowski	Method development for metal detection at cellular levels
14:30-14:45	OL17	M. Tvrdoňová	Simultaneous imaging of proteins and elements in tissues by LA-ICP-MS
14:45-15:00	OL18	E. Pospíšilová	Laser ablation-based methods in the analysis of clay ground layers in painting
15:00-15:15	OL19	V.Dillingerová	Multivariate statistical analysis of archaeological samples and their visualisation
15:15-15:45	CP5	HPST	ICP-MS systems by Agilent Technologies in the Czech Republic and their capabilities
15:45-16:30	**COFFEE BREAK**		
Session 11 Mass spectrometry *Chair:* **Jan Preisler**			
16:30-17:00	IL9	G. Allmaier	From nanoparticle separation/detection by differential mobility analysis to high energy collision induced dissociation MS
17:00-17:15	OL20	T.Černohorský	New approach to matrix modification in ETV ICP-MS

17:15-17:30	OL21	J. Patočka (CZ)	Practical use of carbon nanoparticles as a transport efficiency modifier for ETV-ICP-TOF-MS
19:00-24:00	**CONFERENCE DINNER**		

Thursday 31 May

Session 12 Plasma spectroscopy *(ICP-MS, ICP-OES, ETV)* **_Chair:_ Jozef Kaiser**			
9:30-10:15	PL6	M. de Loos-Vollebregt	Dealing with the matrix and background in analytical atomic spectroscopy
10:15-10:30	OL22	S. Matějková (CZ)	Use of electrothermal evaporation coupled with atomic emission spectroscopy (ETV-ICP-OES) in analysis of small amounts of organic and biological samples
10:30-10:45	OL23	K. Novotný (CZ)	Comparison of different spectral resolution ICP-OES spectrometers for the determination of rare earth elements
10:45-11:30	**COFFEE BREAK**		
Session 13 Real sample analysis **_Chair:_ Yaroslav Bazel´**			
11:30-12:00	IL10	J. Čáslavský (CZ)	Mass spectrometry in environmental analysis
12:00-12:15	OL24	P. Roubíček (CZ)	Can dynamic image analyse method replace classical sieve analysis?
12:15-12:30	OL25	A. Krejčová (CZ)	Testing the reliability of the washing process in hair analysis through a contamination study
12:30-13:00	**CLOSING CEREMONY** (V. Kanický, M. Miglierini)		
13:00	**LUNCH**		

Microsymposium Challenges in Raman spectroscopy

PROGRAMME

Wednesday 30 May

11:20-11:30	**Microsymposium Challenges in Raman Spectroscopy-opening**		
Session M1			***Chair:* Blanka Vlčková**
11:30-12:00	IL-M1	M. Procházka	Rationally designed metal nanostructures for SERS detection of biologically important molecules
12:00-12:30	IL-M2	K. Machalová-Šišková	Raman and surface-enhanced Raman spectroscopic studies of the large cytoplasmic loop of sodium-potassium pump
12.30-13.00	IL-M3	M. Kloz	Spectral watermarking approach to femtosecond Raman Spectroscopy
13:00-14:00	**LUNCH**		
Session M2			***Chair:* Renato Zenobi**
14:00-14:30	IL-M4	L. Kavan	Raman spectroelectrochemistry of nanocarbons and titania
14:30-15:00	IL-M5	J. Kalbáčová-Vejpravová	Cryomagnetic Raman micro-spectroscopy - beyond phonons
15:00-15:30	IL-M6	M. Kalbáč	In situ Raman spectroelectrochemistry of carbon nanostructures
15:30-16:00	IL-M7	V. Valeš	Enhanced Raman scattering on functionalized graphene substrates
16:00-16:30	**COFFEE BREAK**		
Session M3			***Chair:* Jürgen Popp**
16:30-17:00	IL-M8	J. Štěpánek	Raman scattering and physical chemistry of biomolecules
17:00-17:30	IL-M9	P. Mojzeš	Raman microscopy of microalgae: surprising insights and challenges in the unexplored world
17:30-18:00	IL-M10	M. Michl	Intramolecular excitation energy and charge transfer: fluorescence, transient absorption and resonance Raman studies

Thursday 31 May

Session M4			***Chair:* Marek Procházka**
8:45-9:15	IL-M11	I. Němec	Vibrational spectroscopic characterisation of hydrogen-bonded molecular crystal for nonlinear optics
9:15-9:45	IL-M12	I. Matulková	Vibrational spectroscopic studies of salts of 2,4,6-triaminopyrimidinium and phosphoric acid prepared for non-linear optical applications
9.45-10:15	IL-M13	I. Šloufová	Terpyridine-based ligands and their metal complexes: Raman and surface-enhanced Raman study
10:15-10:45	IL-M14	M. Dendisová	Copper nanostructures: Profits and drawbacks for SEVS techniques
10:45-11:30	**COFFEE BREAK**		
Session M5			***Chair:* Ivan Němec**
11:30-12:00	IL-M15	V. Baumruk	Raman optical activity
12:15-12:30	IL-M16	B. Vlčková	Towards SERS and SERRS on single molecule level

POSTER SECTIONS PROGRAMME

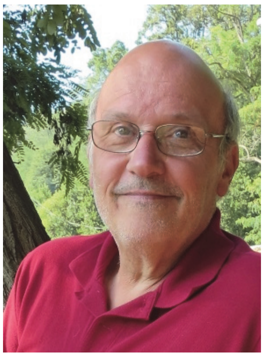
Monday 28 May (18:15-19:15) POSTER SECTION 1

MP 1	M. Holá	Fascination with laser ablation
MP 2	E. Vaníčková	Analysis of metal layers by LA-ICP-MS
MP 3	F. Gregar	In-line aerosol mass monitoring during laser ablation inductively coupled plasma mass spectrometry analysis
MP 4	M. Hložková	Fundamental study of laser beam-minerals interaction and utilization of LA-ICP-MS in geology
MP 5	K. Novotný	Influence of laser wavelength and laser pulse energy on the depth profiling of historical paintings by LIBS
MP 6	A.V. Dik	New approach to design of experiments for LIBS
MP 7	S. Musil	Hydride generation of tellurium for AAS and AFS
MP 8	S. Musil	Photochemical vapor generation of molybdenum with ICP-MS detection
MP 9	J. Smolejová	Electrochemical generation of volatile Te species for AFS detection
MP 10	M. Svoboda	Optimization of atomization conditions for bismuth, lead and tin hydrides for development of hydride atomizers
MP 11	M. Svoboda	Arsenic speciation analysis by hydride generation – cryotrapping – gas chromatography – atomic absorption spectrometry
MP 12	I. Petry-Podgórska	Volatile species generation for speciation analysis of mercury – preliminary studies
MP 13	J. Sysalová	Mercury species contaminations around the abandoned gold mine Libčice due to the use of amalgamation processes in the former gold mining
MP 14	A. Kaňa	Cationic arsenic species in food samples
MP 15	M. Vosmanská	Development of analytical method for total chromium using inductively coupled plasma mass spectrometry
MP 16	T. Matoušek	Influence of addition of organic solvent to ICP-MS plasma on sensitivity and limits of detection for elements forming volatile species and potential internal standard elements
MP 17	M. Loula	Effect of instrumental parameters on nanoparticle peak width in single particle ICP-MS
MP 18	I. Hagarová	Quantification of silver nanoparticles in the presence of Ag(I] species using cloud point extraction followed by ETAAS
MP 19	J. Komárek	Determination of mercury in soil by ETAAS
MP 20	O. Zvěřina	Determination of cadmium and iron in one firing with high-resolution continuum source AAS
MP 21	S. Ružičková	Evaluation of microwave assisted decomposition method for HR CS FAAS determination of total element contents in the waste mobile phones printed circuit boards
MP 22	T. Šídová	Optimization of sample preparation procedure for the determination of metals in synthetic organic pigments using atomic absorption spectrometry method
MP 23	D. Remeteiová	Investigation of the US EPA method 3052 utilization for microwave acid digestion of printed circuit boards

Tuesday 29 May (19:00-20:00) POSTER SECTION 2

TP 1	A. Jeništová	The effect of silver nanoparticles on the penetration properties of the skin barrier
TP 2	M. Švecová	Silver hydrosols reduced by flavonoids: what is the effect of immobilization procedures on enhanced Raman signal of riboflavin?
TP 3	T. Helešicová	Raman micro-spectroscopic monitoring of components distribution in poorly soluble pharmaceuticals tablets
TP 4	M. Medvedíková	Diffuse large B-cell lymphoma subtypes classification using vibrational spectroscopy
TP 5	L. Bednárová	Chiral plasmonic nanoassemblies
TP 6	L. Bednárová	Spectroscopic study of tetrathiafulvalene derivatives in charge-transfer complexes
TP 7	P. Táborský	Interaction of intramolecular g-quadruplex DNA structures with selected alkaloids
TP 8	P. Jarošová	Quaternary protoberberine alkaloids selectively stabilize g-quadruplexes
TP 9	J. Kučera	Enhancement of sensitivity in separation techniques with fluorescence detection using deuterated water
TP 10	A. Vacková	Monitoring spectral changes of nucleic acid UV absorption: Application in study of miRNA binding
TP 11	Y. Bazeľ	A combination of liquid phase microextraction and UV-VIS spectrophotometric determination of chromium (VI)
TP 12	Y. Bazeľ	HPLC-UV analysis of selected estrogens
TP 13	J. Švancarová Laštincová	Determination of phenolic acids in white wine by hplc with fluorescence detector
TP 14	A. García-Figueroa	Drop sensing platforms for detection of bromine under headspace liquid-phase microextraction configuration: a comparison of organic and nanostructured receptors
TP 15	J. Juřica	Determination of lansoprazole and its metabolites in human serum for phenotypization of CYP2C19 and CYP3A4
TP 16	D. Čožíková	Stability studies of rifampicin and gentamicin by using simple HPLC-UV and HPLC-FLD methods
TP 17	J. Kulhánek	GC-MS determination of the residual malondialdehyde in hyaluronic acid grafted by linolenic acid
TP 18	K. Kostolanská	Online solid-phase extraction liquid chromatography-mass spectrometry of hair cortisol using a surrogate analyte
TP 19	O. Romanyuk	Electron affinity of polycrystalline diamond films
TP 20	R. Zakl	Development of new preparation procedures and the usage of plasmonic recyclable nanomaterials for enhanced molecular spectroscopic techniques
TP 21	P. Šimůnková	The development of surface- and tip-enhanced vibrational spectroscopic methodologies for studies of pollen grains

Curriculum Vitae of Alessandro D'Ulivo



Alessandro D'Ulivo (born in Pescia, Tuscany, 1954) graduated in Chemistry at University and Pisa (1978) and is a Senior Researcher of Italian National Research Council (since 1981). He is presently developing his research activity at the Institute of Chemistry of Organometallic Compounds of CNR, research unit of Pisa, of which he was head from 2010 to 2013.

He is associate professor of at the Department of Chemistry and Industrial Chemistry, University of Pisa since 1991 and Scuola Normale Superiore of Pisa (2010-2013) teaching Analytical Chemistry and supervising graduate and PhD students for thesis. Awarded of the national scientific qualification of Full Professor in Analytical Chemistry (2013).

He is IUPAC Fellow from 2011and member of the Editorial Advisory Board of Spectrochimica Acta, Part B, Atomic Spectroscopy from 2006. He organized the Colloquium Spectroscopicum Internationale XL, held in Pisa in 2017.

His research interests focus on analytical atomic and mass spectrometry for trace and ultratrace analysis, fundamentals and applications of chemical and photochemical vapor generation technique, mechanistic aspects of the generation of volatile hydrides by aqueous, boranes, atomization mechanisms and interferences in hydride atomizers, hyphenated techniques using chromatography interfaced with atomic or mass spectrometry.

International scientific cooperation includes National Research Council Canada (INMS, Ottawa), Academy of Science of the Czech Republic (Inst. Analytical Chemistry), Laurentian University (Dept. Chemistry, Sudbury), Max Planck Institute for Chemistry (Dept. Biogeochemistry, Mainz, D), Federal University of Santa Catharina, (Florianopolis, Brazil), Departamento de Química, Universidade Federal Federal University of São Carlos (Brazil), Xiamen University (China).

He authored and co-authored 113 scientific papers on international ISI journals, with 3310 citations and H-index=31.

Curriculum Vitae of Norbert Jakubowski

Norbert Jakubowski graduated as “Diplom-Physiker” from the University in Essen/Duisburg. In his diploma research work he focused on the development of plasma based ion sources. He obtained his doctorate (Dr. rer. nat.) in 1991 from the University of Stuttgart/Hohenheim for his thesis: “Analysis of Technical Layers by Use of Glow Discharge Mass Spectromtry (GD-MS)”. In 1981 he joined the Institute for Analytical Sciences (ISAS) in Dortmund to work as a research scientist in the laboratory of inorganic mass spectrometry, where he developed novel instrumentation for plasma ion source based mass spectrometry. Later in 1999, he became the head of the division 1.1 (Inorganic Trace Analysis) of the “Bundesanstalt für Materialforschung und –prüfung (BAM)” in Berlin. Major research field are the development of ion sources based on plasmas combined with mass spectrometry for solving applications in analytical chemistry.

His main activities are mainly focused on analytical chemistry with special interest in development of instruments, methods and problem-orientated procedures based on the use of plasma sources (inductively coupled plasma, glow discharge) for elemental mass spectrometry of solid, liquid and biological/medical samples. He spent research stays in the laboratory of Joe Caruso (University of Cincinnati), Gary Hieftje (University of Bloomington) and Ken Shimizu (Keio University, Japan).

Presently the key topics of his research are related to:

1. Speciation of Se, As, Gd, Cd, Pt in environmental and biological samples. Characterization of metallic nanoparticles (NP).

2. Metallomics in particular to study the interaction of toxic metals and metallic nanoparticles with single biological cells.

3. Bioconjugation of antibodies for clinical multiplex assays;

4. Bio-imaging and development of a quantitative elemental microscope.

He published more than 206 scientific papers and 10 book chapters and edited one book on inorganic mass spectromtry and his articles are cited about 5,000 times. He is a member of the Editorial Advisory Boards of the journals „The Analyst“ and „Metallomics“.

He received the following awards: the „Alan Date Memorial Award, University of Surrey, UK (1991); the „Zimmer International Scholar” given by the University of Cincinnati, USA“; the “Waters Symposium Prize: Pioneers in ICP-MS”, Pittcon 2006, Orlando, USA (2006) and the most prestigeous „European Award for Plasma Spectrochemistry”, Krakow, Poland (2013).

Curriculum Vitae of Josef Komárek

Josef Komárek was born 1946 in Brno. He graduated in chemistry in 1969 at the Faculty of Science of the J. E. Purkyně University (now Masaryk University), where he also earned a degree of Doctor of Natural Sciences (RNDr.) in 1970. In 1977 he received the Candidate of Sciences degree (CSc.) and in 1998 the Doctor of science degree (DrSc.) from the University of Ljubljana in Slovenia. In 1992 he habilitated at the Faculty of Science of the Masaryk University and in 2004 he was appointed professor of Analytical Chemistry.

His first employment in 1969 was at the Department of Geology and Pedology, Faculty of Forestry, University of Agriculture in Brno (now Mendel University), in 1971 he moved to the Veterinary Research Institute in Brno and then in the same year to the Department of Analytical Chemistry, UJEP in Brno. On this position (now the Department of Chemistry of the Masaryk University) he has operated to this day.

Atomic Absorption Spectrometry has been his major research field since his student´s years. His research interests focus on the development of methods for trace analysis of environmental, clinical, geological and metallurgical samples, role of organic reagents in atomic absorption spectrometry, releasing agents for flame atomization, various types of matrix modifiers for electrothermal atomization, cold-vapour technique, Zeeman background correction, flow injection analysis (FIA), FIA-AAS after preconcentration of metal ions on chelating sorbents, by solvent extraction and by dialysis, and AAS in connection with electrochemical deposition of metals. In addition to the AAS, he devotes to the atomic fluorescence spectrometry and the speciation analysis, especially of mercury.

His teaching activity has consisted of lectures Basic analytical chemistry, Trace analysis, Environmental analytical chemistry - inorganic pollutants, Atomic absorption spectrometry and Speciation analysis, and of laboratory courses Environmental analytical chemistry - inorganic pollutants and Materials analysis.

The results of his work have been published in more than 100 scientific articles, of which over 60 articles have been published in impacted domestic and foreign journals. Josef Komárek co-authored one monograph, seven textbooks and about hundred lectures or posters at domestic and foreign seminars and conferences.

Josef Komárek actively participated in organizing a number of seminars and courses in the field of AAS. Since 2005, he has been a member of the Main committee of the Ioannes Marcus Marci Spectroscopic Society and the chairman of its bulletin editorial board. Recently he also organized a series of "Speciation analysis" workshops.

Curriculum Vitae of Margaretha de Loos-Vollebregt

Margaretha de Loos-Vollebregt obtained her PhD in 1980 from Delft University of Technology, Netherlands, Department of Analytical Chemistry. The title of the thesis was 'Zeeman atomic absorption spectroscopy' with supervisor Prof. Dr. Leo de Galan. From 1968 until 2014 she worked as analytical chemist at the Delft University of Technology in various positions (including associate professor). Since 2009 she is guest professor in Atomic Spectroscopy at Ghent University, Belgium.

She has published about 80 papers in international journals (H index 24) and several book chapters. She presented lectures at numerous international conferences and was member of scientific committees for e.g. CSI, ESAS, FACSS and RioConferences. From 1992 until 1997 she was member of the editorial advisory board of Spectrochimica Acta Part B: Atomic Spectroscopy. From 1997 until 2001 she was reviews editor for Spectrochimica Acta Part B: Atomic Spectroscopy and since 2001 she is editor of Spectrochimica Acta Part B: Atomic Spectroscopy. From 1991 until 2016 she was a member of the advisory board of Journal of Analytical Atomic Spectrometry. Since 2006 she is member of the editorial advisory board of Analytica Chimica Acta. She is member of the Royal Dutch Chemical Society (KNCV) and member of the Analytical Chemistry division (KNCV) where she is leading the Dutch working group for atomic spectroscopy. Her scientific interests are in atomic absorption, atomic emission and inorganic mass spectrometry, including instrumental developments, signal processing and sample introduction.

Curriculum Vitae of Marcel Miglierini

Marcel Miglierini graduated in 1981 from the Slovak University of Technology in Bratislava where he works since then at the Institute of Nuclear and Physical Engineering. In 1995, he has received the Doctor of Science degree and in 1997 was appointed as a full professor in physics of condensed matter at the Slovak University of Technology in Bratislava.

In 1990, he was granted the Monbuscho fellowship and has performed an 18-month research at Osaka University in Japan. In 1995, he has obtained scholarship from the Région du Pays de la Loire and accomplished a 11-month stay at Université du Maine, Le Mans, France. Further long-term stays abroad comprise a 10-month research in 1998-99 at the Universität Wien, Austria as a visiting scientist, 2-month lecture stay in 1992 in Japan and a 2-month stay in 2001 at Georg August Universität Göttingen in Germany as a DAAD fellow. Major fields of scientific interests include magnetic and structural properties of disordered materials prepared by rapid quenching and/or mechanical grinding (amorphous metallic glasses, quasicrystals, nanocrystals, powder steels) and their hyperfine interactions, structural positions of iron in archaeological, biological, chemical, geological, mineralogical, and metallurgical systems. They are studied predominantly by nuclear spectroscopy methods (Mössbauer, NMR, electron-positron annihilation, gamma spectroscopy), atomic and magnetic field microscopy and by special analytical techniques based on synchrotron radiation.

He has published 230+ original papers (175+ in international scientific journals) and one chapter in a book. He has acted as editor of 8 scientific proceedings that were published as books by Kluwer and American Institute of Physics. The number of citations indexed in WOS is 1 200+ with h = 16. He has delivered more than 30 invited lectures at universities abroad and had 27 invited lectures at international conferences. He was declared by the Mössbauer Effect Data Center, Asheville, USA as one of the four most productive authors in the field of Mössbauer spectrometry worldwide during the years 1990-2000. In 2011, he was awarded the title Professor of the Year at the Slovak University of Technology in Bratislava and in 2015 he was declared at the same university as the Scientist of the Year.

Since 1994, he organizes the series of international conferences entitled Mössbauer Spectrometry in Materials Science which are regularly held every two years. In 1998 and 2002, he was one of the directors of NATO Advanced Research Workshops. He was a member of organizing and program committees of 20+ international conferences. During 2004-2009, he was a chairman of Knowledge Management Committee of the ENEN Association (European Nuclear Education Network). He has organized and chaired the Winter School of Synchrotron Radiation 2011, 2013, 2014 with international participation.

He represents Slovakia in the International Board on the Application of the Mössbauer Effect (since 1998) and in the consortium CENTRALSYNC which ensures access to the synchrotron source in Grenoble for researchers from the Czech Republic, Hungary, and Slovakia (since 2008). During 2010-2011, 2013-2014, and 2015-2016 he was a chairman of the Steering Committee of this consortium. Since 2003, he is a president of the Slovak Spectroscopic Society.

Curriculum Vitae of Jürgen Popp

Jürgen Popp studied chemistry at the universities of Erlangen and Würzburg. After his PhD in Chemistry he joined Yale University for postdoctoral work. He subsequently returned to Würzburg University where he finished his habilitation in 2002. Since 2002 he holds a chair for Physical Chemistry at the Friedrich-Schiller University Jena, Germany. Since 2006 he is also the scientific director of the Leibniz Institute of Photonic Technology, Jena, Germany.

His research interests are mainly concerned with biophotonics and optical health technology covering the complete range from photonic basic research towards translation into clinically applicable methods. The core of the biophotonic research activities lies in the realization of microspectroscopic imaging approaches and instruments as well as in the implementation of fiber-, chip- and nanoparticle based methods together with chip-based molecular point-of-care or point-of-use concepts to address biomedical, environmental and life-science problems. In particular, his expertise in the development and application of innovative linear and non-linear spectroscopy approaches (with focus on Raman spectroscopy) for multi-contrast and multi-parameter imaging according to the needs of pathology, oncology, and infection/ sepsis should be emphasized. Jürgen Popp is author and co-author of more than 780 journal papers and has been named as an inventor on 12 patents in the field of spectroscopic instrumentation. His work has been cited more than 15.800 times earning him an h-index of 56. Furthermore, he is editor and author of several books (e.g. Handbook of Biophotonics)

Jürgen Popp is a leading partner in various national and international research projects in cooperation with academic, clinical and industrial partners (e.g. Coordinator of “PHOTONICS4LIFE” a European Network of Excellence for Biophotonics, Initiator and CEO of the research campus “InfectoGnostics” a public-private partnership researching new paths in infection diagnosis and infection research.). In doing so, he and his group raised more than 50 Million Euro third party funding. Since 2011, he gave more than 160 invited talks on national and international conferences (among them more than 15 keynote lectures). Jürgen Popp has been organizer and chairman of several large national and international conferences (e.g. ICOB 2012, ICORS 2014, ECONOS 2016 and many more) and of several interdisciplinary and translatory workshops and symposia. In this context, Jürgen Popp shows great national, international and political commitment for interdisciplinary and translation (e.g. as member of the program committee „Optical Technology“ of the German Federal Ministry of Education and Research (BMBF) or as Member Board of Stakeholders European Technology Platform “Photonics21”).

Jürgen Popp is Founding Editor and Editor-in-Chief of the Journal of Biophotonics. In 2012, he received an honorary doctoral degree from Babeş-Bolyai University in Cluj-Napoca, Romania. Professor Jürgen Popp is the recipient of the 2013 Robert Kellner Lecture Award and the prestigious 2016 Pittsburgh Spectroscopy Award. In 2016 he was elected to the American Institute for Medical and Biological Engineering (AIMBE) College of Fellows.

Curriculum Vitae of Renato Zenobi

Renato Zenobi is Professor of Analytical Chemistry at the Organic Chemistry Laboratory of the Swiss Federal Institute of Technology (ETH) Zurich. Born in Zurich in 1961, he received a M.S. degree from the ETH Zurich in 1986, and a Ph.D. at Stanford University in the USA in 1990. This was followed by two postdoctoral appointments at the University of Pittsburgh (1990 - 1991) and at the University of Michigan (1991). Renato Zenobi returned to Switzerland in 1992 as a Werner Fellow at the EPFL, Lausanne, where he established his own research group. He became assistant professor at the ETH in 1995, was promoted to associate professor in 1997, and to full professor in 2000. He was chairman of the Organic Chemistry Laboratory in 2002-2003 and 2011-2012, served as the president of ETH's university assembly (Hochschulversammlung, HV) from 2006 – 2008, and of the lecturer's conference (Konferenz des Lehrkörpers, KdL) at ETH Zurich 2006 - 2010. Zenobi was a visiting professor at the Barnett Institute (Boston) in 2004/2005, and at the Institut Curie (Paris) in 2010. In 2010 he was appointed Associate Editor of *Analytical Chemistry* (American Chemical Society). He has chaired the 2014 International Mass Spectrometry Conference in Geneva, Switzerland.

Zenobi's research areas include laser-based analytical chemistry, electrospray and laser-assisted mass spectrometry, ambient mass spectrometry, and near-field optical microscopy and spectroscopy. He has made important contributions to the understanding of the ion formation mechanism in matrix-assisted laser desorption/ionization (MALDI) mass spectrometry, and to ambient ionization methods. He is well known for the development of analytical tools for the nanoscale, in particular TERS (tip-enhanced Raman spectroscopy), a spectroscopic methodology with ≈ 10 nm spatial resolution.

Renato Zenobi has received many awards for his scientific work, including the Thomas Hirschfeld Award (1989), an Andrew Mellon Fellowship (1990), the Ruzicka Prize (1993), the Heinrich Emanuel Merck-Prize (1998), the Redwood Lectureship from the Royal Society of Chemistry (2005), the Michael Widmer Award (2006), a honorary Professorship at East China Institute of Technology (2007), the Schulich Graduate Lectureship (2009), a honorary membership of the Israel Chemical Society (2009), honorary professorships at the Chinese Academy of Sciences (Changchun), at Hunan University, and at Changchun University of Chinese Medicine (2010), the Mayent-Rothschild Fellowship (Institut Curie, Paris; 2010), the Fresenius Lectureship from the German Chemical Society (2012), the Thomson Medal (International Mass Spectrometry Foundation, 2014), the 2014 RUSNANO prize, the 2015 Fresenius Award (German Chemical Society/GDCh), and an ER

METROHM SPEKTROSKOPIE – BUDIŽ SVĚTLO

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Co očekáváte od Vašeho spektrometru? Rychlost, všestrannost, zaměření na klíčové aplikace a soulad s předpisy? Toto je podstatou Metrohm spektroskopických řešení. Za spektroskopickou divizí společnosti Metrohm stojí více než 50 let usilovné práce a přes 50 technologických patentů v oblasti molekulární spektroskopie.

Naše spektroskopické portfolio staví na dvou základních pilířích. Jedním je oblast VIS-NIR spektrometrů pro kvalitativní i kvantitativní analýzu kapalných a pevných látek nejen v laboratoři, ale i přímo ve výrobním procesu (tzv. NIR procesní analyzátory). Před analýzou není potřeba žádná časově náročná předúprava vzorku a použití rozpouštědel či dalších reakčních činidel je minimalizováno, což vede k dosažení výsledku analýzy za méně než jednu minutu.
Druhým pilířem jsou Metrohm přenosné Ramanovy spektrometry (MIRA) o velikosti mobilního telefonu a váze 750 gramů. MIRA jsou dedikované přístroje pro identifikaci a verifikaci chemických látek ve farmacii (MIRA P) nebo pro identifikaci výbušnin, drog a tisíce různých chemických látek mimo regulované odvětví (MIRA DS). Tyto přístroje používají technologii „Orbital Raster Scan“ pro měření nehomogenních vzorků s maximálním bezpečím a výsledky v řádu vteřin.

Kromě vysoké přesnosti a nenáročnosti měření s našimi přístroji jsme především schopni Vám nabídnout plnou aplikační podporu, kde nezbytnou součástí je servis přímo v České republice. Aplikační oblast Metrohm spektroskopie zahrnuje veškeré typy průmyslů od farmaceutického, petrochemického, polymerního, přes výrobu biopaliv, až po průmysl potravinářský. V jednom měření můžete stanovit nejen chemické parametry, ale i fyzikální parametry, např. hrubost zrn, index tavení atp. Mezi stěžejní vyvinuté aplikace patří například: stanovení obsahu vody v rozpouštědlech, léčivech, kosmetických přípravcích a olejích, dále stanovení aktivních látek ve farmaceutických produktech, kontrola vstupních surovin ve farmaceutickém průmyslu, číslo kyselosti v petrolejových produktech a olejích, kontrola kvality biopaliv, stanovení aromátů v benzínu, příprava standardů s definovaným cetanovým a oktanovým číslem, stanovení obsahu methanolu v biopalivech, kontrola polymerizačního procesu a mnoho dalších aplikací. Aplikační portfolio společnosti Metrohm je dostupné na webových stránkách: www.metrohm.com/cs-cz/aplikace.

Zavedení analýzy do procesu může být rychlejší než dříve. Metrohm poskytuje pre-kalibrační modely, které minimalizují čas potřebný pro vývoj analytické metody a následné testování. Hlavními pre-kalibračními modely jsou: predikce biomethanolového potenciálu v biomase, stanovení hydroxylového čísla v polyolech nebo stanovení mastných kyselin v palmovém oleji. Pro více informací neváhejte kontaktovat naše aplikační specialisty.

CHEMICAL VAPOR GENERATION BY AQUEOUS BORANES: FROM ANALYTICAL APPLICATIONS TO MECHANISTIC INVESTIGATIONS

Alessandro D'ULIVO

National Research Council, Institute of Chemistry of Organometallic Compounds, S.S. of Pisa, Via G. Moruzzi, 1, 56124 Pisa, Italy
dulivo@pi.iccom.cnr.it

Since1971, Chemical Vapor Generation (CVG) by aqueous borane reagents has been employed as an analytical derivatization technique for the conversion of aqueous ions of several metals and semi-metals to their volatile derivatives. At present CVG is a popular technique and it has been widely employed in the determination and speciation of several elements at ultratrace level by atomic and mass spectrometry. More recently, starting since 2003, dedicated studies were developed with the aim to clarify the mechanisms governing the chemistry of CVG.

In a first phase, the attention was focused on the removal of erroneous concepts and the clarification of controversial aspects of CVG of volatile hydrides. The studies developed during this step served to reconcile CVG with the evidence reported in the fundamental chemistry literature concerning the mechanisms of hydrolysis of boranes, $NaBH_4$ (THB) and amine-boranes (ABs), and the mechanism of hydrogen transfer from borane to analytical substrate [1,2].

Due to the particular conditions in which analytical CVG operates i.e., elevated acidities, high borane to analyte molar ratios, presence of foreign species and chemical additives, the use of dedicated experiments is necessary, in particular to investigate the mechanism of action of additives and the mechanisms of hydrolysis of ABs [3,4]. Some of the evidences obtained under analytical conditions for the hydrolysis of amine-boranes cannot be explained in the light of the current knowledge and suggests the needing of a revision of the mechanism of acid-catalyzed hydrolysis which is currently accepted in the literature for ABs.

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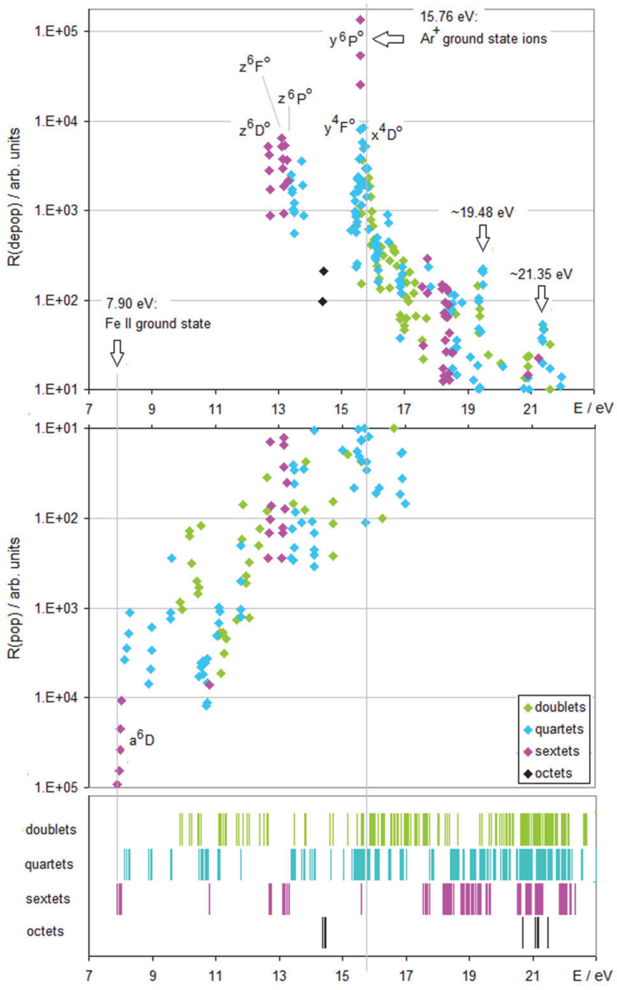
ADVANCES IN GLOW DISCHARGE EMISSION SPECTROSCOPY: SELECTIVE EXCITATION, TRANSITION RATE DIAGRAMS AND BEYOND

Zdeněk WEISS

Institute of Physics of the Czech Academy of Sciences, Department of Materials Analysis
Na Slovance 2, 182 21 Praha 8, Czech Republic
weissz@fzu.cz

Glow Discharge Optical Emission Spectroscopy (GD-OES) [1] is a powerful tool for elemental analysis of metals and alloys. It allows also depth profiling of inorganic coatings and surface-modified materials, with depths ranging from tens of nanometers to more than 100 µm. Recent developments in understanding the glow discharge excitation will be reviewed, in particular the concept of transition rate (TR) diagrams [2], see the TR diagram of Fe II in Fe-Ar plasma below.



From emission spectrum, it is possible to establish relative rates at which individual states of an atom or ion are radiatively depopulated (the top plot) and populated by cascading (the middle plot, values increasing downwards). Bottom plot shows all existing FeII levels sorted by their spin multiplicities. Any peak of R(depop), not balanced by a peak of R(pop) at the same energy, indicates a selective collisional excitation. Here, the peak at ≈15.7 eV of R(depop) indicates the Ar^+-Fe charge transfer reaction,

$$Ar^+ + Fe^0 \rightarrow Ar^0 + Fe^{+*} ,$$

selectively populating the sextet- and quartet FeII levels in the vicinity of the Ar ionization energy (15.76 eV). Here, energy is given relative to the ground state of Fe *atom*.

This concept is best applicable to non-equilibrium plasmas, e.g. glow discharges, in which radiative deexcitation of short-lived states strongly prevails over their collisional deexcitation by free electrons.

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TRACE DETERMINATION OF SELENIUM BY HYDRIDE GENERATION IN-ATOMIZER TRAPPING ATOMIC ABSORPTION SPECTROMETRY

Jan KRATZER[1], Ignacio MACHADO[1,2], Dominik VANĚK[1,3], Stanislav MUSIL[1], Milan SVOBODA[1], Jiří DĚDINA[1]

[1]The Czech Academy of Sciences, Institute of Analytical Chemistry, Veveří 97, 602 00 Brno, Czech Republic
[2]Faculty of Chemistry, Universidad de la República, Gral. Flores 2124, 625 00 Montevideo, Uruguay
[3]University of Chemistry and Technology Prague, Technická 5, 166 28 Prague, Czech Republic
jkratzer@biomed.cas.cz

Selenium and its compounds are essential for life, but its physiological function is ambivalent. Its toxic levels are less than an order of magnitude above those required for health. Hydride generation (HG) is an expedient approach to efficient Se introduction into a spectrometric detector. Atomic absorption spectrometry (AAS) fulfils the criteria of a reliable and cheap detector to be coupled with HG. However, a preconcentration step must be included to reach sufficiently low detection limit. A compact quartz trap-and-atomizer device based on a modified externally heated quartz tube atomizer was designed in our laboratory to preconcentrate Se on a quartz surface. The preconcentration was controlled by both surface temperature and atmosphere composition reaching 70% overall preconcentration efficiency [1]. Gold was reported as a suitable surface for Se preconcentration with subsequent AAS or AFS detection [2]. Preconcentration efficiency of 100% was reached [2].

A modular design of quartz trap-and-atomizer device was constructed allowing fast and simple replacement of preconcentration fillings. Three types of gold-based fillings in forms of wire, foil and amalgamator (used for Hg preconcentration) were tested. Gold wire was selected as the best owing to preconcentration efficiency (100 %) and peak profile. Moreover, trapping of Se hydride in a novel quartz dielectric barrier discharge (DBD) plasma atomizer was also optimized and studied for the first time reaching 65 % overall preconcentration efficiency. The mechanism of selenium collection and release in both atomizers was studied by means of a ^{75}Se radioactive indicator. Incomplete Se volatilization was found in the DBD.

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DIELECTRIC BARRIER DISCHARGES – PLASMA FUNDAMENTALS AND APPLICATIONS IN ANALYTICAL CHEMISTRY

BRANDT S[1], KLUTE FD[1], SCHÜTZ A[1], BURHENN S[1], VOGEL P[1], VEZA D[2], VADLA C[3], HORVATIC V[3], FRANZKE J[1]

[1]ISAS - Leibniz-Institut für Analytische Wissenschaften – ISAS – e.V.,
Bunsen-Kirchhoff-Str. 11, 44139 Dortmund, Germany
[2]Department of Physics, Faculty of Science, University of Zagreb, Bijenicka 32, 10000 Zagreb, Croatia
[3]Institute of Physics, Bijenicka 46, 10000 Zagreb, Croatia
franzke@isas.de

Sixteen years ago the potential of dielectric barrier discharge plasma was presented for use in analytical element spectrometry [1]. It was a miniature planar DBD, characterized by small size, low power consumption, low gas temperature and excellent dissociation capability for molecular species. Several years later a capillary shaped DBD was presented by Na et al. [2] applied as an efficient method for molecular mass spectrometry resulting in the development of a variety of methods now commonly termed Ambient Mass Spectrometry (AMS), which experienced a very rapid development during the last years.

Here themes will be presented and tried to be characterized where dielectric barriers developed at ISAS were used in the field of Analytical Chemistry like “diode laser spectrometry at low pressure DBDs” [1], “DBD as soft ionization source at ambient air”[3-5] and “Atmospheric pressure DBD for OES” [6].

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PLASMA PENCIL IN ANALYTICAL SPECTROCHEMISTRY – ACHIEVEMENTS AND PROSPECTS

Aleš HRDLIČKA[1,2], Magda DVOŘÁKOVÁ[2], Pavel SLAVÍČEK[3], Viktor KANICKÝ[1,2]

[1]Central European Institute of Technology, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic
[2]Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
[3]Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
ales2003h@centrum.cz

Plasma pencil is a capacitively coupled radiofrequency (13.56 MHz) jet discharge operated in argon, helium or gas mixtures at the atmospheric pressure. It was originally designed for surface modifications of cultural heritage objects. It has been also tested in analytical spectrochemistry [1, 2] as an alternative excitation source. Due to lower excitation temperatures of about 2700-4000 K it exhibits matrix interferences by easily ionisable elements (EIE) [3] and nowadays possible influence of anions from dissociated salts is investigated. E.g. the influence of EIE on Cu and Zn emission is apparently driven by excitation energies of Cu and Zn lines and ionization energies of EIE. However, the depression effect of sulfates on Zn emission is unexpectedly stronger than on Cu one from lowest (mg l^{-1}) sulfate concentrations. Therefore it would be very interesting to exploit this effect for indirect determination of sulfates or sulfur in water solution. Results of this research could eventually shift the analytical capabilities of the plasma pencil towards non-metals which cannot be efficiently excited.

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MATRIX EFFECTS IN PLASMA PENCIL AND ANALYSIS OF REAL SAMPLES

Magda DVOŘÁKOVÁ[1], Aleš HRDLIČKA[1,2], Pavel SLAVÍČEK[3], Viktor KANICKÝ[1,2]

[1]Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
[2]Central European Institute of Technology, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic
[3]Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
mdvorakova38@gmail.com

Plasma pencil is a capacitively coupled discharge (CCP), which is tested as an alternative excitation source for determination of elements concentrations in solutions [1, 2]. The discharge can excite elements of 1st and 2nd group of the periodic table and also some other metals of which melting and boiling temperatures are not high related to the pencil plasma temperature. Among them mainly copper and zinc emissions were already studied under various conditions. It was shown that intensities of their atomic lines are suppressed by the presence of easily ionisable elements (EIE: 1st and 2nd group of the periodic table) in the sample solution [3]. The suppression was also found in the presence of nitric acid. Significant differences were also found for different anions in combination with sodium cation in the solution. It seems that the most intensive depression effect is caused by chlorides, less effect is observed for nitrates and sulphates and the dependence on the sulphate concentration is not monotonous. To find out if a plasma pencil can be used as an alternative excitation source, we have analyzed real drinking water samples by plasma pencil and ICP-OES and we can say that the yielded results do not differ significantly.

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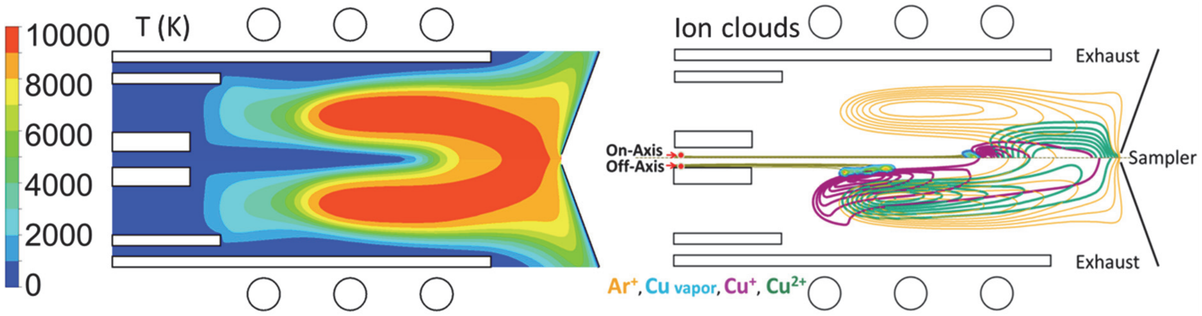
PARTICLE JOURNEY THROUGH AN ICP TORCH: WHAT MODELING REVEALS?

Maryam AGHAEI and Annemie BOGAERTS

Research group PLASMANT, Chemistry department, University of Antwerp, BE2610 Antwerp, Belgium
maryam.aghaei@uantwerpen.be

An inductively coupled plasma, connected to a mass spectrometer, is computationally investigated. After obtaining stable plasma properties for Ar, we introduce the sample particles into the ICP with the discrete phase model. During each iteration, we calculate the exchange of mass, momentum and energy between plasma and particles. By means of this model, we can track the particles to determine their position, their phase (liquid or vapor), velocity and temperature, as well as the ionization of the vapor atoms (ion clouds).

Indeed, due to different boiling and ionization temperatures as well as different viscosity and diffusion of different materials, the position at which the sample cloud may move in the radial direction to the outer region is different. Hence, we show to what extent these differences affect the ion cloud transport towards sampler. Moreover, particles are injected with different sizes in order to find in which range a complete evaporation and ionization inside the torch can be guaranteed. Recently, a direct comparison with experiment is performed in order to find the optimum size of gold nano-particles at a certain operating condition. Studying the radial diffusion, the effect of on- and off-axis injection is also studied. We clearly show that the ion clouds of on-axis injected material are located closer to the sampler with less radial diffusion. This guarantees a higher transport efficiency through the sampler cone. Moreover, our model reveals the optimum ranges of applied power and flow rates, which ensure the proper position of ion clouds inside the torch, i.e., close enough to the sampler to increase the fraction that can enter the mass spectrometer and with minimum loss of material toward the exhausts as well as a sufficiently high plasma temperature for efficient ionization [1].



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ALUMINIUM AND ANTIMONY BIOEXTRACTION FROM ALUMINOSILICATES AND FERRIC OXOHYDROXIDES IN PRESENCE OF FILAMENTOUS FUNGUS *ASPERGILLUS NIGER*

Filip POLÁK[1,3], Martin URÍK[1,3], Marek BUJDOŠ[1,3], Marcel B. Miglierini[2,3]

[1] Institute of Laboratory Research on Geomaterials, Faculty of Natural Sciences, Comenius University in Bratislava, Mlynská dolina, Ilkovičova 6, 842 15 Bratislava, Slovakia
[2] Institute of Nuclear and Physical Engineering, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia
[3] Slovak Spectroscopic Society, member of the Association of Slovak Scientific and Technological Societies, Mlynská dolina, 842 15 Bratislava, Slovakia
filip.a.polak@gmail.com

Aluminosilicates and ferric oxohydroxides are natural solid phases that serve as pool and geochemical barrier, respectively, for various metals in soils and sediments. Most experiments dedicated to evaluation of mobility of toxic elements associated with these phases, e.g. aluminium or antimony, neglect the influence of biotic factors. However, microbial weathering of mineral or amorphous phases may lead to release of aforementioned elements. Therefore, this contribution investigates bioextraction of aluminium and antimony from aluminosilicates and ferric oxohydroxides, respectively, via activity of *Aspergillus niger*, a common soil fungus. Its effect on bioextraction of metals and microstructure of solid phases was evaluated using atomic absorption spectroscopy with flame atomization, Mössbauer spectroscopy, X-ray powder diffraction and capillary isotachophoresis. Our results indicate that during static cultivation of *A. niger* 3.2% of aluminium was bioextracted from aluminosilicates along with other metals and metalloids bounded in its structure. Bioextraction of antimony from ferric oxohydroxides was more successful, hence the 35.8% of antimony was mobilized from antimony unsaturated oxohydroxides. These findings conclude that microorganisms may significantly influence the mobility of aluminium or antimony in the environment.

Acknowledgements
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SORPTION STUDIES OF SELENIUM AND IODINE FROM AQUEOUS SOLUTIONS ON NATURAL AND SYNTHETIC MATERIALS

Michaela MATULOVÁ[1,2], Marek BUJDOŠ[1,2]

[1]Institute of Laboratory Research on Geomaterials, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 842 15 Bratislava, Slovakia
[2]Slovak Spectroscopic Society, member of the Association of Slovak Scientific and Technological Societies, Mlynská dolina, 842 15 Bratislava, Slovakia
matulova22@uniba.sk

Sorption is important process influencing the environmental mobility of elements like selenium and iodine. Selenium is an essential and toxic element of high mobility in the environment. Selenium occurs mainly as selenite and selenate [1]. Iodine occurs mainly as iodide and iodate, with high sorption reactivity with certain minerals, soils, sediments and organic matter [2]. ^{79}Se and ^{129}I are long-lived fission products. These radioisotopes are two of the main radionuclides produced in a spent fuel repository.

We assume that better understanding of selenium and iodine mobility will help to understand their mobility in case of defection of barrier in a spent fuel repository. Iron oxy-hydroxides might play an important role in the migration of elements in the environment, also soil is an important transport medium for radioactive and non-radioactive elements.

This work evaluates the sorption properties of selenium onto goethite and iodine onto soil. The sorption of selenite and selenate was fitted with Langmuir and Freundlich isotherms, for selenite $S_{max} = 7{,}0\ \mathrm{mg\cdot g^{-1}}$, $K_L = 21{,}0\ \mathrm{l\cdot mg^{-1}}$, $K_F = 6{,}0\ \mathrm{mg\cdot g^{-1}\cdot l}$, for selenate $S_{max} = 3{,}8\ \mathrm{mg\cdot g^{-1}}$, $K_L = 8{,}2\ \mathrm{l\cdot mg^{-1}}$, $K_F = 3{,}1\ \mathrm{mg\cdot g^{-1}\cdot l}$. We found out high affinity goethite to selenium ions. Also iodine and iodate was fitted with Langmuir and Freundlich isotherms, for iodide $S_{max} = 14{,}1\ \mathrm{mg\cdot g^{-1}}$, $K_L = 0{,}07\ \mathrm{l\cdot mg^{-1}}$, $K_F = 1{,}26\ \mathrm{mg\cdot g^{-1}}$ and for iodate $S_{max} = 45{,}1\ \mathrm{mg\cdot g^{-1}}$, $K_L = 0{,}07\ \mathrm{l\cdot mg^{-1}}$, $K_F = 3{,}7\ \mathrm{mg\cdot g^{-1}}$. Samples of selenium were measured by flame atomic absorption spectrometry (FAAS) and samples of iodine were measured by inductively coupled plasma mass spectrometry (ICP MS).

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NEXSA - SMALL SPOT XPS AND MULTI-TECHNIQUE ANALYSIS WITH RAMAN

Pavel Janderka

Pragolab s.r.o., Nad Krocínkou 55, 190 00 Praha, Czech Republic
janderka@pragolab.cz

X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy are two popular analytical techniques due to their flexibility, ease of use, and the wealth of information they provide. Until recently analysis of a material with both of these techniques required the use of two different instruments, however the development of coincident XPS - Raman allows for straightforward and quick utilization of both techniques opening up new exciting materials characterization opportunities.

XPS is an extremely versatile technique that has found widespread use in a myriad of application areas, from contact lenses to aerospace materials. XPS is unique in that it can quantify the elemental and chemical composition of a material's surface with extreme selectivity; the typical information depth of XPS being less than 10 nanometres. Raman spectroscopy is utilized in many similar application areas as it requires little sample preparation, is nondestructive, provides information on molecular structure, and enables users to identify materials quickly, thanks to extensive spectral libraries.

Coincident XPS and Raman spectroscopy has not been possible. Instead samples have had to be transferred between instruments; which not only increases the amount of time required to acquire data, but also adds a degree of uncertainty as to whether the analysis has been collected from the same region of the sample. To overcome these problems, the Thermo Scientific™ Nexsa™ spectrometer has been integrated with the Thermo Scientific™ iXR™ Raman Spectrometer to provide a multi-modal analysis platform[1,2,3].

The system aligns the XPS analysis position exactly with the Raman analysis position, ensuring that the data is collected from the same position.

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EXPERIMENTAL SEPARATION OF MOBILE ELEMENTS' FRACTION USING EXTRACTIONS WITH EXTRACELLULAR FUNGAL METABOLITES

Martin URÍK[1,2], Marek BUJDOŠ[1,2], Ingrid HAGAROVÁ[1,2], Filip POLÁK[1,2], Peter MATÚŠ[1,2], Jana KUBOVÁ[2]

[1]Institute of Laboratory Research on Geomaterials, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 842 15 Bratislava, Slovakia
[2]Slovak Spectroscopic Society, member of the Association of Slovak Scientific and Technological Societies, Mlynská dolina, 842 15 Bratislava, Slovakia
urik@fns.uniba.sk

Our extensive research on fungal transformation of selenium, mercury, aluminium, arsenic, antimony and other hazardous substances highlighted that metabolic activity of filamentous fungi do affect the environmental behavior of metals and metalloids. Filamentous fungi naturally produce various acidifying and chelating metabolites into their extracellular space. Since the chemical properties of naturally occurring fungal extracellular metabolites undeniably affect translocation of environmental contaminants, our research group suggested application of fungal metabolites for assessing the mobility of metals and metalloids. To quantify the fungal impact on mobile metals and metalloids' fraction, we have applied various methods of atomic and mass spectrometry and experimented with bioextraction procedures using fungal metabolites on diverse environmental and synthetic solid phases. This approach showed promising results regarding the separation of mobile fraction of metals and metalloids, an important task in analytical geochemistry.

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DETERMINATION OF IODINE FRACTIONS IN SOILS USING INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY AFTER APPLICATION OF SINGLE AND SEQUENTIAL EXTRACTION TECHNIQUES

Eva DUBORSKÁ, Martin URÍK, Marek BUJDOŠ, Michaela MATULOVÁ, Jana KUBOVÁ,
Peter MATÚŠ

Institute of Laboratory Research on Geomaterials, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 842 15 Bratislava, Slovakia
Slovak Spectroscopic Society, member of the Association of Slovak Scientific and Technological Societies, Mlynská dolina, 842 15 Bratislava, Slovakia
peter.matus@uniba.sk

Iodine (mainly as iodide I^- and iodate IO^{-3} ions), is an essential element indispensable for the proper hormone production of the thyroid gland. Iodine has also 37 known isotopes, all undergo radioactive decay except ^{127}I, which is stable. In spite of iodine essentiality and radioactivity, there are only a few studies which are concerned with its distribution in environmental matrices, especially in soils. Thus, this work evaluates the effect of various geochemical factors on iodine mobility in seven agricultural and forest soils from five areas of Slovakia. These effects were evaluated through analytical methods, including single and sequential extraction techniques and inductively coupled plasma mass spectrometry (ICP MS). The effects of soil characteristics on these processes were also evaluated. Our research provides additional information on recent knowledge of iodine geochemistry in soils and can be also utilized for studies on mobility of radioactive iodine isotopes.

Using single extraction technique, total soil iodine content was evaluated. More than 2.5 $mg.kg^{-1}$ iodine, which is the average total soil iodine content for inland areas, was determined in four soils. Soil characteristics which positively correlated with total soil iodine content were soil organic matter content, amorphous aluminum oxide content, clay content and total concentration of aluminum and iron.

Sequential extraction experiments showed that the most of the soil iodine is bound to oxides (39.4 % in average), humic acids (30.5 % in average) and residual fraction (15.1 % in average). Easily extractable fraction contained less than 10 % of total iodine content. Furthermore, only 4.4 % iodine was water-extractable.

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METHOD DEVELOPMENT FOR SPECIATION ANALYSIS OF VOLATILE MERCURY FORMS IN AMBIENT AIR AND FLUE GASES FROM INCINERATION PLANTS

Jaroslav ŠVEHLA[1,2], Jan KRATZER[2], Milan SVOBODA[2], Karel SVOBODA[1], Michal ŠYC[1]
Tomáš RUŽOVIČ[1]

[1]Institute of Chemical Process Fundamentals of the CAS, Rozvojova 2/135, 165 02 Prague 6, Czech Republic
[2]Institute of Analytical Chemistry of the CAS, Veveří 97, 60200 Brno, Czech Republic, svehla.jaroslav@gmail.com

Abstract

Flue gas from fossil fuels and waste combustion contains different oxides of carbon, nitrogen, sulfur, hydrogen halides, arsenic, dioxins, etc. and also considerable amounts of mercury. The new, tightened EU-limits for Hg-emissions from combustion processes will be applied also in the Czech Republic since 2021. The paper introduces the development of a new procedure for speciation analysis of gaseous mercury forms (Hg^0 (g), $HgCl_2$ (g), $MeHg^+$ (g)) in flue gas, biogas and ambient air. For the continuous measurement of Hg^0, the VM-3000 UV spectrometer (Mercury Instrument) was employed. It measures the absorbance of cold vapors of elemental mercury at room temperature at wavelength 254 nm. However, it does not detect $HgCl_2$ vapors which form a significant fraction of Hg emissions particularly from waste incinerators [1,2]. Atomic absorption spectrometry (AAS) with heated quartz tube atomizer (900 °C) was used for determination of gaseous $HgCl_2$. Potential of AAS for on-line speciation analysis of gaseous Hg^0 (non-heated atomizer) and $HgCl_2$ (heated atomizer) in flue gases will be discussed. The risk of transport losses and/or changes in speciation analysis during sampling will be shown. Direct separation of Hg gaseous species by gas chromatography with spectrometric detection will be outlined. In a pilot study, the possibility of pre-concentration of gaseous Hg species on the commercial Au-based amalgamator, followed by their gradual thermo-desorption, with subsequent spectrometric detection is investigated.

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INFLUENCE OF ZINC INITIAL SPECIATION ON ITS DISTRIBUTION IN AQUEOUS MEDIA IN PRESENCE OF FILAMENTOUS FUNGUS OR SOILS

Martin ŠEBESTA[1,2], Martin URÍK[1,2], Marek KOLENČÍK[2,3], Marek BUJDOŠ[1,2], Lucia KOŘENKOVÁ[1,2], Peter MATÚŠ[1,2]

[1]*Institute of Laboratory Research on Geomaterials, Faculty of Natural Sciences, Comenius University in Bratislava, Mlynská dolina, Ilkovičova 6, 842 15 Bratislava, Slovakia*
[2]*Slovak Spectroscopic Society, member of the Association of Slovak Scientific and Technological Societies, Mlynská dolina, Ilkovičova 6, 842 15 Bratislava, Slovakia*
[3]*Slovak University of Agriculture in Nitra, Faculty of Agrobiology and Food Resources, Department of soil science and geology, Trieda A. Hlinku 2, 949 76 Nitra, Slovakia*
martin.sebesta@uniba.sk

ZnO nanoparticles can be easily released to the environment from many commercial products that contain them, e.g. sunscreens, zinc ointments. Through sewers, they often get to the waste water treatment plants where they bind into activated sludge, which, under right conditions, may be applied on the agricultural fields as a fertilizer. ZnO nanoparticles also have potential to be an effective source of zinc for zinc deficient soils. To compare distribution between ZnO nanoparticles, commercial ZnO powder and dissolved Zn between liquid and solid phase of Slovak soils a 24-hour batch experiment was conducted. Sequential centrifugation and ultrafiltration were applied to separate Zn in supernatant into four size-fractions. Flame atomic absorption spectrometry (F AAS) was used to measure Zn concentrations in the separated samples. A further experiment was conducted to see the difference these three forms of Zn have on the filamentous fungus *Aspergillus niger*, as well as on the formation of biogenic mineral phases induced by presence of fungal exometabolites. The biogenic mineral phases were studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

ZnO nanoparticles were the least bound to the solid phase and $ZnSO_4$ had the highest amount of Zn bound to the solid phase in the neutral soil. This trend turned and ZnO microparticles and nanoparticles were bound more to the acidic soils. All three forms of Zn showed different size distribution in the liquid phase of neutral soils. In acidic soils all three forms were mostly dissolved. The fungus responded differently to the free forms of Zn, which was more easily uptaken by fungus from ZnO nanoparticles compared to that of $ZnSO_4$. This highlights the influence of Zn speciation on its bioaccumulation by filamentous fungi and on the distribution of Zn in soils and soil solutions. These findings may help to evaluate the potential risk of intentional and unintentional release and ecotoxicity of ZnO nanoparticles to the environment.

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USING OF IMMERSION PROBE FOR KINETIC SPECTROPHOTOMETRIC DETERMINATION OF DISSOLVED CHROMIUM SPECIES IN WATER SAMPLES

Ján TÓTH, Yaroslav BAZEĽ

Department of Analytical Chemistry, Faculty of Science, Pavol Jozef Šafárik University in Košice, Moyzesova 11, 041 80 Košice, Slovak Republic
jantoth92@gmail.com

The aim of this work is the development, optimization and validation of new spectrophotometric kinetic method for determination of dissolved species of chromium in water samples using polymethine dye (2Z)-1,3,3-trimethyl-2-[(E)-3-(1,3,3-trimethylindol-1-ium-2-yl) prop-2-enylidene] indole chloride also known as Astraphloxine FF. The chemical reaction is research spectrophotometrically with immersion probe. The method is based on the impact of chromium (VI) concentration to the speed of decrease the Astraphloxine FF concentration. The experimental data were evaluated using four experimental data analysis methods specifically by the method of the average rate constant, by the method of the initial rate constant, by the method of constant time and by the method of change the volume of absorption peak in time. Two procedures were described during the development of the analytical method. The first procedure is for determination of chromium (VI) and under the optimal conditions the linear concentration range was 0.005 – 0.5 mg/L. The reaction mixture for first procedure contains sulphuric acid, chromium (VI) or sample and Astraphloxine FF in this order. The second procedure is for determination of total Cr(III) + Cr(VI) chromium and under the optimal conditions the linear concentration range was 0.005 – 0.1 mg/L. The reaction mixture for second procedure contains chromium (III) or sample, potassium periodate, sulphuric acid and Astraphloxine FF in this order. For both procedures were optimized the concentration of Astraphloxine FF, the kind of acid, the acid concentration, the effect of temperature, the effect of ionic strength, the order of reactant addition, the concentration of potassium periodate and the time required for the quantitative oxidation of Cr(III). For the procedure of Cr(VI) determination were study the effect of interferents with redox properties like $K_2S_2O_8$, $KClO_4$, $KClO_3$, KIO_4, KIO_3, KNO_3, KNO_2 and H_2O_2. The effect of Cr(III) ions were studied too. The most interfering ions were found nitrites and persulphates. The presented work was used for determination of chromium in model samples, tap water and also in CRM material with the method of calibration line and the method of standard additions. In the end of the work were calculated the limit of detections (LoD) for everyone method of evaluating the experimental data for both procedures. Under the optimal conditions by using the method of the average rate constant for evaluation of experimental data for the determination of Cr(VI) was found LoD = 1.87 ng/mL and for the determination of total Cr(III) + Cr(VI) chromium was found LoD = 1.90 ng/mL. It has been developed and validated new analytical method for determination of trace amounts of chromium in water samples.

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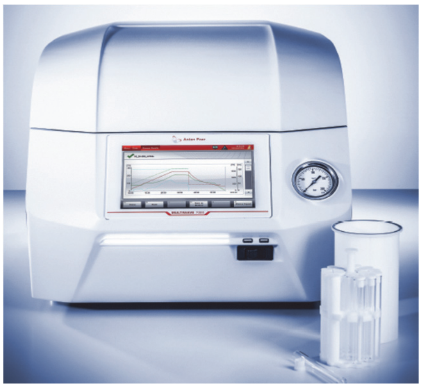
ANTON PAAR MULTIWAVE 7000 – MICROWAVE DIGESTION AT ITS BEST

Michal BÁRTÍK[1], Monika BABÍKOVÁ[2]

[1]Anton Paar Czech Republic s.r.o., Strakonická 3309/2e, 150 00 Praha 5, Czech Republic
[2]Anton Paar Slovakia s.r.o., Aupark Tower, Einsteinova 24, 851 01 Bratislava, Slovakia
michal.bartik@anton-paar.com, monika.babikova@anton-paar.com



Over 35 years ago, Anton Paar developed the first digestion system with a nitrogen pressurized digestion chamber and pressure-sealed vessels – HPA.

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Multiwave 7000 „stands for“ complete digestions of virtually any sample type, a streamlined workflow, lightweight accessories, budget-friendly, easy-to-handle consumables, and minimized cleaning time. There is no need for method development.

Multiwave 7000 provides digestion conditions up to 300°C and up to 199 bar. All kinds of samples such as food, environmental, polymer, cosmetic, pharmaceutical, geological, chemical and petrochemical samples with different reaction mixtures can be digested even in the same run using the same method.

Multiwave 7000 enables the use of different racks and vials according to the required sample amount, sample volume, sample throughput and reaction mixture.

SYNCHROTRON RADIATION ADIDED MÖSSBAUER SPECTROMETRY

Marcel B. MIGLIERINI[1,2]

[1]Slovak University of Technology in Bratislava, Faculty of Electrical Engineering and Information Technology, Institute of Nuclear and Physical Engineering, Ilkovičova 3,
812 19 Bratislava, Slovakia
[2]Slovak Spectroscopic Society, member of the Association of Slovak Scientific and Technological Societies, Ilkovičova 6, 842 15 Bratislava, Slovakia
marcel.miglierini@stuba.sk

Mössbauer spectrometry can be effectively used for investigation of a broad range of materials on an atomic level. Due to its unique properties, it can probe the nearest arrangement of the resonant atoms both from structural as well as magnetic point of view. Nevertheless, even it features superior energetic resolution (most probably the best among all spectroscopic methods) the time needed for acquisition of sufficiently good experimental data often extends over several hours. Thus, the use of Mössbauer spectrometry in the study of dynamical rapid processes is strictly limited.

This disadvantage is overcome by synchrotron radiation which is characterized by extremely high brilliance. With the onset of a new generation of synchrotrons and sufficiently sharp monochromatization techniques synchrotron radiation become suitable for excitation of transitions among nuclear levels. Because of high number of photons, the time needed for acquisition of relevant data is short enough to inspect for example structural transformations in real time during *in situ* experiments. Moreover, some of the techniques that are based on the Mössbauer effect are performed in a time domain which opens brand new perspectives.

In this presentation, basic principles of both types of methods, viz. Mössbauer spectrometry and nuclear resonances with synchrotron radiation, will be briefly introduced. This will form a background for introduction of synchrotron-radiation-based techniques including nuclear forward scattering (NFS), nuclear inelastic scattering (NIS), and synchrotron Mössbauer Spectrometry (SMS). Their application potential will be documented by some representative examples.

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PROPERTIES OF NANOCRYSTALLINE ALLOYS AFTER IRRADIATION OF AMORPHOUS PRECURSORS

J.SITEK, D.HOLKOVÁ, J.DEKAN, P.NOVÁK

Institute of Nuclear and Physical Engineering, Slovak University of Technology, Ilkovicova 3, Bratislava, Slovakia

Amorphous precursors of $(Fe_{64}Co_{21}B_{15})_{95}P_4Cu_1$ and $(Fe_{64}Co_{21}B_{15})_{96}P_4$ alloys were irradiated using different types of radiation then by heat treatment nanocrystalline structure was created. Sample were studied by Mössbauer spectroscopy and XRD. Electron-beam was used for irradiation and Cu ions were implanted into the structure of amorphous precursor. All irradiated samples were compared with non-irradiated one. Both types of external factors had an influence on the volumetric fraction of the constituent phases and on their magnetic microstructure. Changes in microstructure were not observed under the doses of 4 MGy. Over this value crystalline phase created in amorphous structure up to approximately 5% After the heat treatment nanocrystalline sample prepared from irradiated precursor contained twice crystalline phase than non-irradiated. Cu ions were implanted into the amorphous $(Fe_{64}Co_{21}B_{15})_{96}P_4$. According to simulated program we estimated that Cu ions created surface area with a thickness of a few micrometers. After heat treatment the implanted sample was nearly identical with the nanocrystalline sample of $(Fe_{64}Co_{21}B_{15})_{95}P_4Cu_1$. Both this two technology of prepare of nanocrystalline alloys indicate that irradiation of amorphous precursor has an influence on the final structure and properties of nanocrystalline alloy.

Keywords: nanocrystalline alloys, radiation damage, Mössbauer spectroscopy

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IRON IN BIOLOGICAL TISSUES

Ivana BONKOVÁ[1,5], Marcel Miglierini[2,5], Tomáš KMJEČ[3], Martin KOPÁNI[4], Marek BUJDOŠ[1,5]

[1]Institute of Laboratory Research on Geomaterials, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 842 15 Bratislava, Slovakia
[2]Institute of Nuclear and Physical Engineering, Faculty of Electrical and Information Technology, Slovak University of Technology in Bratislava, Ilkovičova 3, 812 19 Bratislava, Slovakia
[3]Department of Low Temperature Physics, Faculty of Mathematics and Physics, Charles University in Prague, V Holešovičkách 2, 180 00 Prague, Czech Republic
[4]Department of Medical Physics, Biophysics, Informatics and Telemedicine, Faculty of Medicine, Comenius University in Bratislava, Sasinkova 4, 811 08 Bratislava, Slovakia
[5]Slovak Spectroscopic Society, member of the Association of Slovak Scientific and Technological Societies, Mlynská dolina, 842 15 Bratislava, Slovakia
ivana.bonkova@gmail.com

Iron is essential element for fundamental cell functions and catalyst for chemical reactions. It is also important for processes of synthesis such as DNA synthesis, heme and iron-sulfur cluster synthesis and in electron transfer reactions. On the other hand, iron, in its free form, is a potential cytotoxic metal especially because of its property to form insoluble salts at physiologic pH and to catalyze formation of free radicals. Since the iron can exist in organism mainly in two oxidation states (Fe^{II} and Fe^{III}), it is important to identify these oxidation states.

In the current work, we focus on characterization of iron in biological tissues. We have studied different types of tissues which were obtained from spleen of human, bullock, and horse origin. In addition, samples of human brain were also investigated. Mössbauer spectrometry measurements were performed at room (~300 K) and liquid helium (4.2 K) temperature. A conventional constant acceleration spectrometer with ^{57}Co source in a rhodium matrix was used. The ferritin nanoparticles exhibit superparamagnetic behaviour due to their small dimensions at room temperature. The corresponding Mössbauer spectra show doublet-like patterns. Magnetic features of the investigated samples start to manifest themselves notably at low temperatures. Here, presence of magnetically split components was unveiled. The spectral parameters of individual components confirm the presence of various iron oxides.

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INFLUENCE OF EXTERNAL TREATMENT ON MICROSTRUCTURE OF SELECTED STEELS

Lukáš PAŠTEKA[a,d], Marcel MIGLIERINI[b,d], Tomáš KMJEČ[c], Marek BUJDOŠ[a,d]

[a]Institute of Laboratory Research on Geomaterials, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, 842 15 Bratislava, Slovakia
[b]Institute of Nuclear and Physical Engineering, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology in Bratislava, Ilkovičova 3, 812 19 Bratislava, Slovakia
[c]Department of Low-Temperature Physics, Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, 180 00 Prague, Czech Republic
[d]Slovak Spectroscopic Society, member of the Association of Slovak Scientific and Technological Societies, Mlynská dolina, 842 15 Bratislava, Slovakia
pashty89@gmail.com

Mössbauer spectrometry (MS) is particularly suited technique for characterization of steel materials and for determination of microstructure in these materials. MS can determine arrangement of iron lattice (fcc – face-centered cubic, bcc – body-centered cubic,) as well as iron oxidation state.

In this work, we focus on characterization of corrosion resistant steel materials suited for nuclear industry. Samples was measured by back-scattering Mössbauer spectrometry and Conversion electron Mössbauer spectrometry (CEMS). We investigated the effect of thermal treatments (non-hardened, hardened, hardened with rapid quenching), mechanical (polishing and grinding) and chemical (etching) treatment. Mössbauer spectra showed different microstructures after these treatments.

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LIPID DRIVEN NANODOMAINS ARE FLUID

R. ŠACHL, M. AMARO, A. KOUKALOVÁ, L.VEĽAS and M. HOF

J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 18223 Prague 8, Czech Republic

It is a fundamental question whether sphingomyelin (SM)- and cholesterol (Chol)- driven nanodomains exist in cells and in model membranes. Studies on model membranes revealed SM and Chol driven micrometer-sized liquid-ordered domains. Although the existence of such microdomains has not been proven for the plasma membrane, such lipid mixtures have been used as a model system for 'rafts'. On the other hand, super resolution results indicate that the plasma membrane might organize into nanocompartments. However, due to the limited resolution of those techniques their unambiguous characterization is still missing. In this lecture, a combination of Förster resonance energy transfer and Monte Carlo simulations (MC-FRET) [1] identifies directly 10 nm large nanodomains in liquid-disordered model membranes composed of lipid mixtures containing SM and Chol [2]. Our MC-FRET approach can determine the sizes and concentrations of nanodomains down to 2 nm and enables studying the nanodomain inter-leaflet coupling. Combining MC-FRET with solid-state wide-line and high resolution magic angle spinning NMR as well as with fluorescence correlation spectroscopy [3] we demonstrate that these nanodomains containing hundreds of lipid molecules are fluid [2]. Addition of GM1 ganglioside, a molecule which forms already fluid 6 nm sized clusters in fluid phosphatidylcholine bilayers [4,5], leads to growth of those nanodomains while preserving the fluidity [5].

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DETERMINATION OF ABSOLUTE EMISSION EFFICIENCY OF UP- AND DOWN-CONVERTED LUMINESCENCE AND SOME OTHER ADVANCED OPTICAL CHARACTERIZATION OF FLUORIDES DOPED WITH VARIOUS LANTHANIDE IONS

Jan VALENTA and Michael GREBEN

Department of Chemical Physics & Optics, Faculty of Mathematics & Physics, Charles University, Prague
jan.valenta@mff.cuni.cz

Microcrystals of hexagonal $NaYF_4$, $NaLuF_4$ and $NaGdF_4$ co-doped by Yb^{3+} and $Er^{3+}/Tm^{3+}/Ho^{3+}$ were prepared by the hydrothermal method and the optimum composition was determined to be $NaLuF_4$: Yb^{3+} 15 %, Er^{3+} 1.5 %. The best samples were studied in detail using several advanced methods of luminescence spectroscopy [1]. Namely, absolute power efficiency of both up- and down-converted luminescence (over an extremely broad range 360-1650 nm) under different excitation power using an integrating sphere [2] and a special spectroscopic apparatus with two detection branches [3]. The integrated up-converted signal reaches about 17 % in the excitation power range of 70-100 W/cm^2, while the down-converted emission power efficiency is about 20 % (for excitation by a laser at 975 nm). An important fraction of absorbed power is (re)emitted by Yb^{3+} ions within a band close to the excitation wavelength. In order to prove this loss channel we exploited the time-resolved luminescence kinetics under excitation with modulated laser beam (using TeO_2 acousto-optical crystal) [4]. Detailed characterization of both rise and decay of luminescence at different emission bands enabled us to get insight into the excited state formation and relaxation and determine the value of absorption cross section [5]. Moreover, we have developed the micro-spectroscopy method to study up- and down-conversion emission on the scale of micrometers. The best investigated materials are perfectly suitable for light-conversion applications.

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TIME-RESOLVED LUMINESCENCE SPECTROSCOPY AS A TOOL FOR STUDY OF CHEMICAL REACTIONS OF EU(III) COMPLEXES

Přemysl LUBAL[1,2], Filip SMRČKA[1]

[1]Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
[2]Central European Institute of Technology, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic
lubal@chemi.muni.cz

Lanthanide(III) complexes of macrocyclic ligands are utilized in many areas of medicinal chemistry (*e.g.* ^{153}Sm, ^{166}Ho, ^{177}Lu radioisotopes in nuclear medicine, Gd(III) as contrast agents in MRI or Eu(III)/Tb(III) as luminescence probes). An important factor for MRI and luminescence probes is determination of number of the water molecules coordinated to Ln(III) central ion as well as thermodynamic stability and kinetic inertness of the complexes [1]. Time-resolved luminescence spectroscopy of Eu(III) ion and its complexes with macrocyclic DOTA-like ligands (as a model Ln(III) complexes for measurement of luminescence decay) is used for determination of the number of water molecules in the first coordination sphere [1-5]. This measurement can be employed for estimation of stability constants [5] as well as for postulation of reaction mechanism of Eu(III) complexation by ligands [2-5] or Eu(III) complex dissociation [2-5]. Some advantages and limitations of this new experimental method will be discussed [5]. The results can be utilized for optimization of ligand structure to design the better chelators for Ln(III) endowed with a fast complexation and a slow decomplexation.

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NMR SPECTROSCOPY METHODS FOR STUDIES OF BIOMOLECULAR STRUCTURE AND DYNAMICS

Radovan FIALA

Central European Institute of Technology, Masaryk University, Kamenice 5, 625 00 Brno,
Czech Republic
radovan.fiala@ceitec.muni.cz

NMR spectroscopy has been an indispensable tool in chemical laboratories for decades. The gradual progress in the technology of magnets, electronics and computational tools together with methodological advances allowed expanding NMR to many disciplines ranging from material science to biology and medicine. In structural biology, NMR spectroscopy ranks together with the leading X-ray crystallography and quickly expanding cryo-electron microscopy among the 'Big Three' methods for determining structures of the molecules essential for living organisms such as proteins and nucleic acids. NMR has an advantage in its ability to study the compounds in their natural environment, namely in water solution, and at temperatures at which they perform their biological roles. Attempts are being made to study the structures of proteins and nucleic acids inside the living cells. NMR is also suitable for studies of complexes and can provide information about intramolecular dynamics.

The molecules of proteins and nucleic acids consist of many repetitions of identical building units, namely amino acids and nucleotides, respectively. This quickly leads to severe overlaps of the signals in the spectra. Resolution, as well as sensitivity, increases with increasing magnetic field. High-field spectrometers with proton resonance frequencies from 600 MHz to 1,000 MHz are typically used for biomolecular studies. A new generation of 1.2 GHz spectrometers is under development. Further increase in sensitivity is brought by cryogenic probes in which the thermal noise is minimized by keeping the coils and preamplifiers at a low temperature (16 to 20 K).

However, the high magnetic field alone is not sufficient to solve the signal overlap problem. A more efficient way to increasing the resolution is multidimensional NMR spectroscopy. Two- and three-dimensional NMR spectra are used routinely to study proteins and nucleic acids. Large numbers of NMR techniques relying on specific networks of coupled spins in proteins and nucleic acids have been developed [1]. Their application usually requires samples enriched with ^{13}C and ^{15}N to a high degree.

There are two principle limits to increasing the number of measured dimensions – relaxation and experimental time. For flexible, slowly relaxing molecules such as inherently disordered proteins (IDPs) spectra with up to five dimensions can be obtained. To overcome the problem of time-consuming acquisition of large numbers of experimental points necessary for extra dimensions, non-uniform sampling (NUS) techniques are being employed.

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DISENTANGLING PUZZLES – ATOMIC RESOLUTION STUDIES OF PROTEIN DISORDER

Vladimír SKLENÁŘ

Central European Institute of Technology, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic
vladimir.sklenar@ceitec.muni.cz

As the classical paradigm of structural biology states "one protein - one structure - one function", it is generally believed that the protein structure and its function are directly interrelated. Although it is commonly true for a large number of proteins, many of them are biologically active without having a unique and stable 3D structure. Those proteins, which in their native conditions sample a multitude of diverse conformational states characterized by high spatiotemporal heterogeneity, are most often termed as intrinsically disordered proteins (IDPs) or natively unfolded (UF) proteins. With the growing evidence of their important roles in fundamental cellular processes, there is an urgent need to characterize the conformational behavior of IDPs at the highest possible level. Among of all available techniques of modern structural biology NMR spectroscopy represents the ultimate tool for studies of unstructured or partially disordered proteins at atomic resolution.

The lecture will review recent methodology developed in our lab, which significantly shortens time needed for thorough description of unstructured or partially disordered proteins. To facilitate the atomic resolution studies, we have designed a suite of high-dimensional (4D-5D) NMR experiments, which combines 13C-direct detection, non-uniform sampling, and non-standard data processing procedures to substantially enhance the attainable resolution. The power of the developed methodology is documented on studies and disorder characterization of 20 kDa delta subunit of RNA polymerase unique for gram-positive bacteria and 49.2 kDa microtubule-associated protein 2c.

LOCAL STRUCTURE OF GARNETS STUDIED BY NMR

Helena ŠTĚPÁNKOVÁ[1], Vojtěch CHLAN[1], Yuriy ZAGORODNIY[2], Valentin LAGUTA[2],
Yevhen FOMICHOV[1], Jiří ENGLICH[1], Jaroslav KOHOUT[1], Pavel NOVÁK[3]

[1]Charles University, Faculty of Mathematics and Physics,
V Holešovičkách 2, 180 00 Prague Czech Republic
[2]Institute for Problems of Materials Science NAS Ukraine,
Krjijanovsky 3, 03142 Kyiv, Ukraine
[3]Institute of Physics of ASCR, Cukrovarnická 10, 162 53 Prague 6, Czech Republic
stepanko@nbox.troja.mff.cuni.cz

Nuclear magnetic resonance (NMR) spectroscopy has become a unique tool in organic chemistry, biochemistry and biology, but it has been also successfully applied to inorganic solid state and materials research. Its benefit lies in the fact that the local magnetic and electric fields present at atomic nuclei and monitored by NMR are able to provide information on both the static properties and the dynamics of the studied materials on the atomic scale, including detection of defects or impurities. These findings can then be very useful for the understanding of the macroscopic properties and help to control the preparation processes or/and subsequent treatment.

Results of NMR spectroscopy in investigation of garnet structures of various physical properties will be presented including non-magnetic aluminum/gallium garnets and magnetic iron garnets. We will show different NMR approaches to their study and illustrate possibilities of determining the type and concentration of cationic defects and preferences in occupying of non-equivalent crystallographic positions by impurities or cation substitutions.

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CLINICAL RAMAN SPECTROSCOPY - DIAGNOSIS BEFORE THERAPY

Juergen POPP[1,2]

[1]*Leibniz Institute of Photonic Technology, Jena, Germany*
[2]*Institute of Physical Chemistry & Abbe-Center of Photonics, Friedrich-Schiller University Jena, Germany*
Juergen.popp@leibniz-ipht.de

During the last years Raman spectroscopic approaches (e.g. Raman microspectroscopy, surface enhanced Raman spectroscopy (SERS), coherent Raman imaging i.e. coherent ant-Stokes Raman scattering (CARS) and stimulated Raman scattering (SRS) etc.) have shown their potential to provide a clinician with clinically relevant information to meet current diagnostic challenges in various fields of medical need. Within this contribution, we will highlight our efforts in utilizing a broad variety of Raman spectroscopic approaches for an early diagnosis and targeted therapy of infectious diseases and cancer.

Infectious diseases are one of the major reasons of deaths worldwide. Successful treatment of infection relies on timely identification of the pathogen and its antibiotic resistance pattern in order to select the appropriate antibiotic treatment as early as possible. Classical microbiological analysis methods rely on time-consuming overnight cultures. Fast culture-independent analysis methods could thus lead to huge improvements and help save lives. It will be shown that Raman spectroscopy in combination with chemometric strategies and chip-based sampling show great promise for a fast and targeted identification of pathogens together with their antibiotics resistance pattern and plays a key role in turning this vision into reality.

In addition, we will highlight our efforts on the combination of Raman approaches with other spectroscopic technologies to solve challenges clinical pathology are currently facing like e.g. determination of the tumor type and grade and intraoperative delineation of tumor margins. We will amongst other introduce a compact multimodal nonlinear CARS/SHG(second harmonic generation)/TPEF(two-photon excited autofluorescence) microscope in combination with novel fiber lasers for use in clinics. The system offers great potential to complement established clinical pathological diagnostic tools and to augment standard intraoperative clinical assessment with multimodal images to highlight tumor boundaries. Furthermore, efforts towards Raman endospectroscopy, i.e. coupling spectroscopic systems via optical fibers to the point of measurements for in-vivo tissue screening to reliably diagnose and screen cancer will be introduced.

Overall the coverage of topics extends from: (I) fundamental research (e.g. innovative plasmonic nanostructures for Raman signal enhancement) to (II) specific technological developments (e.g. Raman / SERS lab-on-a-chip devices, high-content Raman cell analysis platform, etc.), while also (III) including the latest applications or clinical trials / case reports

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TIP-ENHANCED RAMAN SPECTROSCOPY - PRINCIPLES AND APPLICATIONS

Renato ZENOBI

Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zürich, Switzerland
zenobi@org.chem.ethz.ch

Tip-enhanced Raman Spectroscopy (TERS) is a nanoscale chemical analysis and imaging method with a spatial resolution on the order of 10 nm. TERS relies on enhancement of the local electromagnetic field in the vicinity of a plasmonic nanostructure that is scanned over a sample by means of a scanning probe microscope, using either AFM or STM feedback. Analogous to SERS, the local enhancement of Raman scattered light is many orders of magnitude in TERS, large enough to render monomolecular films spectroscopically visible that would otherwise be optically too thin to be analyzed with conventional vibrational spectroscopy.

The working principle and experimental realization of TERS will be presented [1]. An important advance concerns the production long-lived silver TERS tips. Thanks to the presence of a chemical protection layer, these live for many weeks as opposed to the typical lifetime of ≈1 day for bare Ag tips [2], and can be operated in liquids. The focus of this presentation will be on applications of TERS to the spatially resolved chemical analysis of molecular and biological nanostructures, including self-assembled monolayers, a novel class of materials, 2D polymers [3], membranes, and biological nano-structures such as amyloid forming proteins [4]. The Figure (right hand side) shows a high-resolution TERS map of Amyloid-β fibrils.

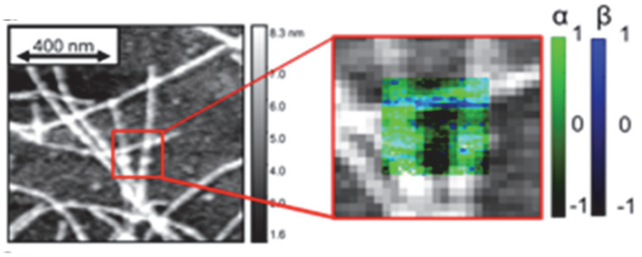

Figure. Distribution of α□helices and β□sheets in $A\beta_{1-42}$ fibrils: typical spectra of α□helices (green) and β□sheets (blue). AFM image (left) with a TERS map (7.5 nm x 7.5 nm pixel size) overlayd (right).

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NICOLET CZ - THE MOLECULAR SPECTROSCOPY COMPANY

Ján PÁSZTOR[1]

[1]Nicolet CZ s.r.o., Klapálkova 2242/9, 149 00 Praha 4, Czech Republic
pasztor@nicoletcz.cz

Nicolet CZ company profile. Brief history and recent instrumentation in molecular spectroscopy:

1. IR-SNOM
2. Raman
3. FT-IR

Dedicated to the memory of Assoc. Prof. RNDr. Bohuslav Strauch, CSc., our proud teacher, supervisor and friend.

3D CHEMICAL IMAGING THROUGH A COMBINATION OF LASER-INDUCED BREAKDOWN SPECTROSCOPY AND COMPUTED TOMOGRAPHY

Jozef KAISER[1,2], Pavel PORIZKA[1,2], Tomas ZIKMUND[1], Jakub KLUS[1,2], David PROCHAZKA[1,2], Marketa TESAROVA[1], Jakub SALPLACHTA[1], and Adam BRINEK[1]

[1]Central European Institute of Technology, Brno University of Technology, Purkynova 123, 61200 Brno, Czech Republic
[2]AtomTrace a.s., Kolejní 9, 61200 Brno, Czech Republic

In this project, we propose a new paradigm shifting the conventional imaging analysis from 2D to 3D. The novelty of the project is in the synergy of X-Ray Computed Tomography (CT) and Laser-Induced Breakdown Spectroscopy (LIBS) techniques. We aim to develop a platform, including optimized measurement methodology and data processing, providing 3D chemical imaging of a sample.

Throughout the project, optimized protocols for i) sample preparation, ii) CT and consecutive LIBS analysis, and iii) data processing will be delivered. On top of the analytical part, mathematical algorithms (multivariate data analysis algorithms; MVDAA) will be implemented to combine the structural and chemical information. This data processing step will enhance the information obtained from the CT and LIBS analyses themselves. Moreover, the utilization of MVDA will potentially lead to the easier segmentation of CT data and even to the automatized creation of 3D elemental images.

We set to demonstrate this novel idea on the specially designed sample. The key part of the project is the implementation of MVDA algorithms, random forest method in this case. Combination of CT and LIBS data is discussed in detail and future obstacles and prospects are critically evaluated.

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DIMENSIONALITY REDUCTION OF MULTI-VARIATE LASER SPECTROSCOPY DATA

Pavel POŘÍZKA[1,2], Jakub KLUS[1,2], Frédéric PELASCHINI[3], Cécile FABRE[4], David PROCHAZKA[1,2], Vincent MOTTO-ROS[5,6], Jozef KAISER[1,2]

[1]Central European Institute of Technology, Brno University of Technology, CZ-61200 Brno, Czech Republic
[2]AtomTrace a.s., CZ-61200 Brno, Czech Republic
[3]GeoRessources, UMR CNRS, Université de Lorraine, F-54500 Vandoeuvre-les-Nancy, France
[4]CRITT Matériaux Alsace, F-67305 Schiltigheim, France
[5]Institute Lumière Matière, Claude Bernard University Lyon, F-69100 Villeurbanne, France
[6]Ablatom SAS, F-69622 Villeurbanne Cedex, France

State-of-the-art Laser-Induced Breakdown Spectroscopy (LIBS) instruments enable high repetition rate analysis. With this experimental settings, the mapping of sample surfaces provides large data sets. The richness of information is in spectra (objects) as well as wavelengths (variables). Processing such multivariate data is, thus, a challenging task demanding more sophisticated approaches. Utilization of advanced statistical algorithms, referred to as multivariate data analysis algorithms or chemometrics, are of great interest in contemporary data processing [1-3]. Moreover, elemental composition (relation of individual elements) and structural complexity (relation of individual matrices) provides additional valuable information in understanding of the heterogeneity of, *e.g.*, biological and geological samples. In our work, we bring an introduction to the utilization of Principal Component Analysis to processing of LIBS data. Our efforts tackled mainly the dimensionality reduction in both, objects and variables. Such algorithm leads to an increase in the turn-around time of the multivariate data processing and to a reduction of demands on the computing power. We demonstrated our endeavors on the processing of multi-elemental maps of a geological sample. The original size of the map was 2000x1190 pixels and the spectra contained 2048 variables, resulting in a matrix of 2 380 000x2048 data points. We achieved a conversion to 1 % on the side of objects and 0.44 % on the side of variables of the original data matrix. The data processing brought the same results based on original data matrix as well as on data obtained through such significant information conversion.

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METHOD DEVELOPMENT FOR METAL DETECTION AT CELLULAR LEVELS

Norbert JAKUBOWSKI[1]

[1]Bundesanstalt für Materialforschung und -prüfung (BAM), Richard-Willstaetter
-Str. 11, 12489 Berlin, Germany
Norbert.jakubowski@bam.de

An overview about different analytical approaches will be presented of how to detect metals in individual biological cells by use of ICP-MS. For this purpose, we are using different sample introduction systems and ICP-MS for detection, imaging and quantification of metals at cellular levels.

By use of laser ablation, we have studied the up-take by and distribution of nanoparticles in single cells. Recently we have developed staining techniques to measure the protein and DNA content of cells indirectly and identifying the cell status by immunoassays using metal-tagging of antibodies. New research based on cell arrays will be shortly discussed.

Using pneumatic nebulization and microdroplet generation, we have also studied the up-take of nanoparticles and toxic metals as well as essential elements in single cells using different ICP-MS mass spectrometric concepts (sector field instrument, triple-quad instrument, time of flight (CyTOF) instrument).

The different ICP-MS based methods will be compared concerning their analytical figures of merit and their strengths and weaknesses will be discussed.

SIMULTANEOUS IMAGING OF PROTEINS AND ELEMENTS IN TISSUES BY LA-ICP-MS

Michaela TVRDOŇOVÁ[1,2], Lena ASCHER[3], Norbert JAKUBOWSKI[3], Marketa VACULOVIČOVÁ[4,5], Marcela VLČNOVSKÁ[5], Viktor KANICKÝ[1] and Tomas VACULOVIČ[1,2]

[1]Department of Chemistry, Faculty of Science, Masaryk University in Brno, Kotlarska 2, 611 37 Brno,
[2]CEITEC Masaryk University in Brno Kamenice 5, 625 00 Brno,
[3]BAM Federal Institut for Materials Research and Testing, Richard-Willstätter-Straße 11, 12489 Berlin
[4]Brno Univ Technol, Cent European Inst Technol, Purkynova 123, CZ-61200 Brno, Czech Republic,
[5]Mendel Univ Brno, Dept Chem & Biochem, Zemedelska 1, CZ-61300 Brno, Czech Republic
358018@mail.muni.cz

Laser ablation with inductively coupled plasma is still more used in life science as biology and biomedicine and the utilization of metals and proteins determination simultaneously is also growing up. [1,2] We have developed a new strategy of antibody labeling (it can specific binds to proteins) by nanoparticles which is composed of thousands of atoms and thus increases the sensitivity enormously and of course decreases the limit of detection, compare to lanthanoids labeling. The ability of successfully tagged antibodies bounds to antigen (protein) was proved by dot blot on membrane imaged by LA-ICP-MS. It should be universal method to image simultaneously distribution of elements and proteins as well. One of the many possible applications is binding of labelled antibodies to the tumour tissues containing metallothionein (known as a transporter of Cu, Zn and heavy metals) and image their distribution in different tumour stage.

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LASER ABLATION-BASED METHODS IN THE ANALYSIS OF CLAY GROUND LAYERS IN PAINTINGS

Eva POSPÍŠILOVÁ[1,2], Karel NOVOTNÝ[1,3], Markéta HOLÁ[1,3], Janka HRADILOVÁ[2], David HRADIL[2,4], Jozef KAISER[5], Viktor KANICKÝ[1,3]

[1]Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, Brno, 61137, Czech Republic
[2]Academy of Fine Arts in Prague, ALMA laboratory, U Akademie 4, Prague 7, CZ-17022, Czech Republic
[3]Central European Institute of Technology, Masaryk University, Kamenice 753/5, Brno, 62500, Czech Republic
[4]Institute of Inorganic Chemistry of the AS CR, v.v.i., ALMA laboratory, Husinec-Řež, CZ-25068 Czech Republic
[5]Central European Institute of Technology, Brno University of Technology (CEITEC BUT), Purkyňova 123, Brno, CZ-61200, Czech Republic
379264@mail.muni.cz

Application of scientific methods in the analysis of is an essential tool in revelation of the material composition, painting technique, answering the question of their origin and age. Use of non-destructive or micro-destructive techniques is always favoured. Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) and laser-induced breakdown spectroscopy (LIBS) enable direct analysis of solid samples without the need of previous sample preparation. Examination of trace element fingerprints of individual pigments helps to determine provenance of the materials used which can help in authentication of the works of art.

The aim of this study is to optimize the process to identify and link groups of pigments to the same region of origin based on their composition and trace element fingerprint using LA-ICP-MS. Abilities of qualitative and quantitative analysis of particular elements by means of LIBS, chosen based on the LA-ICP-MS results, are examined. Possible classification of pigments containing clay minerals from European region and their assignment to the same geographic source is investigated.

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MULTIVARIATE STATISTICAL ANALYSIS OF ARCHAEOLOGICAL SAMPLES AND THEIR VISUALISATION

Veronika DILLINGEROVÁ[1,2], Tomáš VACULOVIČ[1,2], Kateřina TOMKOVÁ[3], Viktor KANICKÝ[1,2]

[1]Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
[2]Central European Institute of Technology, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic
[3]Institute of Archaeology of the CAS, Prague, V. V. I.
veronika@dilli.sk

Historical contact between Bavaria and Bohemia was shown in different fields. Archaeology was also influenced by that, so when it comes to findings from these two areas, it is important to investigate their connection. This work aims to find differences or similarities between glass beads found in Bavaria and Bohemia.

Elemental composition of glass beads was measured by LA-ICP-MS. From an archaeological point of view, it is usually important to compare main oxides, such as K_2O and MgO to differentiate soda-lime natron glass from plant ash glass. However, this study focusses on the use of machine learning algorithms to find patterns in trace elements of the glass beads. With a low number of observations - glass beads (only 51) it is important to find the most suitable algorithm. Therefore, we decided to compare multiple machine learning algorithms for this data set. Its main purpose is to show the possibilities of complex algorithms, such as k-nearest neighbours (KNN), decision trees, e.g. random forest (RF) or linear discriminant analysis (LDA). First of all, an exploratory analysis was performed to determine variables - elements with high distinguishing power. Programming language python with sci-kit learn library and software SAS Enterprise guide was used.

This study compared multiple machine learning algorithms for finding differences and similarities of the set of glass beads from Bohemia and Bavaria. These algorithms work on different principles, so in some cases it can be beneficial to use more than just a one. Especially in this one, when each one of them can discover various interesting facts about the observed dataset.

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ICP-MS SYSTÉMY AGILENT TECHNOLOGIES V ČR A JEJICH MOŽNOSTI

Ivo NOVOTNÝ[1], Martin JUŘÍČEK[1]

[1]HPST, s.r.o., Na Jetelce 69/2, 190 00 Praha 9, Czech Republic
ivo.novotny@hpst.cz, martin.juricek@hpst.cz

Počet ICP-MS systému instalovaných v České republice v posledních letech narůstá a tento trend se zdá být aktuální i pro nejbližší roky. Důvodů je mnoho, ale jedním z těch nejvýznamnějších je postupné nahrazování klasických technik AAS nebo ICP-OES právě technickou ICP-MS, která díky vývoji technologií překonává své historické limitace a dnes je robustní technikou zvládající široké spektrum matric. Jak různorodé může být aplikační použití dnešních moderních ICP-MS spektrometrů, bylo patrné na loňském setkání českých uživatelů ICP-MS systému, kde se slovo čistá nebo jednoduchá matrice téměř neobjevilo. Až tímto průřezem reálných aplikací od těch různorodých výzkumně-vědeckých, přes rutinní kontrolní až po náročné průmyslové častokrát pochopíme skutečnou sílu a reálné možnosti nejmodernějších technologií, dnes rutinně používaných v oblasti ICP-MS analýz.

S posouváním požadavků na robustnost ICP-MS systémů jde ruku v ruce také nutnost vypořádat se s přítomností interferentů pocházejících z matrice vzorku. Díky unikátní technologii kolizně reakční cely jsou ICP-MS systémy Agilent Technologies schopné velmi efektivně odstranit nežádoucí víceatomové interferenty. Kritickým ukazatelem robustnosti systému je však důsledné odstranění dvojnásobně nabitých iontů, jejichž signál interferuje na analytech o poloviční hmotnosti. Vznik tohoto typu interferujících iontů může být do jisté míry potlačen precizní regulací výkonu plazmatu. Běžně používané korekční rovnice vyžadují přesnou znalost izotopického složení vzorků a chemizmy a jejich chování v plazmatu, tudíž tento způsob eliminace není vhodný pro praktické využití na alespoň trochu rutinnějších pracovištích. Úplná eliminace signálu dvojnásobně nabitých iontů byla donedávna možná jen na ICP systémech s vysokým rozlišením. Jednoduché a velmi účinné řešení přinesl až ICP/MS/MS Agilent Technologies, který díky vřazené reakční cele mezi dva plnohodnotné kvadrupóly s jednotkovým rozlišením umožňuje efektivně a beze zbytku odstranit dvojnásobně nabité interferující ionty přesně kontrolovaným reakčním mechanizmem. Názornou ukázkou funkčnosti tohoto uspořádání může být například stanovení nízké koncentrace arsenu v geologické matrici obsahující prvky vzácných zemin samarium a neodym. Jejich dvojnásobně nabité ionty interferují na monoizotopickém iontu arsenu a na ICP-MS/MS jsou účinně odstraněné řízenou reakcí s kyslíkem.

FROM NANOPARTICLE SEPRATION/DETECTION BY DIFFERENTIAL MOBILITY ANALYSIS TO HIGH ENERGY COLLISION INDUCED DISSOCIATION MASS SPECTROMETRY

Victor WEISS[1], Ernst PITTENAUER[1], Günter ALLMAIER[1]

[1]*Institute of Chemical Technologies and Analytics, Vienna University of Technology (TU Wien), Getreidemarkt 9, A-1060 Vienna, Austria*
Guenter.allmaier@tuwien.ac.at

The characterization of different kinds of liposome, virus-like particles (VLP) and exosome preparations plays a growing role due to the fact of the increasing use and development drug delivery systems as well as biological relevance of extracellular vesicles (EVs) also termed exosomes. The physico-chemical characterization (size and molecular mass) by means of nano electrospray (charge reduction by Po-210 or soft X-ray radiation) in combination with differential mobility analysis (nanoES-DMA, aka GEMMA, gas-phase electrophoretic mobility molecular analysis or macroIMS) with subsequent size-fractionation and MALDI mass spectrometry is gaining growing interest. The focus is on size-dependent lipid and protein compositions and drug loads in case of liposomes or VLPs. In case of liposomes, VLPs and especially of EVs the present lipidome and the detected proteins are of extraordinary interest due the variation of composition due to wide range of sizes. The size covers single-digit nanometers up to a couple of hundreds nanometers. Nano ES-DMA will allow the determination of the dry diameter of such nanoparticles and their size distributions [1, 2]. Afterwards nES-DMA size-separated liposomes, VLPs and EVs were collected by means of an electrostatic nanoparticle collector at atmospheric pressure on high quality MALDI MS targets or other suitable surfaces (e.g. mica surface for atomic force microscopy) and subsequently analyzed by matrix-assisted laser desorption ionization (MALDI) to determine the molecular mass of lipid species, the encapsulated drug molecules as well as proteins in case of EVs. This will be the first step in the structural characterization of such complex mixtures. It will be followed in case of the different detected lipid classes as well as drug compound(s) by tandem MS. Particular MALDI TOF (time-of-flight)/RTOF (reflectron) mass spectrometers with true high energy (20 eV) CID (collision induced dissociation) will be applied to obtain detailed structural information of the individual lipids and drugs as well as potential degradation products. Such size-correlated data might open up new ideas of optimization of liposome and VLP preparations as well as EVs functional grouping.

NEW APPROACH TO MATRIX MODIFICATION IN ETV ICP-MS

Tomáš ČERNOHORSKÝ[1], Jan PATOČKA[1], Anna KREJČOVÁ[1], Lenka BENDAKOVSKÁ[1]

[1]*Department of Environmental and Chemical Engineering, University of Pardubice,*
CZ-532 10 Pardubice, Czech Republic.
tomas.cernohorsky@upce.cz

This lecture will explain the differences between principles of the matrix modification (MM) in ETA AAS and ETV ICP-MS with the subsequent demonstration of a new approach to MM in ETV ICP-MS based on the use of carbon nanoparticles as a new matrix modifier.

ETV ICP-MS is not frequently used technique, mainly due to persistent problems with commercially available systems and also due to methodical problems. The most frequent methodology error is the use of an inappropriate matrix modifier, which was selected with the use of experiences from ETA AAS.

It should be noted that MM has a fundamentally different target in ETA AAS and ETV ICP-MS. The main goal in the case of ETA AAS is the formation of free atoms of analyte or their time separation from the matrix components that could cause problems in the background correction. The main goal of ETV in the connection with ICP-MS is creating of fine particles, which can be transported with high efficiency into the plasma. Sometimes, the time separation of the analyte from interfering matrix components can also play the role, but this is important only for few special cases.

We will demonstrate the influence on sensitivity, reproducibility and accuracy in the Tl and Au analysis when the approach to the matrix modification was changed from “conventional” MM to “in situ particle creating” MM using carbon NPs as MM, which drastically improve the transport efficiency in ETV ICP-MS. For example, Tl is one of the most difficult analytes for ETA AAS, especially in the case of samples containing chlorides, *aqua regia* or slurry samples. Combined MM effects are necessary (Tl stabilization and removing of the matrix in the TT step together with the matrix modification in gas phase in the AT step). The situation in ETV ICP-MS is completely different, “conventional” MMs are extremely ineffective and only causes high transportation loses even when the sample matrix is effectively removed during the TT step. It is necessary to use MMs, which improve the transport efficiency by creating suitable nanoparticles. These nanoparticles are working as a carrier and can improve the transport efficiency. Few articles described positive effect of high concentrations of organic acids, which probably create carbon particles having positive effect on the analyte transport to the plasma. We also observed this positive effect but high concentration of organic acids also caused the instability of the plasma, so we started to use carbon NPs as a transport carrier. Carbon NPs are robust transport efficiency modifier, which alone allowed quantitative analysis of Tl, even though the pyrolysis step was simplified and no analyte stabilizing MM was used. The sensitivity increased hundred times in comparison with the conventional MM.

The electrothermal vaporization unit GF 5000 connected to the inductively coupled plasma orthogonal acceleration time of flight mass spectrometer (oaTOF-ICP-MS) Optimass 9500 (both GBC Scientific Equipment, Australia) was used for this study.

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PRACTICAL USE OF CARBON NANOPARTICLES AS A TRANSPORT EFFICIENCY MODIFIER FOR ETV-ICP-TOF-MS

Jan PATOČKA[1], Tomáš ČERNOHORSKÝ[1], Anna KREJČOVÁ[1], Lenka BENDAKOVSKÁ[1]

[1]Department of Environmental and Chemical Engineering, University of Pardubice,
CZ-532 10 Pardubice, Czech Republic
jan.patocka@student.upce.cz

In this study, the transport effect of carbon NPs used as a modifier for ETV-ICP-MS was investigated. Thallium was analyzed in CRMs BCR 679 (white cabbage, digested and slurried) and GBW 10052 (green tea, slurried) and in samples of spruce needles (slurried). Gold was analyzed in CRM GBW 07601 (human hair, digested) to confirm that the transport effect of carbon nanoparticles is not specific for Tl and occurs for other elements as well.

The electrothermal vaporization unit GF 5000 connected to the inductively coupled plasma orthogonal acceleration time of flight mass spectrometer (oaTOF-ICP-MS) (both from GBC Scientific Equipment, Australia) was used for the analysis.

The spruce needle samples were cut, dried and cryogenically grinded in liquid nitrogen using the Freezer/Mill 6970 (SPEX Sample Prep, USA). The digestion of samples was done in the microwave system Speedwave™ MWS-2 (Berghof, Germany) using 65% HNO_3. All samples and calibration standards contained carbon NPs and were made in 0.1% Triton X-100.

The optimization of working conditions was done for standard solution 0.5 µg L of Tl and Au. The pyrolysis and vaporization temperatures were 400 and 1900 °C for Tl and 500 and 2700 °C for Au. Carbon NPs concentration was 2.5 g L for Tl and 1 g L for Au. The optimized working conditions were used for the analysis of digested and slurried CRMs and spruce needles. For the quantification, external calibration standard solutions were used.

The obtained results for Tl in CRM BCR 679 (the certified value 3 ±0.3 µg kg) were 3.17 ±0.23 µg kg (solution) and 2.70 ±0.1 µg kg (slurry) and in CRM GBW 10052 (the certified value 57 ±11 µg kg) 50.5 ±2.73 µg kg (slurry). The result for Au in CRM GBW 07601 (the informatory value 2.1 ±2 µg kg) was 2.15 ±0.12 µg kg (solution). The instrumental limits of detection were 0.026 and 0.016 ng L for Tl and Au. The recoveries and repeatabilities measured on calibration standards were in the range 100 - 111 % and 2.9 - 6.7 % for Tl and 99 - 100 % and 0.2 - 2.3 % for Au.

Carbon NPs turned out to be a robust transport efficiency modifier that alone allowed quantitative analysis of Tl and Au, even though the pyrolysis step was simplified and no matrix modifier was used. The transport efficiency modifying seems to be very important factor when using ETV-ICP-MS and it should be taken into account when applying the knowledge of modifiers from ET-AAS.

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DEALING WITH THE MATRIX AND BACKGROUND IN ANALYTICAL ATOMIC SPECTROSCOPY

Margaretha de LOOS-VOLLEBREGT

Department of Chemistry, Ghent University, Krijgslaan 281 – S12, 9000 Ghent, Belgium
margaretha.deloos@ugent.be

In analytical atomic spectroscopy the composition of the sample is an import factor that should be taken into account. From the early days of flame atomic absorption spectrometry (FAAS), it is well known that the matrix may influence the sensitivity and/or cause a background signal. In order to obtain correct analytical results, various background correction systems have been developed for electrothermal atomization atomic absorption (ETAAS) and FAAS and matrix modification is widely used in ETAAS. In inductively coupled plasma atomic emission spectrometry (ICP-AES) the analyte emission signal is superimposed on a background signal consisting of plasma radiation and matrix emission. When separating these signals by manual or automated background correction, there are many instances in which the data reduction fails, e.g., with noisy analyte signals, nonlinear background signals, large and heavily structured background, and spectral interferences. On the basis of scans and using spectral fitting or Kalman filter procedures more accurate and precise results and lower detection limits have been obtained. Such approaches do not use a search for peak position or specific background points and peak area instead of peak height is processed. To tackle problematic polyatomic interferences in inductively coupled plasma mass spectrometry (ICP-MS), software approaches have been developed based on data reduction of the measured total mass spectrum through multicomponent analysis (MCA). The full isotopic patterns for all elements and expected interferents are used in the modelling, leading to concentration estimates for all elements (and interferents). Amongst matrix effects that have been observed in atomic absorption, emission and mass spectrometry, especially carbon containing samples are known to cause problems in ICP-AES and ICP-MS. The signal of some hard-to-ionize elements is selectively enhanced in the presence of carbon, sulfur or phosphorus. This effect has been explained by increased ionization due to a charge transfer reaction between the concomitant ions and analyte atoms, followed by an ion-electron recombination process. This results in an increased population of ions as well as excited analyte atoms in the plasma [1,2]. In ICP-MS the sensitivity for P, As, Se, Sb, Te, I, Au and Hg is higher for carbon-containing solutions than without carbon, whereas P, As. Se and Te are also enhanced in the presence of sulfuric acid. The atomic emission intensities of P, As, Se, Te and I are enhanced by a carbon- or sulfur-containing matrix whereas Hg emission is only enhanced in the presence of carbon.

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USE OF ELECTROTHERMAL EVAPORATION COUPLED WITH ATOMIC EMISSION SPECTROSCOPY (ETV-ICP-OES) IN THE ANALYSIS OF SMALL AMOUNTS OF ORGANIC AND BIOLOGICAL SAMPLES

Stanislava MATĚJKOVÁ[1], Luisa ŠERÁ[2], Martin LOULA[1,2], Jan MENGR[3]

[1]Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo sqr. 542/2 166 10 Prague 6 Czech Republic
[2]University of Chemistry and Technology, Department of Analytical Chemistry, Technická 5, Prague, Czech Republic, 166 28
[3]Charles University, Faculty of Science, Department of Ecology, Viničná 7, 128 44, Prague, Czech Republic
matejkova@uochb.cas.cz

Electro-thermal evaporation combined with the inductively coupled plasma spectrometer allows rapid, direct and simultaneous multi-element analysis in different types of samples without additional preparation steps. The controlled evaporation of the analyzed material with the optimized temperature program and the use of a reaction gas allow usually a matrix-free calibration with various types of standard materials. The advanced and user-friendly instrumentation enables automation of the analysis. The detection limits in the raw material of the samples are improved, as the material is transported with almost 100% efficiency into the plasma. This allows us a trace analysis of very small sample amounts (a few milligrams or less), which makes this method well-suited for environmental, forensic, biomedical and clinical applications, where it is often necessary to analyze small quantities of matter. We have employed the advantages of the method in many cases, for example:

1/ Content of newly developed Ni-complexes [1], which are potentially applicable as a harmless ^{19}F MRI (magnetic resonance imaging) contrast agents with significantly enhanced signal and short acquisition time, was determined in the treated cells. The problem was a small amount of cell culture and expected low concentrations in the ppm range. We used successfully the ETV-ICP-OES with the "*in situ*" enrichment.

2/ During an ongoing pharmacokinetic study, the time-dependent concentrations of the carborane-based candidate drugs were measured using either only boron or together boron and cobalt contents in fresh frozen mouse tissues (serum, brain, and liver).

3/ The quantity of heavy metals and other elements in the collected insect samples from both contaminated post-industrial and unpolluted areas was determined. Total of 18 elements (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sr, V, and Zn) were simultaneously determined in about 1 mg of dried and ground insect sample aliquots.

4/ A method for the determination of biologically important main (Ca, K, Mg, P, S) and minor elements (Ba, Co, Cu, Fe, Mn, Na, Se, Sr, Zn) in plants has been developed.

5/ The method was used to determine metal contaminants in a graphene material.

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COMPARISON OF DIFFERENT SPECTRAL RESOLUTION ICP-OES SPECTROMETERS FOR THE DETERMINATION OF RARE EARTH ELEMENTS

Karel NOVOTNÝ[1,2], Barbora TICOVÁ[1], Viktor KANICKÝ[1,2]

[1]*Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, Brno, 61137, Czech Republic*
[2]*Central European Institute of Technology, Masaryk University, Kamenice 753/5, Brno, 62500, Czech Republic*
codl@sci.muni.cz

ICP-OES spectrometers with low and high spectral resolving power were compared with regard to the determination of rare earth elements (REEs). Due to large number of mutual spectral interferences of REEs the correction (interference) factors were used for interferences correction. This approach was useful for spectrometer with low spectral resolving power, where the corrections were found significant. As was expected in case spectrometers with high spectral resolving power considerably better results were obtained without corrections and further results improvement by using correction factors was insignificant. To confirm the effectiveness of corrections the model samples of rare earth elements were measured. As a real sample certified ore containing rare earth elements reference material REE-1 from the Strange Lake deposit, Quebec, Canada was used. Our results for both types of spectrometers confirm assumption that high spectral resolving power spectrometers provide better and reliable result than low spectral resolving power spectrometers with utilization of correction factors.

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MASS SPECTROMETRY IN ENVIRONMENTAL ANALYSIS

Josef ČÁSLAVSKÝ[1]

[1]*Department of Chemistry and Technology of Environmental Protection, Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic*
caslavsky@fch.vut.cz

The care for the environment has long been outside the interest of so-called developed human societies. On the opposite side, access to the environment for nations designated as primitive to the environment in which they lived was significantly different. The Indian Chief Seattle's message to the US President and the Congress in 1854 may be evidence of this. Here the behavior of the white man in the newly populated areas of America has been subjected to strong criticism. Almost hundred years later, the unaccustomed access to the environment in USA and also in Europe has become the cause of a series of events that have claimed a number of casualties and confirmed the truth of the Old Indian's words.

Mass spectrometry soon became a highly valued method in the monitoring of the contamination of all environmental compartments and substantially simplified the identification and quantification of previously unknown contaminants. The first successful case was the identification of chloroform in drinking water containing organic compounds treated by chlorination in 1974 [1]. Two years later, the number of compounds identified in drinking water exceeded 1500 [2].

This contribution will describe the role of mass spectrometry in monitoring of the environmental contamination by traditional but still relevant contaminants like DDT and its metabolites or polychlorinated biphenyls, but attention will be paid mainly to the group of so-called contaminants of emerging concern like pharmaceuticals, personal care products (PCPs) and endocrine disrupting compounds (EDCs).

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CAN DYNAMIC IMAGE ANALYSIS REPLACE CONVENTIONAL SIEVE ANALYSIS?

Pavel ROUBÍČEK

České lupkové závody a.s., Pecínov 1171, 271 01 Nové Strašecí, Czech Republic
roubicek@cluz.cz

Dynamic Image Analysis (DIA) - also called digital image processing - is a modern method involving the projection of particle silhouettes in transmitted light. The particles freely fall from a feeding chute and a high-speed camera is used to capture the size and shape of each individual particle. This information is transmitted to a computer and the grain size distribution is determined by software evaluation. This presentation will show the comparisons between granulometric analysis obtained by classical sieve analysis and by dynamic image analysis. The measured material is burnt clay sand with grain size 0,063-0,500mm (AFS50). Samples were analyzed with the Fritsch Analysette 28 ImageSizer with the objective 58µ-7400µ. To reach the acceptable statistical error it is necessary to measure more then 300 000 particles. But the differences between the results obtained by sieve analysis and by DIA are still too high. Therefore, separately for each grain range measured by DIA, the intensities were recalculated to obtain a better fit with sieve analysis. But the differences between these two methods were still too high. It was also tested whether the precision cannot be improved by slightly shifting the size of grains for each range measured by DIA, but improvement still was not good enough. It is shown that the reason is in a very high overlap between the histogram for each range of grain size distribution. The best result, which brings the finally acceptable accuracy, was obtained by calibration DIA instrument with a set of monofractions . A new software program was prepared and it recalculates the original results according to this calibration. The software assumes a measured result from DIA as a spectrum of more overlapping peaks with split pseudo-Voigt distribution and calculates the contribution of each range of grains to the total grain size distribution. Split pseudo-Voigt distribution has been used because it has a very good match with the measured shape of peaks from monofractions.

TESTING THE RELIABILITY OF THE WASHING PROCESS IN HAIR ANALYSIS THROUGH A CONTAMINATION STUDY

Anna KREJČOVÁ[1], Lenka BENDAKOVSKÁ[1]

[1]*Department of Environmental and Chemical Engineering, University of Pardubice,*
CZ-532 10 Pardubice, Czech Republic
anna.krejcova@upce.cz

Human hair and animal fur are useful materials for monitoring of health effect if an organism is exposed to compounds as various persistent bioaccumulative or doping substances and heavy metals. These compounds enter to the body by various routes and they are firmly incorporated in the hair protein structure. When assessing their effects on the body, it is necessary to distinguish them from a contamination from the environment trapped on hair surface. An effort to separate the internal and external contamination leads us to use a washing step prior to analysis. Unclearness, irreproducibility and incomparability in health, environmental and similar studies is often a result of own, “home-made” cleaning procedure because there is no standardized, generally accepted procedure. A strong washing agent can disrupt the hair internal structure and release substances of interest in the cleaning step. Therefore, the washing procedure used needs to be considered very carefully. In literature, the procedure given by IAEA (using acetone and water) is used a little more often than others.

An efficiency of washing agents was studied in the two-step experiment: (i) the effect of single agents (nitric acid, acetone, Triton X-100, EDTA) under various conditions (temperature, time, and agitation support) was assessed; the most suitable one was selected, and (ii) a contamination study was carried out to find out whether all artificially added contaminant were removed in the next washing step.

A homogenized bulk sample of horse hair was used. Fifteen elements including rather exogenous contaminants (sodium, potassium) and rather endogenously built elements (sulphur, copper) were analyzed using ICP-OES. As well as, mechanical changes in the hair surface visible under an electron microscope were evaluated. The external artificial contaminants were solid (soil, river sediment, fly ash) and liquid (0.1-1-10 mg L^{-1} of Cu, Zn, As, Cd, Pb in an artificial sweat at pH 3-5.5-8). A defined portion of the horse hair sample was carefully mixed with a defined amount of the solid contaminant or soaked in the contaminant solution. Than the washing procedure and next ICP-OES analysis was applied.

Significant differences between cleaning agents were found: each of them revealed different washing strength for specific elements. Hot water was selected for the second part of experiment. The artificial contamination is not removable quantitatively: (i) elements coming from solid contamination are partly adsorbed on the hair surface during the washing step; (ii) the elements from the fortified artificial sweat were adsorbed and not washed back. These result revealed the washing step as the more critical as had been predicted.

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Assoc. Prof. RNDr. Bohuslav Strauch, CSc. (1929-2017)

Assoc. Prof. RNDr. **Bohuslav Strauch**, CSc., the excellent Czech spectroscopist and inorganic chemist, scientist and teacher, the active representative as well as the honorary member of the Ioannes Marcus Marci Spectroscopic Society (IMMSS) and the recipient of the IMM medal, died unexpectedly at the end of last summer.

B. Strauch has been well known to Czech as well as international scientific community as a pioneer of Raman spectroscopy in Czechoslovakia. In 1960, he assembled (at the Dept. of Inorganic Chemistry, Faculty of Science, Charles University in Prague) the first spectrograph for Raman spectral measurements. The spectrograph was equipped with a Hg lamp source and a photographic plate detector. The success and the international recognition of the measurements carried out with this spectrograph enabled B. Strauch to acquire, for the Dept. of Inorganic Chemistry, one of the first commercially available Raman spectrometers with laser excitation, namely the JRS-S1 JEOL spectrometer with an Ar ion laser excitation. Utilization of this spectrometer has immensely broadened the scope of the measured samples and enabled also the employment of new methods, such as resonance Raman spectroscopy.

The internationally recognized scientific work of B. Strauch was focused mainly on vibrational spectroscopic study of inorganic compounds, transition metal complexes and biologically important molecules. In addition to the publications in local as well as international scientific journals, B. Strauch is also well known as the author of a book chapter in Horák, M. Papoušek D. et al.: *Infrared spectra and molecular structure*, (in Czech), Academia, Prague 1974. Dissemination of information about modern vibrational spectroscopy methods and techniques has been an important point of B. Strauch's scientific as well as educational activities. His review articles „Laser Raman spectroscopy and „Raman spectroscopy with Fourier transformation“ were published first in Czech, and later, in a upgraded English version, as chapters in the book „*Instrumentation in Analytical Chemistry*“, (J. Zyka, Ed), Volume 2, Ellis Horwood, London, 1994.

The last mentioned goal motivated also B. Strauch's activities within the Czechoslovak Spectroscopic Society, and, subsequently, within the Ioannes Marcus Marci Spectroscopic Society. In the period of 1977-1993, he was in charge of the Vibrational spectroscopy scientific group of the Society. Since 1978, B. Strauch was the chief organizer as well as lecturer of the „Measurements of Vibrational Spectra“ courses for spectroscopist working in applied research and industry, and also for students. Owing to the great success of this course, its sequel entitled „Interpretation of Vibrational Spectra“ was launched in 1993. Both courses have been very popular and they have been organized annually until now. Although B. Strauch has, later on, transfered the leadership and organization of these courses to Prof. Pavel Matejka, he himself remained the excellent and popular lecturer at these courses until last year.

Assoc. Prof. B. Strauch was a wonderful person known for a variety of his interests. One of them was the life, work and legacy of Iohannes Marcus Marci. By translating the book Thaumantias-About the Rainbow and about the Nature, Origin and Causes of its Observed Colors by Ioaness Marcus Marci (1648) from Latin to Czech, he enabled Czech spectroscopist to learn about the excellent ideas and explanations of our great scientist and the patron of our Spectroscopic Society.

RATIONALLY DESIGNED METAL NANOSTRUCTURES FOR SERS DETECTION OF BIOLOGICALLY IMPORTANT MOLECULES

Marek PROCHÁZKA[1], Jan PROŠKA[2], Ondřej KYLIÁN[3]

[1]Charles University, Faculty of Mathematics and Physics, Institute of Physics, Ke Karlovu 3, 121 16 Prague 2, Czech Republic
[2]Czech Technical University, Faculty of Nuclear Science and Physical Engineering, Department of Physical Electronics, Břehová 7, 115 19 Prague 1, Czech Republic
[3]Charles University, Faculty of Mathematics and Physics, Department of Macromolecular Physics, V Holešovičkách 2, 180 00 Prague 8, Czech Republic
prochaz@karlov.mff.cuni.cz

Surface-enhanced Raman scattering (SERS) is an extremely sensitive spectroscopic technique employed in a wide variety of (bio)analytical, biomedical and sensing applications [1]. The rational design is employed still more frequently to generate metal nanostructures providing high SERS enhancement and/or high spectral reproducibility. Reproducibility is intrinsically ensured at periodic substrates while high enhancement requires optimized frequencies of localized surface plasmon resonance of metal nanostructure.

In this contribution we prepared and tested a set of rationally designed gold and silver nanostructures for sensitive and reproducible SERS detection of various biologically important molecules (classical biomolecules, drugs, poisons, food contaminants, etc.) [2,3]. Gold "film-over nanospheres" (FON) based on gold-coated assembly of polystyrene or SiO_2 nanospheres has been prepared by nanosphere lithography. Silver substrates are represented by uniform silver nanoislands growing on magnetron-sputtered polytetrafluoroethylene film [4,5]. The sensitivity and spectral reproducibility of particular nanostructure for particular molecule will be discussed.

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RAMAN AND SURFACE-ENHANCED RAMAN SPECTROSCOPIC STUDIES OF THE LARGE CYTOPLASMIC LOOP OF SODIUM-POTASSIUM PUMP

Karolína MACHALOVA SISKOVA[1], Jaroslava SEFLOVA[1], Petra CECHOVA[1], Josef KAPITAN[2], Igor CHOURPA[3]

[1]Department of Biophysics, CRH, Faculty of Science, Palacký University, Šlechtitelů 27, 78371 Olomouc, Czech Republic
[2]Department of Optics, Faculty of Science, Palacký University, 17. Listopadu 12, 77146 Olomouc, Czech Republic
[3]Université François Rabelais de Tours, EA6295 'Nanomédicaments et Nanosondes', 31 avenue Monge, 37200 Tours, France
karolina.siskova@upol.cz

In our contribution we will deal with the large cytoplasmic loop (labelled as C45) of a vital transmembrane protein, Na^+/K^+-ATPase (NKA), an enzyme which is ubiquitous in all animal cells. Malfunctions of this enzyme are related to many diseases such as: hypertension, diabetic neuropathies, renal failure, neurological disorders etc. [1-4]. C45 loop plays a significant role in the NKA function. Moreover, it is soluble in buffered aqueous solutions representing thus an ideal task for Raman and Surface-Enhanced Raman scattering (SERS) spectroscopies. In our very recent paper [4], we have identified the binding sites of cisplatin (the most widely used chemotherapeutic drug for the treatment of various types of cancer) on the C45 loop of NKA. Hence, we are trying to distinguish the differences between the C45 loop with and without cisplatin spectroscopically by using Raman and SERS. As for SERS measurements, silver and/or gold nanoparticles are employed with a special interest in their functional surface modifications. Molecular dynamic simulations of the C45 loop were performed in selected cases as well in order to support our interpretation of the spectra.

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SPECTRAL WATERMARKING APPROACH TO FEMTOSECOND RAMAN SPECTROSCOPY

Miroslav KLOZ[1,2], Jörn WEISSENBORN[1], Yusaku HONTANI[1], John T.M. KENNIS[1]

[1]*Department of Physics, VU University Amsterdam, Boelelaan 1081HV, Amsterdam, The Netherlands, m.kloz@vu.nl*
[2]*Institute of Physics ASCR, v.v.i. (FZU), ELI-Beamlines Project, 182 21 Prague, Czech Republic*

It is now more than 50 years since the discovery of stimulated Raman phenomena and more than 15 years since establishing the femtosecond stimulated Raman spectroscopy (FSRS) technique. Nevertheless, stimulated Raman measurements as an analytical probe have not become a widespread and universal tool, as major problems persisted through unresolved issues of parasitic signals and insufficient sensitivity of applied detection techniques.

Here, we attempt to solve both issues simultaneously by a simple but radical shift in the experimental approach. The traditional way is to generate FSRS signal by a single narrowband picosecond pulse. Such approach is easiest to implement, but in several independent ways not practical for actual Raman data acquisition. We developed a new approach where the FSRS signal is generated by pseudorandom waveforms instead of by a single narrowband pulse. The acquired Raman spectra are then convoluted by the applied waveform, and based on the knowledge of the waveform they can be unambiguously deconvoluted with no loss of spectral resolution. The power of the technique is dual. First, the deconvolution works as a very efficient filter that rejects parasitic signals and offsets automatically and with high fidelity, doing away with human bias in baseline estimation. The second gain is hidden in the delocalization of the signal over a broad interval on the detector array, greatly reducing the so called "fixed pattern noise". In fact, very similar approaches have for decades been a workhorse in many technologies such as Wi-Fi data transfers. With the Wavelet-Resolved FSRS (WR-FSRS) we managed to record femtosecond transient Raman spectra to a sensitivity approaching units of μOD in only tens of seconds of accumulation time. To our best knowledge WR-FSRS increases the resolving power of FSRS experiments at least one order of magnitude while making data processing entirely automatic, rendering the experiment accessible to researchers without FSRS expertise. Based on the data we acquired, we believe that WR-FSRS can be a breakthrough in the field time-resolved Raman spectroscopy.

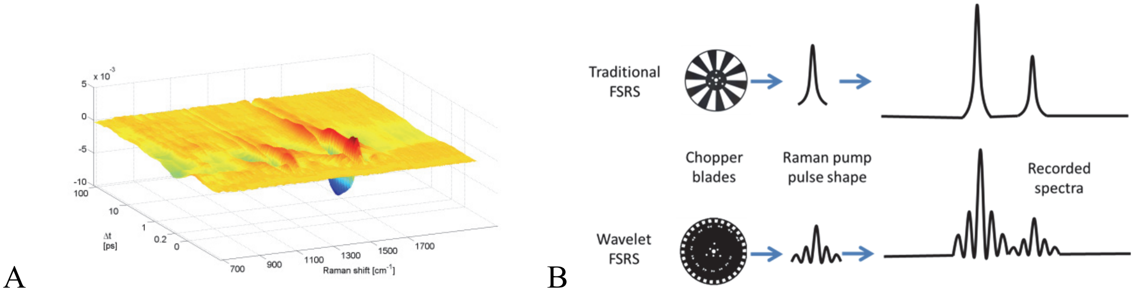

Fig. 1: A: Ultrafast vibrational dynamics (fs to ns) of the peridinin-chlorophyll protein (PCP), aphotosynthetic light-harvesting complex of red algae. Each time-resolved FSRS spectrum is the result of only 4 seconds of data accumulation, resulting in baseline noise of ~100μOD. The entire experiment results from only 5 minutes of acquisition time on 1 kHz laser system. B: Wavelet generation through a specially designed chopper blade allows to implement WR-FSRS with minimal extra costs in comparison to traditional FSRS, as no programmable pulse shaper is needed.

RAMAN SPECTROELECTROCHEMISTRY OF NANOCARBONS AND TITANIA

Ladislav KAVAN[1]

[1]*J. Heyrovsky Institute of Physical Chemistry, Dolejskova 3, 18223 Prague 8, Czech Republic*
kavan@jh-inst.cas.cz

The paper highlights selected examples of Raman spectra of electrochemically active nanomaterials which are mostly investigated *in-situ*. Carbon-based nanomaterials include: electrochemical carbon (sp, polyyne) [1], B-doped nanodiamond (sp^3) [2] and palette of sp^2 nanocarbons (fullerenes, carbon nanotubes, fullerene peapods and graphene) [3-5]. They have been studied in our group during the last 20+ years, sometimes in truly pioneering works.

Titania (TiO_2) finds salient applications in energy conversion (solar cells) [6] and storage (solar fuels, batteries) [7]. Raman spectroscopy is a powerful tool for investigation of various phases of titania, particularly if these studies are refined by isotope labelling (^{16}O, ^{17}O, ^{18}O) [8]. The second-order Raman scattering in rutile, and the overlapping Raman features in anatase can be thus addressed in detail.

Lithium/sodium storage in TiO_2 anatase, rutile, monoclinic TiO_2(B) and in $Li_4Ti_5O_{12}$ (spinel) is applicable for the development of anodes for Li-ion batteries, and possibly also for the Na-ion batteries [9]. Nanostructured materials provide faster charging/discharging compared to that in traditional micron-sized electrode materials. The enhanced contribution of capacitive Li-storage in nanomaterials and faradaic pseudocapacitance in monoclinic TiO_2(B) are of particular interest. Raman spectroelectrochemistry of Li-insertion in anatase confirmed reversible phase transitions (tetragonal/orthorhombic) during electrochemical Li-charging/discharging [10]. These studies were upgraded by Raman spectroelectrochemistry of ^6Li and ^7Li insertion into anatase. Furthermore, Li-insertion into TiO_2 presents the most sensitive analytical tool for detecting trace anatase impurities in rutile and TiO_2(B) [11].

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CRYOMAGNETIC RAMAN MICRO-SPECTROSCOPY - BEYOND PHONONS

Jana KALBACOVA VEJPRAVOVA[1], Tim VERHAGEN[1], Vaclav VALES[2], Martin KALBAC[2]

[1]Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 121 16 Prague, Czech Republic
[2]Department of Low-dimensional Systems, J. Heyrovsky Institute of Physical Chemistry CAS, Dolejskova 3, 182 00 Prague 8, Czech Republic
jana@mag.mff.cuni.cz

The incursion of low-dimensional materials bared exciting physical phenomena underlying progressive concepts for nanoelectronics and quantum computing. However, the key functional principles of these unique species are usually accessible at rather extreme conditions as low temperatures and high magnetic fields, typically using magnetotransport experiments requiring a sufficiently conductive system. However, thanks to the unique nature of Raman scattering processes in the graphene and its relatives (TMD – transition metal dichalcogenides), precisious information about the electronic band structure can be obtained in metallic, semiconducting and insulating systems as well as non-trivial electronic degrees of freedom can be accesed and even controlled. The Raman scattering is also a powerfull tool for observation of spin state switching in spin-crossover molecules, thanks to the significant electron(spin)-phonon coupling. Thus the Raman spectroscopy at extreme conditions enables *in situ* tracing of topographic defects mirrored in charge-strain spatial distribution of the 2Ds, investigation of mixing of the non-trivial electronic states with phonons or inspecting spin state switching in various low-dimensional materials [1-4].

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IN SITU RAMAN SPECTROELECTROCHEMISTRY OF CARBON NANOSTRUCTURES

Martin KALBAC[1]

[1]J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, CZ-18223 Prague 8, Czech Republic. Tel: 420 2 6605 3804; Fax: 420 2 8658 2307
kalbac@jh-inst.cas.cz

Raman spectroscopy is a widely used tool to study carbon nanostructures (carbon nanotubes, graphene). It is very powerful method because it can reveal electronic properties, defects, doping or strain in these materials. Furthermore, the Raman spectroscopy can be combined with electrochemistry. The so called *in-situ* Raman spectroelectrochemistry enables to perform detailed studies of electronic properties of carbon nanostructures, both in their neutral and doped states. The controlled doping of carbon nanostructures leads to a defined shift of the Fermi level and for this reason electrochemical doping provides a simple way to control the transport and optical properties of these materials. Here, we review our studies on carbon nanostructures, which revealed several important phenomena, for example tuning of the electronic structure in carbon nanotubes or partial canceling of quantum interference in single layer graphene by doping.

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ENHANCED RAMAN SCATTERING ON FUNCTIONALIZED GRAPHENE SUBSTRATES

Václav VALEŠ[1], Petr KOVAŘÍČEK[1], Michaela FRIDRICHOVÁ[1], Xiang JI[2], Xi LING[2], Jing KONG[2], Mildred S DRESSELHAUS[2], Martin KALBÁČ[1]

[1]*LDM, J Heyrovský Institute of Physical Chemistry, ASCR, v.v.i., Dolejškova 3, 182 23 Praha, Czechia*
[2]*Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, MA 02139, United States of America*
vaclav.vales@jh-inst.cas.cz

The concept of graphene-enhanced Raman scattering (GERS) was proposed and experimentally demonstrated in 2010. An enhancement of the Raman signal of molecules in very low concentrations in vicinity of graphene was observed. In addition, the photoluminescence of molecules placed on graphene is quenched.

In our work we used functionalized graphene to experimentally probe the theoretical GERS conditions with Rhodamine 6G (R6G) molecules by assuming the change of the Fermi level of graphene due to its functionalization. We showed that the photoluminescence of R6G was quenched also with functionalized graphene. We were able to qualitatively validate the theoretical GERS conditions by comparing several R6G Raman modes on differently functionalized graphene layers. Moreover, we studied the effect of the degree of fluorination on the GERS effect. The fluorination induces sp^3 defects in graphene. We found that high fluorination degree leads to loss of the GERS enhancement, however it can be restored upon fluorine removal.

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RAMAN SCATTERING AND PHYSICAL CHEMISTRY OF BIOMOLECULES

Josef ŠTĚPÁNEK

Institute of Physics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 121 16 Praha 2, Czech Republic
stepjos@karlov.mff.cuni.cz

Employment of high sensitivity CCD detectors and high throughput spectrographs has brought about shortening of the exposition time necessary to obtain Raman spectra with a good signal-to-noise ratio. This has opened large possibilities to carry out various experiments when dependences on the environmental conditions, e.g., temperature, concentrations of interacting molecules, pH, or presence of particular inorganic ions, are recorded as large series of Raman spectra. This makes Raman spectroscopy an effective tool for acquiring the physico-chemical characteristics of interacting large molecules including biomolecules. Its advantage is that proper analysis of Raman spectra can provide not only the physico-chemical parameters but also isolated vibrational spectra of particular molecular states, which can help to uncover the molecular basis of the observed event. Typical example is Raman monitoring of acid-base equilibria, which provides not only the values of pK constants but also vibrational spectra of the studied molecule in individual protonation states, which indicate the sites of the protonation.

For a proper quantitative analysis of Raman spectra series, it is absolutely necessary to subtract correctly the spectrum background. A number of our experiences show how the incorrectly subtracted background spectra have led to completely erroneous conclusions. Despite there is no general applicable procedure of the background subtraction, we have designed a completely automatic procedure to eliminate the impact of a certain set of spectral profiles on the results of the evaluation.

When the obtained series of Raman spectra reflect several processes that are not mutually synchronized, factor analysis is a valuable tool. At first, it enables to determine how many types of the spectral changes can be distinguished with regard to the quality of the acquired data. It also provides a simple quantification of the context of spectral changes with the changing parameters of the experiment. This represents direct base for the fit according a proper thermodynamic model, which then provides both the unknown thermodynamic parameters of the model and isolated normalized Raman spectra of individual species.

Applicable non-resonant Raman experiments require relatively high concentrations of dissolved species. At these conditions, many-molecular interactions are preferred in respect to unimolecular events. In case of a simultaneous presence of unimolecular and bimolecular structural forms, it is thus impossible to discriminate between them by using only the Raman data. It is though possible to combine the temperature dependencies of Raman scattering and of UV absorption in a joint thermodynamic analysis. This approach based on a joint fit of the results of singular value decomposition to a thermodynamic model has been shown to allow determination of the thermodynamic parameters of co-existing unimolecular and bimolecular structural forms and isolation of their Raman spectra.

RAMAN MICROSCOPY OF MICROALGAE: SURPRISING INSIGHTS AND CHALLENGES IN THE UNEXPLORED WORLD

Peter MOJZEŠ[1], Šárka MOUDŘÍKOVÁ[1], Kateřina BIŠOVÁ[2], Vilém ZACHLEDER[2], Ladislav NEDBAL[3], Lu GAO[3], Jana PILÁTOVÁ[4], Alexander SOLOVCHENKO[5]

[1]Institute of Physics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, CZ-121 16 Prague 2, Czech Republic
[2]Laboratory of Cell Cycles of Algae, Centre Algatech, Institute of Microbiology, Czech Academy of Sciences, Opatovický mlýn, CZ-379 81 Třeboň, Czech Republic
[3]Institute of Bio- and Geosciences/Plant Sciences, Forschungszentrum Jülich, Wilhelm-Johnen-Straße, D-52428 Jülich, Germany
[4]Department of Experimental Plant Biology, Faculty of Science, Charles University, Viničná 5, CZ-128 44 Prague 2, Czech Republic
[5]Faculty of Biology, Moscow State University, Leninskie Gori 1/12, 119234, Moscow, Russia
mojzes@karlov.mff.cuni.cz

Autotrophic microalgae use sunlight, carbon dioxide and inorganic nutrients to biosynthesize complex organic compounds interesting as renewable raw materials. The search and phenotyping of suitable algal strains require rapid and simultaneous detection, imaging and quantification of various biomolecules directly within living cells. Confocal Raman microscopy, which combines the molecular specificity of vibrational spectroscopy with spatial resolution of confocal optical microscopy, can be a method of choice, but its routine applicability to microalgae has long been hindered by a strong autofluorescence of photosynthetic pigments. Recently, we have discovered a simple methodology [1] for fast and efficient suppression of the algal fluorescence, which open the door to an unexplored world. Besides simultaneous detection, visualization and quantification of lipids, carbohydrates, proteins and polyphosphates [1, 2], we have shown that Raman microscopy can be useful for identifying various microcrystalline inclusions of unknown or misidentified chemical nature, *e.g.*, guanine microcrystals [3]. Recent progress in the field, advantages, limitations and pitfalls of the method will be demonstrated and discussed.

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INTRAMOLECULAR EXCITATION ENERGY AND CHARGE TRANSFER: FLUORESCENCE, TRANSIENT ABSORPTION AND RESONANCE RAMAN STUDIES

Miroslav DVOŘÁK[1], Tomáš STANĚK[1], Numan ALMONASY[2], Miloš NEPRAŠ[2]
and Martin MICHL[1]

[1]*Department of Physical Electronics, Faculty of Nuclear Siences and Physical Engineering, Czech Technical University in Prague, V Holešovičkách 2, 180 00 Prague 8, Czech Republic*
[2]*Institute of Organic Chemistry and Technology, Faculty of Chemical Technology, University of Pardubice, Studentská 95, 532 10 Pardubice, Czech Republic*
martin.michl@fjfi.cvut.cz

Both excitation energy transfer (EET) and charge transfer belong to the phenomena which frequently govern the photophysics of molecular systems. They play crucial role in processes important for e.g. light harvesting and artificial photosynthesis, organic photovoltaics or organic LED applications. In this contribution, we report on the experimental and theoretical studies of intramolecular EET occuring in compounds containing multiple chromophoric moieties covalently bound via an s-triazine conjugated bridge. This type of EET, nowadays often referred to as “through-bond”, is more efficient and takes place on shorter time scale than the “through-space” Förster dipole-dipole type EET. However, despite the intensive research, the intrinsic nature of the “through-bond” EET process still remains unclear. Additionally, we will present how resonance Raman spectroscopy can contribute to elucidation of the photophysics of a pyrene-triazine compound involving intramolecular charge transfer.

VIBRATIONAL SPECTROSCOPIC CHARACTERISATION OF HYDROGEN-BONDED MOLECULAR CRYSTALS FOR NONLINEAR OPTICS

Ivan NĚMEC[1], Irena MATULKOVÁ[1], Ivana CÍSAŘOVÁ[1], Róbert GYEPES[1], Přemysl VANĚK[2]

[1]Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 8, 128 43 Prague 2, Czech Republic
[2]Department of Dielectrics, Institute of Physics, The Academy of Sciences of Czech Republic, Na Slovance 2, 182 21 Prague 8, Czech Republic
agnemec@natur.cuni.cz

The hydrogen-bonded molecular crystals represent very promising result of crystal engineering of materials, which are especially attractive for the applications in nonlinear optics (NLO). The studied crystalline salts and co-crystals are based on properly arranged organic nitrogen-containing molecules (e.g. aminopyrimidines, guanidine and their derivatives) acting as carriers of NLO properties. The energy of formed hydrogen bonds counteracts the natural tendencies of the organic molecules (ions) to form centrosymmetric pairs. In addition, the formed hydrogen-bonded structures frequently gain advantageous chemical and physical properties.

Several molecular crystals exhibit exceptional NLO properties based on $\chi^{(2)}$- and $\chi^{(3)}$-nonlinearities. Examples of these properties that can be employed for technical applications include harmonic generation (e.g. second harmonic generation – SHG), sum- and difference-generation, intensity dependence of the complex refractive index, light-by light scattering, and stimulated light scattering. Recent application of hydrogen-bonded salts of organic molecules (e.g. salt of carbamoyl-guanidine [1]) is based on stimulated Raman scattering (SRS). This $\chi^{(3)}$ NLO phenomenon is used for the development of compact and efficient frequency converters of the one-micron laser emission based on neodymium or ytterbium lasants. [2]

Selected vibrational spectroscopic aspects will be presented in this contribution. The main emphasis will be focused on the assignment of vibrational spectra (IR and Raman) of representative molecular crystals of aminopyrimidines and guanidine derivatives, which is based on quantum chemical calculations and X-ray diffraction results. Moreover details concerning phase characterisation, hydrogen bonding and monitoring of observed phase transformations will be presented and discussed.

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VIBRATIONAL SPECTROSCOPIC STUDIES OF SALTS OF 2,4,6-TRIAMINOPYRIMIDINIUM AND PHOSPHORIC ACID PREPARED FOR NON-LINEAR OPTICAL APPLICATIONS

Irena MATULKOVÁ[1], Ivana CÍSAŘOVÁ[1], Přemysl VANĚK[2] AND Ivan NĚMEC[1]

[1]*Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 8, 128 43 Prague 2, Czech Republic*
[2]*Institute of Physics, Academy of Sciences of the Czech Republic, v.v.i., Na Slovance 2, 182 21 Prague 8, Czech Republic*
matulkov@natur.cuni.cz

The most molecular crystals used in the field of the second order non-linear optics are based on the aromatic nitrogen containing organic bases which are responsible for the carrying of the non-linear optical properties. The promising organic bases are selected and predicted according to the *ab initio* calculation of hyperpolarisability tensor.

The main target of this presentation is focused on the combination of spectroscopic and diffraction techniques. This combination together with the detailed assignment of vibrational bands supported by theoretical studies allows us the deeper understanding of the observed thermal effects.

This presentation is focused on the characterisation of the salts of 2,4,6-triaminopyrimidinium and phosphoric acid. The possibilities of hydrogen interactions together with the variety of protonation degree of triaminopyrimidine and phosphoric acid can lead to the versatile crystal arrangements grown from same or different molar ratio. Five polymorphs were crystallised at room temperature from mixture of phosphoric acid and triaminopyrimidine. All prepared salts are basically studied by the methods of X-ray diffraction, optical and vibrational spectroscopy. Not only the transparency, but also the thermal stability of the prepared materials is very important for their potential optical applications. If some thermal effects are observed during DSC measurement, the temperature-dependent infrared and Raman spectroscopies supported by the temperature-dependent crystal structure analysis are applied for fundamental monitoring of thermal behaviour. Last but not least the non-linear optical characterisation especially second harmonic generation of the non-centrosymmetric compounds is tested on powder samples.

Two of prepared salts belong are very promising material in the field of second order non-linear optic. Additionally, $P1$ polymorph occur the thermal change concerning the H-atom migration.

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TERPYRIDINE-BASED LIGANDS AND THEIR METAL COMPLEXES: RAMAN AND SURFACE-ENHANCED RAMAN STUDY

Ivana ŠLOUFOVÁ[1], Blanka VLČKOVÁ[1], Jiří VOHLÍDAL[1], Peter MOJZEŠ[2], Marek PROCHÁZKA[2], Irena MATULKOVÁ[3], Markéta PRUSKOVÁ[1], Veronika SUTROVÁ[1,4], Miroslav ŠLOUF[4], Jan SVOBODA[4]

[1]Charles University, Faculty of Science, Department of Physical and Macromolecular Chemistry, Hlavova 2030, 128 40 Prague 2, Czech Republic
[2]Charles University, Faculty of Mathematics and Physics, Institute of Physics, Ke Karlovu 5, Prague 2, 121 16, Czech Republic
[3]Charles University, Faculty of Science, Department of Inorganic Chemistry, Hlavova 2030, 128 40 Prague 2, Czech Republic
[4]Institute of Macromolecular Chemistry CAS, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Rep.
sloufovi@natur.cuni.cz

Ligands derived from 2,2´:6´,2´´-terpyridine (tpy) are utilized in the "bottom-up" self-assembly fabrication of nanocomposites. Their high binding affinity towards transition metal ions are employed in forming various metallo-supramolecular architectures. Linear α,ω-bis(*tpy*) conjugated oligomers have been studied as building blocks for electromagnetic-field-responsive metallo-supramolecular polymers [1].

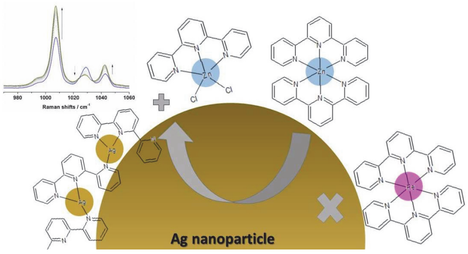

Fig. 1 – Decomposition and ligand replacement observed for $[Zn(tpy)_2]^{2+}$ complex

In our contribution we summarize our contribution to the tpy chemistry via the Raman spectroscopy methods (RS, RRS, SERS). We present (i) the SERS excitation profiles of iron complexes of tpy-based ligands [2], (ii) formation of Ag nanoparticle (NP) and Au NP surface complexes with and without charge transfer resonance, together with the relationship between the morphology and the optical responses of the 2D-arrays of metal NPs of various tpy-based ligands [3], and (iii) the decomposition and the ligand exchange reaction of $[Zn(tpy)_2]^{2+}$ complex on the Ag NP surface (Fig.1) accompanied by formation of Ag-tpy surface complex [4].

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COPPER NANOSTRUCTURES: PROFITS AND DRAWBACKS FOR SEVS TECHNIQUES

Marcela DENDISOVÁ[1], Marie ŠVECOVÁ[1,2], Adéla JENIŠTOVÁ[1], Martin KRÁL[1], David PALOUNEK[1], Alžběta PARCHAŇSKÁ[1], Milan PLICKA[1], Pavel MATĚJKA[1]

[1]Department of Physical Chemistry, Faculty of Chemical Engineering, University of Chemistry and Technology Prague, Technická 5, 166 28 Praha, Czech Republic
[2]Department of Analytical Chemistry, Faculty of Chemical Engineering, University of Chemistry and Technology Prague, Technická 5, 166 28 Praha, Czech Republic
marcela.dendisova@vscht.cz

Surface-enhanced vibration spectroscopy (SEVS) is a powerful physico-chemical tool for study of layer on the surface of nanostructured substrates. The SEVS techniques include surface-enhanced Raman scattering and surface-enhanced infrared absorption. The crucial parameter for SEVS spectroscopy is a metal plasmonic substrate with specific surface. The most used metals are gold, silver and copper in the form of nanoparticles/colloids[1] or large-scaled substrate/roughness electrode. The enhancement factor of copper surfaces is comparable with gold surfaces, it can reach the value of ca. 10^5. The main property of copper is its specific reactivity and complexation abilities. It exhibits high affinity with functional groups contained nitrogen, sulfur and oxygen. For this reason, the copper substrates are suitable for detection of various organic molecules and bio-molecules. Other its physical properties are utilized for studies of adsorption processes between an adsorbed molecule and the surface. These adsorption processes and possible surface reactions are affected by temperature, applied potential[2], used excitation wavelength[3], etc. The risk property of copper is its oxidation. Copper surface enhances the signal if it is in the form of Cu^0 not in the oxidized form of CuO.

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RAMAN OPTICAL ACTIVITY

Vladimír BAUMRUK

Institute of Physics of Charles University, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 121 16 Prague 2, Czech Republic
baumruk@karlov.mff.cuni.cz

In my contribution I would like to introduce Raman optical activity (ROA) and summarize its current development and future prospects. ROA measures vibrational optical activity by means of a small difference in the intensity of Raman scattering from chiral molecules in right- and left-circularly polarized incident light or, equivalently, a small circularly polarized component in the scattered light. Thanks to new developments in instrumentation, ROA may be applied to a wide range of chiral molecular species. Application of ab initio methods to the analysis of experimental ROA spectra holds great promise for the determination of the three-dimensional structure and conformational distribution in unprecedented detail[1]. We have also started to measure ROA spectra in the whole region of fundamental molecular vibrations (150-4000 cm^{-1})[2]. The many structure-sensitive bands in the ROA spectra of aqueous solutions of biomolecules provide detailed structural information including, in the case of proteins, the tertiary fold in addition to secondary structure elements such as helix and sheet. ROA studies of unfolded and partially folded proteins can provide new insight into the residual structure in denatured proteins and the abnormal behavior of proteins responsible for misfolding diseases. Determination of absolute configuration of small and medium sized molecules in solution highlights the power of ROA. Enantiomeric purity of drugs is essential for their biological activity.

We have investigated the performance of Raman optical activity (ROA) spectroscopy in distinguishing four possible stereoisomers of the synthetic precursor used for the production of taxol from baccatin III[3]. Taxol is one of the best-selling medicaments used in the treatment of ovarian, lung, and breast cancers and Kaposi's sarcoma. In a low yield, it may be isolated from the bark of the Pacific yew tree (Taxus brevifolia); however, its industrial production is largely dependent on the precursor. It is shown that for reliable comparison of the experimental and computed Raman and ROA intensities a large number of conformers had to be averaged, to properly account for molecular flexibility in solution. In addition, if combined with the density functional theory computations, ROA spectra provide convenient and economic means of absolute configuration determination.

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TOWARDS SERS AND SERRS ON SINGLE MOLECULE LEVEL

Blanka VLČKOVÁ[1], Veronika SUTROVÁ[1,2], Ivana ŠLOUFOVÁ[1], Ewa PAVLOVA[2]

[1] Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 43, Prague 2, Czech Republic
[2]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic
vlc@natur.cuni.cz

Detection of single molecules is one of the most interesting developments in SERS spectroscopy in the last two decades. Observation of SERS and SERRS (surface-enhanced /resonance/ Raman scattering) on single molecule level is conditioned by generation of strong nanoscale localized electromagnetic fields (dubbed hot spots) in SERS substrates by an external optical excitation as well as by an efficient localization of molecules into them [1]. While the hot spots in dimers of Ag nanoparticles (NPs) were proven to be sufficiently strong for single molecule SERS [e.g. 2,3] this point is still under debate for fractal aggregates, in particular for adsorbates with a weak or no contribution of molecular resonance to SERS.

In our contribution to these issues, we will focus first on providing evidence for single molecule SERRS and SE(R)RS of $[Ru(bpy)_3]^{2+}$ complex dication incorporated into 3D Ag nanosponge aggregate assembled from the adsorbate containing, fused fractal aggregates (D=1.87) of Ag NPs by the strategy reported by us earlier for other adsorbates [4]. The following very low concentration values of the $[Ru(bpy)_3]^{2+}$ spectral detection limits were obtained at four excitations: SERRS (445 nm)- 1×10^{-15} M; SE(R)RS (532 nm)- 1×10^{-14} M; SERS (632 nm)- 5×10^{-13} M; SERS (780 nm)- 8×10^{-11} M. Furthermore, the observed signal-on/signal-off fluctuations of SE(R)RS of $[Ru(bpy)_3]^{2+}$ upon micro-Raman spectral mapping at 532 nm excitation are consistent with the calculated presence of 0.3 $[Ru(bpy)_3]^{2+}$ cations in the spectrally probed volume of the aggregate. Various factors contributing to the achievement of single molecule SE(R)RS of $[Ru(bpy)_3]^{2+}$ will be considered and discussed. In addition to that, the strategies of tailoring the Ag nanosponge aggregates for surface-enhanced luminescence studies and of modification of the aggregates preparation for incorporation of hydrophobic adsorbate species will be presented and discussed as well.

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FASCINATION WITH LASER ABLATION

Markéta HOLÁ[1,2], Jana JURMANOVÁ[3], Viktor KANICKÝ[1,2]

[1]Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
[2]Central European Institute of Technology, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic
[3]Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
mhola@sci.muni.cz

Laser ablation (LA) is defined as a process of removing material from a solid (or occasionally liquid) surface by irradiating it with a laser beam. Its use is constantly expanding to the fields industry, medicine, biology and chemical analysis. LA as a sample technique for Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a method widely used in analytical chemistry for the direct elemental analysis of solid samples.

Studying of laser ablation craters as a "side product" of LA-ICP-MS analysis can be fascinating. The detailed study of crater formation during ns LA (Analyte G2 Photon Machines) was performed by FEG SEM (Field Emission Gun Scanning Electron Microscope) MIRA3 with a high brightness Schottky emitter.

Let's look at ablation from a different point of view. More artistically, more playfully, more 3 D…

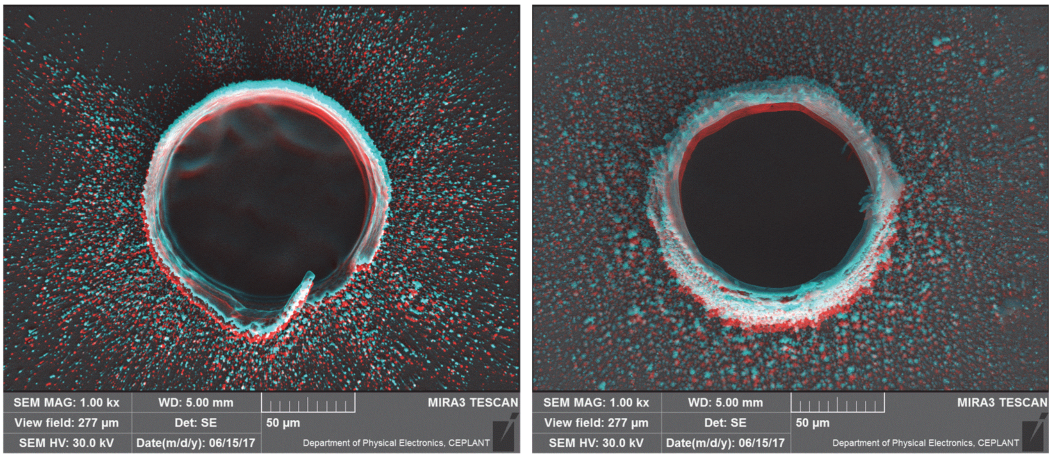

Fig. 1 Ablation crater after 100 and 800 pulses (8 J cm^{-2}) on steel sample.

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ANALYSIS OF METAL LAYERS BY LA-ICP-MS

Elena VANÍČKOVÁ[1], Markéta HOLÁ[1,2], Karel RAPOUCH[3], Viktor KANICKÝ[1,2]

[1]Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
[2]Central European Institute of Technology, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic
[3]Technical museum in Brno, Purkyňova 105, 612 00 Brno, Czech Republic
elena.vanickova@gmail.com

LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) was applied as a semi-destructive method for analysis of metal layers on samples of cultural heritage. The system consists of an Analyte G2 LA system (Photon Machines Inc., Redmond, WA, USA) and an Agilent 7500ce ICP-MS analyser (Agilent Technologies, Japan). The LA system operates at a wavelength of 193 nm with a pulse duration of 4 ns.

The laser ablation was performed using spot mode with the diameter of 160 µm, fluence of 5 J cm^2 and repetition rate of 10 Hz. The method was developed using five samples of zinc-coated iron sheets with defined layer length and composition. Six real samples of watch cases were analysed, the layer composition and thickness was determined (Fig. 1). The analytical results were compared with X-ray fluorescence spectroscopy analysis. The layer thickness was additionally determined by Scanning Electron Microscopy on the cross section of selected samples.

Fig. 1 Real samples of watches with different case coatings

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IN-LINE AEROSOL MASS MONITORING DURING LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY ANALYSIS

Markéta HOLÁ [1,2], Jakub ONDRÁČEK [3], Filip GREGAR [2], Viktor KANICKÝ [1,2]

[1]Central European Institute of Technology (CEITEC), Masaryk University, Kamenice 5, 62500 Brno, Czech Republic
[2]Department of Chemistry, Faculty of Science, Masaryk University, Žerotínovo náměstí 9, 60200 Brno, Czech Republic
[3]Institute of Chemical Process Fundamentals of the CAS, Rozvojová 135, 16500 Prague, Czech Republic
460720@mail.muni.cz

The mass aerosol generated by laser ablation (LA) and transported to inductively coupled plasma mass spectrometer (ICP-MS) was monitored during LA-ICP-MS analysis of different solid samples. DustTrak DrX aerosol monitor was plugged in-line between laser ablation unit and ICP-MS. This unique arrangement provides real-time aerosol mass readings without sample dilution in the size range 0.1-15 µm.

The normalization of LA-ICP-MS signal to total particle mass concentration leads to the reduction of RSD by up to 70 % for the analysis and can serve as internal standardization for the samples with inhomogeneous matrices.

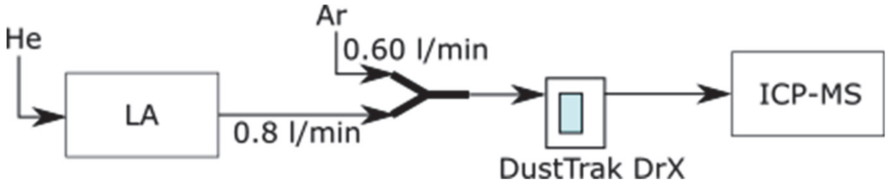

Fig. 1 Schematics of measurement set-up for laser ablation system coupled with ICP-MS and DustTrak DrX.

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FUNDAMENTAL STUDY OF LASER BEAM-MINERALS INTERACTION AND UTILIZATION OF LA-ICP-MS IN GEOLOGY

Michaela HLOŽKOVÁ[1], Michaela VAŠINOVÁ GALIOVÁ[2], Radek ŠKODA[3],
Jindřich KYNICKÝ[2], Viktor KANICKÝ[1,4]

[1]*Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic*
[2]*Department of Pedology and Geology, Faculty of Forestry and Wood Technology, Mendel University in Brno, Zemědělská 3, 613 00 Brno, Czech Republic*
[3]*Department of Geological Sciences, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic*
[4]*Central European Institute of Technology, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic*
hlozkova.michaela@mail.muni.cz

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has become powerful technique and it benefits high sensitivity, multielemental capability, high spatial resolution and minimal sample preparation. It is well known that ablated mass quantity and aerosol composition are affected by laser-beam properties, e.g. wavelength, pulse length, repetition rate, fluence, diameter of laser beam, and moreover, orientation of mineral grains.

This exploratory study was focused on investigation of the influence of mineral grains orientation on absorption of laser radiation. Experiments were performed using quadrupole-based ICP-MS and sector field ICP-MS connected with two different laser ablation systems operating at wavelenght of 213nm (Nd:YAG solid state laser) and 193nm (ArF* excimer laser), respectively. The influence of crystal axis position on interaction of laser beam and apatite, mica and tourmaline was tested for 44 elements from Li to U. Selection of elements was carried out with respect to cover of the entire mass spectrum and presence of individual elements in analyzed minerals. Spot diameter of 80 µm, 60s ablation dwell time and 60s Ar-He gas blank were kept constant. Repetition rates 5, 10 and 20 Hz were applied in combination with fluencies in the range of 3-10 $J \cdot cm^{-2}$.

Time-profiles were investigated with respect to orientation of mineral grains. In this context, the effect of wavelength on the absorption of laser radiation and the signal intensity was observed in several different crystal axis orientations in analyzed minerals. Moreover, the elemental mapping within selected area between individual craters was carried out in order to determine modification of chemical composition around ablated craters caused by thermal effects.

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INFLUENCE OF LASER WAVELENGTH AND LASER PULSE ENERGY ON THE DEPTH PROFILING OF HISTORICAL PAINTINGS BY LIBS

Eva POSPÍŠILOVÁ[1,2], Karel NOVOTNÝ[1,3], Richard ŠEVČÍK[1], Janka HRADILOVÁ[2], David HRADIL[2,4], Pavel POŘÍZKA[5], Josef KAISER[5], Viktor KANICKÝ[1,3]

[1]Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, Brno, 61137, Czech Republic
[2]Academy of Fine Arts in Prague, ALMA laboratory, U Akademie 4, Prague 7, CZ-17022, Czech Republic
[3]Central European Institute of Technology, Masaryk University, Kamenice 753/5, Brno, 62500, Czech Republic
[4]Institute of Inorganic Chemistry of the AS CR, v.v.i., ALMA laboratory, Husinec-Řež, CZ-25068 Czech Republic
[5]Central European Institute of Technology, Brno University of Technology (CEITEC BUT), Purkyňova 123, Brno, CZ-61200, Czech Republic
codl@sci.muni.cz

Laser-induced breakdown spectroscopy (LIBS) has a high potential in analysis of the objects of cultural heritage. However it is a microdestructive technique and it is essential to optimize effects of laser radiation on particular material examined. Model samples of historical painting were therefore analyzed by two different instruments to obtain information on the chemical composition and the depth profile of the multilayered surface. Two different LIBS systems were used for investigation laser wavelength and laser pulse energy influence on shape of crater and depth profile parameters.

The first system was composed of Q-switched Nd:YAG laser Quantel CFR Ultra (laser wavelength 532 nm, pulse duration ~10 ns and echelle spectrometer Emu-65 (Catalina Scientific, USA). Samples were analyzed using laser energy of 40 mJ, 60 mJ and 85 mJ.

Second system was modified New Wave UP-266 MACRO with Nd:YAG laser operating at fourth harmonic frequency 266 nm where plasma emission was transported by means of optical fiber into the entrance of a monochromator Czerny Turner (Jobin Yvon, TRIAX 320) and detected with the ICCD detector (PI max 3 Princeton). Samples were analyzed using energy of approximately 11 mJ with a crater diameter of approximately 100 µm.

Multilayered samples were prepared on a wooden support (5 x 10 cm) following original painting techniques with each layer partly revealed. That allowed verification the depth profile analysis. Photographs of the samples were taken with Nikon D90 camera, equipped with AF-S Micro NIKKOR 60 mm 1:2, 86 ED lens. Detailed photographs of craters were taken with Nikon eclipse E200 microscope (reflected light mode) equipped with KL3 light source and Nikon D90 camera using NK Remote software.

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NEW APPROACH TO DESIGN OF EXPERIMENTS FOR LIBS.

Anthon DIK[1], Vitaliy FOMIN[1]

[1]Department of Inorganic and Technical Chemistry, Faculty of Chemistry, Academician E.A. Buketov Karaganda State University, Universitetskaya str. 28, Karaganda, Republic of Kazakhstan
anthonydik@protonmail.com

Among the methods that make it possible to improve the quality of LIBS analysis, an important place is occupied by design of experiments (DoE). One of the methods of DoE, potentially suitable for use in emission spectral analysis, is stochastic-determinated design of experiment (SDDoE). The essence of SDDoE lies in the original methods of obtaining a replica from the full factorial experiment and subsequent mathematical processing of the results. For n factors, it suffices to carry out $(n-1)^2$ experiments. When developing the procedure for LIBS, it is required to achieve the maximum possible values of accuracy and reproducibility of the analysis, to lower the detection limit of an element or to achieve an acceptable combination of all these parameters. As an optimized factor, the spectrometer settings are in this case. It is also necessary to take into account the possible influence of the spectral lines on each other when the ratio of the concentrations of chemical elements in the sample changes. With the traditional approach of the SDDoE method, the concentration of each of the sample elements should be considered as a separate factor, which substantially increases the number of necessary experiments. In [1] by the method of computational experiment it was predicted that, under certain limitations, the chemical composition of the sample can be considered as one factor.We carried out an experimental test of the possibility of applying an improved SDDoE technique for LIBS. For this purpose, 5 mixtures of oxides,,,, and were prepared, the weight ratios in which were determined by the Latin square of the 5th order. These oxides were randomly selected. Worn with boric acid and compacted samples were used to adjust and calibrate the "LAES Matrix Continuum" device with the use of the SDDoE. The energy of the pump lamp, the delay times of the first and second gates, the delay in the start of the detection of the spectrum, and the duration of the exposure were the optimized parameters. It has been experimentally shown that empirical formulas can be obtained for the total concentration of a mixture of oxides in a boric acid matrix from 0.1 to 10%, linking the intensity of the lines of the elements to be determined with the concentration and parameters of the recording of the spectrum. The accuracy of the obtained calibration formulas was from 0.9 to 0.99.

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HYDRIDE GENERATION OF TELLURIUM FOR AAS AND AFS

Kateřina BUFKOVÁ[1,2], Tomáš MATOUŠEK[1], Jiří DĚDINA[1], Stanislav MUSIL[1]

[1]Department of Trace Element Analysis, Institute of Analytical Chemistry of the Czech Academy of Sciences, Veveří 97, 602 00 Brno, Czech Republic
[2]Department of Analytical Chemistry, Faculty of Science, Charles University, Albertov 8, 128 43 Prague, Czech Republic
stanomusil@biomed.cas.cz

Tellurium is an element quite rare in nature but increasingly used and vital for modern technologies such as those needed for modern communication, computing and the production of clean energy. Increased use also brings increasing demand for analytical methods for Te determination. Despite the fast progress of analytical methodology, Te determination at low concentrations still poses a considerable challenge. This is one of the reasons why this element is also among the less studied ones.

As a first step in development of sensitive methods, the conditions of hydride generation (HG) of tellurium have been investigated. HG has been carried out in a home-made generator in the flow injection mode. A sample (1 ml) is injected into the carrier (HCl) by an injection valve and subsequently mixed with an alkaline solution of $NaBH_4$. Atomic absorption spectrometry (AAS, ContrAA 300, Analytik Jena) has been utilized as a detector, using the most sensitive absorption line at 214.3 nm. TeH_2 has been atomized in a diffusion flame (DF) atomizer. The reason why the DF flame has been chosen for the purpose of optimizing the conditions of HG is the fact that it has been found extremely robust. Furthermore, utterly the same atomizer can be simply utilized for atomic fluorescence spectrometry (AFS) which is our future main aim.

It was verified that efficient HG can be achieved only from Te(IV) while no TeH_2 is generated from Te(VI). The prereduction of Te(VI) can be easily carried out by heating the stock solution of Te(VI) in 6M HCl at 95 °C in a thermoblock for 1 hour. The optimal conditions of HG have been found rather at high concentrations of both HCl (2-6 M) and $NaBH_4$ ($\geq$ 2%). No effect of a reaction coil volume has been observed. The atomization in the DF was also thoroughly investigated by means of AAS detection. The key parameters were as follows: flow rates and composition of the gas phase, *i.e.* carrier Ar an H_2, and observation height.

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PHOTOCHEMICAL VAPOR GENERATION OF MOLYBDENUM WITH ICP-MS DETECTION

Jakub ŠOUKAL[1,2], Ralph E. STURGEON[3], Stanislav MUSIL[1]

[1]Department of Trace Element Analysis, Institute of Analytical Chemistry of the Czech Academy of Sciences, Veveří 97, 602 00 Brno, Czech Republic
[2]Department of Analytical Chemistry, Faculty of Science, Charles University, Albertov 8, 128 43 Prague, Czech Republic
[3]National Research Council of Canada, 1200 Montreal Road, Ottawa, Ontario K1A 0R6, Canada
stanomusil@biomed.cas.cz

Photochemical vapor generation (PVG) is an expanding and promising sample introduction technique for analytical atomic spectrometry applicable not only to mercury and hydride forming elements (Se, As, Sb, Te, Pb, Bi) but also nonmetals (I, Br, Cl, S) and transition metals (Ni, Fe, Co, Cu, Cd, Os). In this work, we present the PVG of Mo which has never been earlier reported.

PVG was accomplished using a 19 W high-efficiency flow-through photoreactor (Beijing, Titan Instruments Co. Ltd.) in a flow injection mode. The generated volatile product (most probably molybdenum hexacarbonyl) was directed by an argon carrier gas to a plastic gas-liquid separator and introduced into the spray chamber of an Agilent 7700x inductively coupled plasma mass spectrometer.

Details of optimization of generation conditions (type and concentration of photochemical agent, irradiation time, influence of various modifiers, etc.) will be presented. Particular attention was paid to the determination of generation efficiency relative to that for liquid nebulization, as well as to interferences from common inorganic anions (Cl^-, NO_3^-, SO_4^{2-} and NO_2^-) likely to be encountered during analytical application to real samples. The accuracy and feasibility of this sensitive methodology (limit of detection around 1 ppt) was successfully verified by analysis of two seawater Certified Reference Materials (NASS-7 and CASS-6) and by analysis of two samples of dietary supplements.

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ELECTOCHEMICAL GENERATION OF VOLATILE Te SPECIES FOR AFS DETECTION

Jana SMOLEJOVÁ[1], Eliška NOVÁKOVÁ[1], Jalub HRANÍČEK[1]

[1]Charles University, Faculty of Science, Department of Analytical Chemistry, Hlavova 2030/8, Prague 2, CZ 128 43, Czech Republic
smolejoj@natur.cuni.cz

Tellurium is a non-biogenic metallic element with semiconductor properties widely used in rewritable CDs and DVDs and solar panels. Its increasing use may cause environmental pollution e.g. through the leaching of Te from these materials on landfills. Therefore, sensitive methods for the determination of Te should be developed. Te can be determined in dissolved samples at ng ml^{-1} levels by ICP-MS [1] or using volatile species generation with AFS detection [2]. Electrochemical generation of volatile species (EcVG) has been developed to overcome the drawbacks of chemical hydride generation, namely the problems associated with the limited stability of $NaBH_4$ reduction agent. Reduction of the analyte and production of H_2 in EcVG are achieved using electric current in a mineral acid medium.

This poster contribution proposes a method for the determination of tellurite based on the electrochemical generation of its volatile species coupled to AFS detection. We achieved the limit of detection for tellurite 0.00130 ng ml^{-1} using a miniaturized electrolytic cell. We studied the influence of selected interferents likely to appear in expected wastewater samples along with their tendency to cause direct or memory interference. We tested methods for removing the adsorbed interferents from the lead cathode surface. The accuracy of the method was validated using NIST SRM 1643f certified reference material. We also examined the stability of the generated volatile species. The effect of the transport tubing temperature on the observed signal showed some interesting trends.

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OPTIMIZATION OF ATOMIZATION CONDITIONS FOR BISMUTH, LEAD AND TIN HYDRIDES FOR DEVELOPMENT OF HYDRIDE ATOMIZERS

Barbora ŠTÁDLEROVÁ[1,2], Milan SVOBODA[2], Jiří DĚDINA[2]

[1]Charles University in Prague, Faculty of Science, Department of Analytical Chemistry, Hlavova 2030, 128 43 Prague, Czech Republic
[2]Institute of Analytical Chemistry of the CAS, Veveří 97, 602 00 Brno, Czech Republic, svoboda750@biomed.cas.cz

Hydride atomizers for AAS and AFS are well known. Quartz tube atomizer and miniature diffusion flame are the most popular. The multiatomizer (developed in 2000) as well as the flame-in-gas-shield atomizer (developed in 1997) extended the group of atomizers for hydride forming elements [1,2].

The multiatomizer differs from the quartz tube atomizer in the second inner horizontal tube (with orifices). The space between inner and outer horizontal arm serves for an injection of a flow of oxygen/air into the inner tube. The horizontal arms are resistively externally heated (700 - 1100 °C). Created clouds of H radicals in the orifices of the inner horizontal tube serve for the atomization.

The flame-in-gas shield atomizer significantly modifies the miniature diffusion flame with use of an argon shielded burner and the capillary centered inside the vertical tube serves to introduce the very small flow of oxygen. The hydrogen-oxygen micro-flame at the end of the capillary creates H radicals which serves for the atomization.

The carrier gas flow and hydrogen-oxygen ratio in the mentioned atomizers are critical parameters for the creation of radicals and thus for efficient hydride atomization. Moreover the flow of argon „shield“ in flame-in-gas-shield atomizer is also important and has significant effect to sensitivity and on baseline noise. An optimization of the described critical parameters leads to efficient bismuthine, stannane and plumbane atomization. The comparison of analytical characteristics of quartz tube atomizer, multiatomizer, miniature diffusion flame and flame-in-gas shield atomizer with AAS detection was made. The optimization study helps to better understanding of the processes inside the atomizers and will be used for future development of the new atomizer/s which will inherently contribute to the presently known group of atomizers for hydride forming elements.

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ARSENIC SPECIATION ANALYSIS BY HYDRIDE GENERATION – CRYOTRAPPING – GAS CHROMATOGRAPHY – ATOMIC ABSORPTION SPECTROMETRY

Štěpánka PETREŇOVÁ[1,2], Milan SVOBODA[2], Jiří DĚDINA[2]

[1]Charles University in Prague, Faculty of Science, Department of Analytical Chemistry, Hlavova 2030, 128 43 Prague, Czech Republic
[2]Institute of Analytical Chemistry of the CAS, Veveří 97, 602 00 Brno, Czech Republic,
svoboda750@biomed.cas.cz

The development of both methodology and instrumentation for arsenic speciation analysis based on generation of substituted hydrides by cryogenic trapping, gas chromatography with atomic absorption spectrometry detection will be presented.

A novel and simple cryogenic trap (CT) design based on a U shaped nonpolar fused silica capillary (U-capillary)[1] was connected to a gas chromatograph with a capillary column. All generated substituted hydrides - arsanes (AsH_3, CH_3AsH_2, C_2H_5AsH, $(CH_3)_3As$) from a flow injection hydride generator (HG) were trapped inside the U-capillary and after heating at ambient temperature were transported directly to the column of the gas chromatograph. Thereafter separated arsanes gradually reached the multiatomizer[2] of the AAS or FID of the gas chromatograph. The connections between hydride generator, U-capillary, gas chromatograph and AAS were optimized to eliminate loss of all generated arsanes. Also the parameters of the separation in the gas chromatograph (type of column, carrier gas, temperature program, time of injection) were optimized to reach appropriate peak area, shape and resolution. The comparison among HG-AAS, HG-CT-AAS and HG-CT-GC-AAS resulted in the conclusion that the procedure was lossless for all arsanes. Moreover the comparison with HG-CT-FID-GC demonstrates analytical performance of HG-CT-GC-AAS. Finally the HG-CT-GC-AAS system was validated with reference materials and real matrices as a urine.

The HG-CT-GC-AAS system is an example of more accessible hyphenated method than for example HG-CT-AAS with U-tube cryogenic trap[3] and powerful alternative to HPLC methods with combination of inherent advantages of HG.

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VOLATILE SPECIES GENERATION FOR SPECIATION ANALYSIS OF MERCURY – PRELIMINARY STUDIES

Inga PETRY-PODGÓRSKA[1], Michaela MIGAŠOVÁ[2], Radek ŽÍDEK[2], Jaroslav ŠVEHLA[3], Jan KRATZER[1]

[1]Institute of Analytical Chemistry of the CAS, v.v.i., Veveří 97, 60200 Brno, Czech Republic,
[2]Department of Analytical Chemistry, Faculty of Science, Charles University;Albertov 6, 128 43 Prague, Czech Republic
[3]Institute of Chemical Process Fundamentals of the CAS, v.v.i., Rozvojová 2/135, 165 02 Prague, Czech Republic
podgorska@iach.cz

A variety of mercury species can be found in the environment. They differ by their physicochemical properties and also toxicity. Due to growing interest to maintain control on the mercury levels in the habitat there is a need to have fast and reliable method of detection and quantification of those species. A HPLC as separation technique is usually coupled to a sensitive spectrometric detector (ICP-MS) to reach this goal.

However, generation of volatile species (VSG) with spectrometric detection (AAS, ICP-MS) can also be used as an alternative. Its advantages reside in high analyte introduction efficiency into the detector and its separation from matrix improving thus the detection limit and minimizing interferences. A separation step must follow the VSG prior to detection or conditions for selective VSG must be found. Preliminary results presented in this work are focused on thorough optimization of VSG conditions of four mercury compounds (Hg^{2+}, $MeHg^{+}$, $EtHg^{+}$ and $PhHg^{+}$) with AAS detection. Reductant ($NaBH_4$ or $SnCl_2$) and acid (HCl) concentration, carrier gas flow rate and atomization temperature were optimized as well as the design of the gas-liquid separator (GLS). Generation efficiency of individual mercury species was subsequently quantified by trapping them in a gold-based amalgamator and subsequent detection by single purpose atomic absorption spectrometer AMA-254. $SnCl_2$ was found to convert Hg^{2+} to a corresponding volatile compound (Hg^0) exclusively, whereas the other three organomercury compounds are not generated. This reducing agent can be thus employed for selective VSG enabling determination of Hg^{2+} only while all four Hg species can be quantified when $NaBH_4$ is used. Generation efficiency of Hg^0 from Hg^{2+} was 60 % in a flow injection mode with a GLS with forced outlet. 100 % generation efficiency was found in a batch apparatus setup. Our next goal, development of a separation step based on cryogenic trap and assessment of its performance will also be outlined.

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MERCURY SPECIES CONTAMINATIONS AROUND THE ABANDONED GOLD MINE LIBČICE DUE TO THE USE OF AMALGAMATION PROCESSES IN THE FORMER GOLD MINING

Jiřina SYSALOVÁ[1], Martina UMLAUFOVÁ[2], Jiřina SZÁKOVÁ[2], Ondřej ZVĚŘINA[3], Rostislav ČERVENKA[4], Josef KOMÁREK[5]

[1]*AAS laboratory, University of Chemistry and Technology, 166 28 Prague 6, Czech Republic,*
[2]*Department of Agroenvironmental Chemistry and Plant Nutrition, Czech University of Life Sciences Prague, 165 21 Prague, Czech Republic*
[3]*Department of Public Health, Faculty of Medicine, Masaryk University, Kamenice 753/5, Bohunice, Brno, Czech Republic*
[4]*Research Centre for Toxic Compounds in the Environment (RECETOX), Faculty of Science, Masaryk University, Kotlářská 2, 61137 Brno, Czech Republic*
[5]*Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic*
Jirina.Sysalova@vscht.cz

The abandoned gold mine Libčice is situated in the Central Bohemia, southwest of the village Libčice (GPS 49.7515442N, 14.3019583E). Amalgamation technology, which is the simplest and most efficient technique to extract gold from raw ore, was repeatedly used in this area. The last mining took place during World War II (1940-44).

The present study is focused on formerly contaminated soils as a result of the amalgamation procedure. The main aims were i) to assess how these soils contribute to pollution of the environment, primarily the atmosphere, ii) to assess the mobility of Hg in soils and its uptake by herbaceous vegetation cover, iii) to assess the potential health and environmental risk. For that purpose gaseous elemental mercury (GEM) was measured (Lumex RA-915$^+$ instrument, Lumex Ltd., St.Petersburg, Russia) in released soil gases as the most stable Hg form in air (residence time 1-2 y) and highly contaminated sites may be revealed. Total Hg (T-Hg) (AMA-254, Leco Corp.), elemental mercury (Hg^0) (thermal desorption at 105 °C for 48 hours, Memmert, Germany), and methylmercury ($MeHg^+$) (GC AFS, Agilent Technologies, USA) were determined in contaminated soils from upper layers ($\leq$ 5 cm depth). The accuracy of methods was verified by ERM-CC580 Estuarine Sediment or by standard additions. Mercury species were determined in six selected soils exceeding the preventive values for soil Hg, i.e. 0.3 mg kg^{-1} of T-Hg, where concentrations of T-Hg were up to 3.5 mg kg^{-1}. In these samples, contents of Hg^0 up to 0.45 mg kg^{-1} (a proportion of T-Hg up to 13%) and $MeHg^+$ up to 2.5 µg kg^{-1} (a portion of T-Hg only up to 0.09%) were observed. Appropriate GEM values in soil gases were in the range 8-26 ng m^{-3}. However, the T-Hg values in soils in the vicinity of the mine reached occasionally even up to 15 mg kg^{-1}. These values resulted in enhanced T-Hg contents in the aboveground biomass of herbaceous plants growing at the investigated area. More than 130 samples of plants (divided into 25 families and 54 species) were analysed, and the T-Hg levels occasionally exceeded the threshold limits for maximum allowable contents of Hg in raw feedstuffs. The maximum Hg value was detected in *Epipactis* sp., whereas the highest bioaccumulation factor (ratio of the element content in plants to the T-Hg content in soil) was determined for *Lotus corniculatus*. These results indicate potential environmental risk for soil biota and herbivorous animals in this mining-affected area.

CATIONIC ARSENIC SPECIES IN FOOD SAMPLES

Antonín KAŇA, Lucie SEDLECKÁ, Oto MESTEK

University of Chemistry and Technology Prague, Faculty of Chemical Engineering,
Technická 5, 166 28 Prague, Czech Republic
kanaa@vscht.cz

A method for determining cationic arsenic species in different food products was optimized for maximum performance. The arsenic species were extracted from the matrix by water and quantified by high-performance liquid chromatography (cation-exchange column LC-SCX 300, mobile phase 10 mmol/L pyridine, pH=2.0) coupled to inductively coupled plasma mass spectrometry (HPLC-ICP-MS). The variables affecting each stage of the methodology were optimized. The arsenobetaine (AB) was purchased and the standards of arsenic species arsenocholine (AC), trimethylarsine oxide (TMAO) and tetramethylarsonium ion (TETRA) were synthetized at Department of organic chemistry, UCT Prague. The analytical features of the method (recovery, limit of detection and linearity range) were determined for each species. The lowest limit of detection was obtained for AB (0.014 µg/L), whereas TMAO was the species with the highest limit of detection (0.027 µg/L). The recovery percentage were between 92-105 % for all species using the standard addition method at two concentration levels.

The samples of mushrooms, seaweed and fish were analyzed. AB was found to be main species in fish samples, but also minor species TMAO, AC and TETRA was detected. These species was also found in mushrooms besides the AB. Two additional species present in samples were identified using mass spectrometry with electrospray ionization (ESI-MS). Trimethylarsoniopropionate (TMAP) was found in fish samples, and 2-(2,3-dihydroxypropoxy)-5-(dimethylarsorylmethyl)oxolane-3,4-diol (Arsenosugar 1) was found as main species in seaweed. Other unknown As species were not identified.

DEVELOPMENT OF ANALYTICAL METHOD FOR TOTAL CHROMIUM USING INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Magda VOSMANSKA[1], Shurtsetseg ERDENEBAYAR[1]

[1]*Department of Analytical Chemistry, Faculty of Chemical Engineering, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague, Czech Republic*
Magda.Vosmanska@vscht.cz

Chromium, a naturally occuring element, is considered both essential (chromium (III)) and toxic (chromium (VI)), depending on its chemical form. Exposure to chromium can occur by drinking water, consuming vegetables, fruits, meat, and/or supplements. Industrial exposure can occur during alloy production, stainless steel welding, chrome plating, or leather tanning. Additionally, metal prostheses used in hip and knee replacements contain chromium.

Inductively coupled plasma mass spectrometry (ICP-MS) is a very sensitive commonly used techmique for chromium determination in all the types of samples. However, spectral and non-spectral interferences arising from the complicated matrixes complicate ICP-MS analysis of chromium. A NexION 300D ICP-MS equipped with an universal cell capable of being operated in either dynamic reaction cell (DRC) or KED mode (collision cell) is used for chromium determination. The goal of this work was to compare the use of the DRC mode with ammonia and KED mode with helium for elimination of polyatomic interferences commonly occured in the chromium determination. The model experiments showed the better results obtained by the use of KED mode.

A method for analysis of chromium by ICP-MS using KED mode was developed, the limits of detection and quantification were determined, the linearity of the calibration was verified. The method was applied to certified reference material (CRM) samples.

INFLUENCE OF ADDITION OF ORGANIC SOLVENT TO ICP-MS PLASMA ON SENSITIVITY AND LIMITS OF DETECTION FOR ELEMENTS FORMING VOLATILE SPECIES AND POTENTIAL INTERNAL STANDARD ELEMENTS

Tomáš MATOUŠEK, Stanislav MUSIL, Jiří DĚDINA

Department of Trace Element Analysis, Institute of Analytical Chemistry of the Czech Academy of Sciences, Veveří 97, 602 00 Brno, Czech Republic
matousek@biomed.cas.cz

It has been documented in the literature that an addition of carbon in the form of organic solvent or carbon dioxide gas has a substantial enhancing effect on sensitivity of elements with high ionization potential, most prominently arsenic and selenium. The supposed mechanism is enhanced ionization due to charge transfer reactions with carbon-containing charged species in the plasma [1]. Since most of the elements forming volatile hydrides are hard to ionize, this effect can be deliberately exploited to improve sensitivity of volatile species generation methods with ICP-MS as a detector, if organic solvent solution is co-nebulized along with gas phase analyte introduction.

The behavior of elements forming volatile hydrides (As, Se, Te, Sb, Pb, Bi, Ge) or other volatile species (Ni, Cd) and Hg in the presence of methanol in the plasma was explored. Signal enhancement of other elements commonly used as internal standards for hydride forming elements (In, Rh, Y, Sc along with Bi, Ge and Te mentioned above) was also compared.

Se and As show the highest sensitivity enhancement (approximately 8 times), followed by Te (5 times) and Hg (4 times). All the other elements exhibit only a moderate increase in sensitivity between 2.5 times for Sb and 1.5 times for Pb. A broad optimum of about 8% of methanol in a nebulized solution was common for all the elements. Except As, neither background signals nor their noise was increased with the increased methanol content. Potential implications of background signal sources in relation to limit of detection enhancement are discussed.

A comparison of performance of Ge, Te and Rh as internal standards in As analysis will be also presented.

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EFFECT OF INSTRUMENTAL PARAMETERS ON NANOPARTICLE PEAK WIDTH IN SINGLE PARTICLE ICP-MS

Martin LOULA[1], Antonín KAŇA[1], Oto MESTEK[1]

[1]*Department of Analytical Chemistry, Faculty of Chemical Engineering, University of Chemistry and Technology, Technická 5, 166 28 Prague, Czech Republic*
loulam@vscht.cz

Single particle inductively coupled plasma mass spectrometry (sp-ICP-MS) is a relatively new method capable of characterizing inorganic nanoparticles (NPs) in terms of their size distribution and number concentration. The method is based on analysis of highly diluted NP dispersion. Under such conditions NPs enter the spectrometer individually and each of them creates a separate cloud of ions, which results in signal in form of discrete peaks. The frequency of these peaks is proportional to NPs number concentration and their area is proportional to the third power of NPs diameter. The signal is observed with high frequency (up to 10^5 Hz) and each peak is recorded in several points. Typical peak width at baseline is 0.5-0.7 ms.

With increasing NPs number concentration increases also a probability of multiple peaks overlap. The method cannot distinguish signal of one big NP and overlapped signals of multiple smaller NPs, therefore results of analyses of too concentrated samples can be distorted significantly. The range of acceptable number concentrations could be extended by narrowing the peaks because it would reduce the probability of peak overlaps.

This work studied effects of various instrumental parameters on peak width and peak area of 100 nm Ag NPs. The studied parameters were namely plasma r.f. generator power, nebulizer Ar flow, sample uptake, quadrupole rod offset, RPq, axial field voltage, cell entrance voltage, cell exit voltage and cell rod offset. 100 nm Ag NPs (Sigma Aldrich, St. Luis, MO, USA) were used for the experiments. All analyses were performed using NexION 350D (Perkin Elmer, Concord, Canada) mass spectrometer.

Although no generally employable improvements of peak width were achieved, some interesting trends were observed. Some parameters, e.g. axial field voltage or RPq exhibited no effect on peak width but could affect peak area. Other parameters, e.g. cell entrance and exit voltage, were able to narrow the peaks at cost of significant reduction of peak area. And finally, quadrupole rod offset and cell rod offset could broaden the peaks and significantly reduce peak area at the same time.

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QUANTIFICATION OF SILVER NANOPARTICLES IN THE PRESENCE OF AG(I) SPECIES USING CLOUD POINT EXTRACTION FOLLOWED BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

Ingrid HAGAROVÁ, Martin ŠEBESTA

Comenius University in Bratislava, Faculty of Natural Sciences, Institute of Laboratory Research on Geomaterials, Ilkovičova 6, 842 15 Bratislava, Slovak Republic
Slovak Spectroscopic Society, member of the Association of Slovak Scientific and Technological Societies, Mlynská dolina G, 842 15 Bratislava, Slovak Republic
ingrid.hagarova@uniba.sk

In this work, cloud point extraction (CPE) followed by electrothermal atomic absorption spectrometry (ETAAS) is used for the quantification of silver nanoparticles (AgNPs) in the presence of Ag(I) species. The extraction is well known for the analysis of non-polar substances; either organic compounds or metallic ions after complexation. In this case, two procedures were optimized for reliable quantification of AgNPs in model solutions. In the both, three main parameters were adjusted to obtain optimal analytical results: extraction parameters and additives, enrichment factor, and ETAAS measurement conditions. Non-ionic surfactant Triton X-114 was used in the both optimized procedures. To optimize the CPE procedures, extraction efficiency was determined for aqueous AgNPs solutions under different conditions (pH value, surfactant volume and its concentration, contact time and temperature, centrifugation time) and with two different additives (thiocyanate and EDTA) at an initial sample volume of 40 ml. Finally, separation of aqueous phase and the highly viscous surfactant-rich phase was done. Methanolic solution of 0.2 M HNO_3 was used for the dissolution of the surfactant-rich phase and the prepared sample was pippeted into the graphite tube. All the measurements were made in the presence of palladium nitrate as a chemical modifier.

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DETERMINATION OF MERCURY IN SOIL BY ETAAS

Josef KOMÁREK[1], Hana ZELINKOVÁ[1], Rostislav ČERVENKA[1,2], Jiří MAJEWSKI[1],
Pavel COUFALÍK[1,3], Ondřej ZVĚŘINA[1,4]

[1]*Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic*
[2]*Research Centre for Toxic Compounds in the Environment (RECETOX), Faculty of Science, Masaryk University, Kotlářská 2, 61137 Brno, Czech Republic*
[3]*Institute of Analytical Chemistry of the Czech Academy of Sciences, v.v.i., Veveří 97, 60200 Brno, Czech Republic*
[4]*Department of Public Health, Faculty of Medicine, Masaryk University, Kamenice 753/5, Bohunice, Brno, Czech Republic*
komarek@chemi.muni.cz

The main problem in the determination of mercury by electrothermal atomic absorption spectrometry (ETAAS) is a high volatility of the element and its compounds. Therefore, the thermal stabilization of mercury prior to its atomization is necessary for avoiding losses of the analyte. Due to higher volatility of metal mercury, several oxidizing agents or complexing reagents were used to prevent the reduction of mercury compounds. Another possible approach for the stabilization of mercury is the use of noble metals as modifiers. Such modification of atomizer surface with noble metals can be performed either by thermal or electrochemical way.

In this study, an inner surface of graphite platform for solid sampling (SS) technique was modified with rhenium by replicated electrodeposition from a drop of solution. A total mass of 250 µg of electrodeposited rhenium was used. SS-ETAAS with such modified platforms was used for the determination of total mercury contents in soil samples and for the determination of methylmercury after its selective extraction from soil samples in the L-cysteine solution.

For direct analysis of solid samples, the masses between 0.1 and 10 mg of samples were weighed into modified platforms according to the mercury content. The calibration solutions were used in the form of methyl isobutyl ketone (MIBK)-methanol solutions with the tetramethylene dithiocarbamate (TMDTC) chelates. Reagents containing sulphur stabilize the mercury by the formation of complex and subsequently mercury sulphide. The accuracy of the method was verified by analysis of the certified reference material GBW 07405 Soil.

The extraction of methylmercury from soil samples was based on acidic hydrolysis of the sample with HCl, followed by the extraction with toluene and back-extraction into the aqueous phase with L-cysteine. Optimized procedure includes the multiple extraction of methylmercury and subsequent purification of extracts from inorganic Hg. The extract of L-cysteine was injected into the graphite platform coated with rhenium. The calibration by aqueous solutions of methylmercury in the presence of L-cysteine was used. The proposed analytical method was verified by the certified reference material CC 580 Estuarine Sediment.

DETERMINATION OF CADMIUM AND IRON IN ONE FIRING WITH HIGH-RESOLUTION CONTINUUM SOURCE AAS

Ondřej ZVĚŘINA[1], Pavel COUFALÍK[2], Josef KOMÁREK[3]

[1]Department of Public Health, Faculty of Medicine, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic
[2]Institute of Analytical Chemistry of the Czech Academy of Sciences, v.v.i., Veveří 97, 602 00 Brno, Czech Republic
[3]Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
zverina@med.muni.cz

High-resolution continuum source (HR-CS) has brought many advantages into the field of atomic absorption spectrometry. Possibility of multi-element analysis is one of its most attractive features. The main condition that must be met in such assays is that selected analytical lines are located within the monitored portion of spectra. Despite the fact that CCD array detector reaches the spectral range of only 0.2–1 nm, numerous combinations of atomic lines with suitable sensitivities can be found and used for the simultaneous determination of respective elements.

In this contribution, we present a method for simultaneous determination of cadmium and iron by HR-CS graphite-furnace spectrometer ContrAA 800G by Analytik Jena (Germany).

Liquid samples (e.g. obtained by microwave-assisted digestion) are introduced into the graphite furnace together with $Pd/Mg(NO_3)_2$ modifier. The primary absorption line of cadmium and adjacent secondary line of iron are used for the determination. Atomization is performed as a two-step process in order to meet ideal atomization conditions for both elements. Interferences originating from PO molecular bands are sufficiently suppressed by correction model using least squares background correction. Working range of the method is 0.01–2 $\mu g.L^{-1}$ for Cd and 10–500 $\mu g.L^{-1}$ for Fe, with the possibility of further expansion by reading the signal at lines' wings.

Its sensitivity combined with robustness allow the method to be used in analysis of many matrices including foodstuffs, where both cadmium and iron are elements of great interest.

EVALUATION OF MICROWAVE ASSISTED DECOMPOSITION METHOD FOR HR CS FAAS DETERMINATION OF TOTAL ELEMENT CONTENTS IN THE WASTE MOBILE PHONES PRINTED CIRCUIT BOARDS

Silvia RUŽIČKOVÁ[1], Dagmar REMETEIOVÁ[1], Vladislava MIČKOVÁ[1]

[1]*Technical University of Košice, Faculty of Materials, Metallurgy and Recycling, Institute of Recycling Technologies, Letná 9, 042 00 Košice, Slovakia*
silvia.ruzickova@tuke.sk

Microwave (MW) assisted wet decomposition of printed circuit boards (PCBs) from waste mobile phones (MP) sample was realized. Application of MW energy follows from complexity of sample character as well as attributes respected by analysts in terms of „green chemistry“ principles. Total content of selected metals (Co, Cu, Fe, Ni, Pb, Pd, Sb, Zn) determination in MP PCBs sample, part of waste electrical and electronic equipment (WEEE) as a source of secondary raw material, is necessary step before its next handling or searching the most suitable conditions for next processing.

Mixtures of aqua regia, Lefort aqua regia, with and without hydrogen peroxide were tested in order to achieve total sample decomposition. Time of 10, 15, 20, and 30 minutes and temperature of 190 °C, 200 °C, 210 °C, and 220 °C were applied. Studied decomposition conditions were evaluated by comparison of selected elements total content determined in solutions after sample decomposition in tested mixtures by high resolution continuum source flame atomic absorption spectrometry (HR CS FAAS) method using contrAA 700 spectrometer (Analytic Jena, Germany). As the next one, the weight of solid residue after decomposition and residue after obtained solution filtration was evaluated. Finally, on the basis of calculated relative standard deviation values (RSD) the precision of the most succesful digestion procedure was evaluated.

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OPTIMIZATION OF SAMPLE PREPARATION PROCEDURE FOR THE DETERMINATION OF METALS IN SYNTHETIC ORGANIC PIGMENTS USING ATOMIC ABSORPTION SPECTROMETRY METHOD

Tereza ŠÍDOVÁ[1], Lenka HUSÁKOVÁ[1], Lenka MUSILOVÁ[1], Jan VYŇUCHAL[2], Vlasta LIŠKOVÁ[2]

[1]Department of Analytical Chemistry, Faculty of Chemical Technology, Studentská 573 HB-D, 532 10 Pardubice, Czech Republic
[2]Synthesia, Inc.; Semtín 103; 530 02 Pardubice; Czech Republic
tereza.sidova@upce.cz

Accurate and precise analysis of metals content is the key component to quality control in manufacturing and processing of synthetic organic pigments. In this work a simple and novel approach is described allowing to facilitate the step for sample preparation, which is the most time-consuming and error-prone step of the whole procedure of complex sample analysis. Number of analytical reagents such as HNO_3, H_2SO_4, HCl, NH_4F, H_3PO_4, H_2O_2, etc. and their combinations were investigated for hot-plate digestion of various organic pigments. Mixture of H_3PO_4 and H_2SO_4 with subsequent addition of H_2O_2 was found to be the most efficient for this purpose. The digestion efficiency was evaluated on the basis of the determination of residual carbon content (RCC) by inductively coupled plasma optical emission spectrometry (ICP-OES). Fractional factorial design was employed to study the effects of sample mass, volume of analytical reagents and heating time onto digestion efficiency and for sample preparation optimization. Under the optimized digestion conditions the proposed method was successfully utilized for the determination of Fe, Ni and Cr in different samples (PR 255, PY 150, PY 192 and PO 68) by flame atomic absorption spectrometry (FAAS) and satisfactory results were obtained.

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INVESTIGATION OF THE US EPA METHOD 3052 UTILIZATION FOR MICROWAVE ACID DIGESTION OF PRINTED CIRCUIT BOARDS

Dagmar REMETEIOVÁ[1], Silvia RUŽIČKOVÁ[1], Vladislava MIČKOVÁ[1],
Patrícia KELEMENOVÁ[1]

[1]Technical University of Košice, Faculty of Materials, Metallurgy and Recycling, Institute of Recycling Technologies, Letná 9, 042 00 Košice, Slovakia
dagmar.remeteiova@tuke.sk

The metals content determination is one of critical attributes in characterization of electronic waste for metal recycling. In spite of the fact that end-of-life printed circuit board (PCBs) are considered to be a secondary resource reservoir, there is no the standard procedure for the determination of total metal content in this multicomposite material containing plastics, metals, alloys and ceramics. The United States Environmental Protection Agency (US EPA) Solid Waste 846 Method 3052 is applicable to the microwave (MW) wet acid digestion of solid waste materials with siliceous, organics and other complex matrices [1]. This US EPA method employs of conc. HNO_3 and conc. HF and this mixture with the MW energy combination provide the high energy system with strongest chemical complexation, oxidization and solubilisation power [2]. Even when this method has not been originally designated for PCBs was already for this type of material used [3].

In this work, the originally US EPA Method 3052 and its modifications in the time of digestion and the sample and digestion mixture ratio and the two stage digestion procedures with/without HCl addition to reaction mixture after first stage of digestion on the sample of PCBs from mobile phones, we applied. The efficiency of the MW digestion procedures for the majority elements (Cu, Pb, Zn, Fe, and Ni) release from PCBs was monitored through determination of their content in the solution after digestion by the high resolution continuum source flame atomic absorption spectrometry (HR CS FAAS) on the contrAA 700 spectrometer.

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THE EFFECT OF SILVER NANOPARTICLES ON THE PENETRATION PROPERTIES OF THE SKIN BARRIER

Adéla JENIŠTOVÁ, Pavel MATĚJKA

Department of Physical Chemistry, Faculty of Chemical Engineering, University of Chemistry and Technology Prague, Technická 5, 166 28 Praha 6 - Dejvice, Czech Republic
adela.jenistova@vscht.cz

Topical application of drugs represents the non–invasive alternative treatment of many diseases. Nanoparticles (NPs) are used to accelerate the penetration of medicaments through the skin, for the targeted drug delivery or in the case of surgical implants[1-3]. Moreover, NPs play an important role in cosmetics. The development of biocompatible/environmentally friendly NPs (that do not exhibit negative effects) is necessary. For some medical purposes, silver NPs (AgNPs) are used considering their antibacterial and anti–inflammatory properties. AgNPs can be used further for the localisation of medicaments[2,3]. The topical use of AgNPs is very convenient because they are accumulated (as Ag^0 or Ag^+) in the skin or *hypodermis* and should not penetrate into the vascular system and/or internal organs[2].

In this study, we used solvents generally used in pharmaceutical area namely ethanol, methanol, dimethyl sulfoxide and demineralized water. Gallic acid (GA), which is used in dermatology considering the anti–oxidant, anti–bacterial or anti–tumor effects, was selected as a model analyte. Several AgNPs (exhibiting defined mean diameters of 20, 40, 60 and 100 nm) were added both to the pure solvents and corresponding solutions of GA. The samples of pig skin were treated with these systems containing AgNPs; the kinetic series of IR spectra were recorded by attenuated total reflection technique to clarify the skin changes. Thousands of spectra in arranged series were evaluated by multivariate statistical methods. The obtained results demonstrate the strong influence of AgNPs size on the structural changes of the skin surface. The largest changes of the skin structure were caused by AgNPs with the 20–nm mean diameter which influence strongly the effect of solvents and cause an apparent penetration of the dissolved GA deeper to the skin layers compared to the other systems. This study follows the experiments with vertical Franz diffusion cells where the permeability of the different sizes of AgNPs through the skin samples is tested thoroughly.

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SILVER HYDROSOLS REDUCED BY FLAVONOIDS: WHAT IS THE EFFECT OF IMMOBILIZATION PROCEDURES ON ENHANCED RAMAN SIGNAL OF RIBOFLAVIN?

Marie ŠVECOVÁ[1,2], Jiří JANOUŠEK[1,3], David PALOUNEK[2],
Oleksandr VOLOCHANSKYI[1], Pavel MATĚJKA[2]

[1]Department of Analytical Chemistry, Faculty of Chemical Engineering, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague, Czech Republic
[2]Department of Physical Chemistry, Faculty of Chemical Engineering, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague, Czech Republic
[3]Institute of Organic Chemistry and Biochemistry, Czech Academy of Science, Flemingovo náměstí 542/2, 166 10 Prague, Czech Republic
svecovam@vscht.cz

Colloidal plasmonic nanoparticles (NPs) are very popular as enhancing substrates for techniques of surface-enhanced vibrational spectroscopy (SEVS). SEVS techniques allow us detection of deposited analytes on plasmonic substrates in low concentration range. To improve detection limits down to single-molecular level and for a detailed clarification of interactions between individual analytes and enhancing substrates, it is desirable to connect SEVS techniques with scanning probe microscopy (SPM). Two of these advanced techniques are called tip-enhanced Raman scattering (TERS) and scanning near-field infrared microscopy (SNIM). SNIM and TERS provide better lateral resolution than SEVS and information about interactions comes from only a few molecules, which leads to a more accurate description of analyte orientation on the surface and its interactions with the metallic surface.

Colloidal NPs is necessary to immobilize for the use in TERS and SNIM techniques. This study is focused on comparison of enhanced Raman signal of riboflavin (Rf) adsorbed (i) on the surface of colloidal AgNPs (reduced by flavonoids [1]), (ii) on the deposited/immobilized AgNPs on the SEVS-inactive substrate by a short linker and (iii) on large-scaled electrochemically prepared Ag substrates. The morphology or size and shape of prepared nanofeatures is observed by atomic force microscopy or by transmission/scanning electron microscopy. Rf can be detected in the concentration range from 10^{-4} mol/l to 10^{-9} mol/l.

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RAMAN MICRO-SPECTROSCOPIC MONITORING OF COMPONENTS DISTRIBUTION IN POORLY SOLUBLE PHARMACEUTICALS TABLETS

Tereza Helešicová[1,3], Pavel Matějka[2], Tomáš Pekárek[3]

[1]Department of Analytical Chemistry, Faculty of Chemical Engineering, University of Chemistry and Technology Prague, Technická 5, 166 28 Praha, Czech Republic
[2]Department of Physical Chemistry, Faculty of Chemical Engineering, University of Chemistry and Technology Prague, Technická 5, 166 28 Praha, Czech Republic
[3]Zentiva, k.s., U Kabelovny 130, 102 37 Praha, Czech Republic
helesict@vscht.cz

The problem of many newly developed drug substances in solid form is the very low solubility in aqueous media [1]. The insolubility of the active substances poses a problem during the dosage form formulation process to guarantee an acceptable bioavailability of the drug in the body. Dissolution behavior is the most challenging aspect for different new chemical entities.

The study focuses on the testing of the proposed simple model of poorly soluble tablets containing two main components; ibuprofen as active pharmaceutical ingredient and lactose as excipient with admixture of sodium stearyl fumarate (1 wt%). Micro-spectroscopic Raman mapping/imaging can provide information needed for investigation of the release of a poorly soluble drug from pharmaceutical tablets.

In order to explain the dissolution behavior, Raman microscopy was employed for monitoring of disintegration and/or dissolution of above mentioned test pharmaceuticals tablets allowing determination of the tablet disintegration in an aqueous medium. The time-dependent maps provide results for identification of the surface (interphase) changes and changes in tablet composition, i.e. how and how fast is the soluble excipient washed out. Subsequent detailed analysis of the dried tested tablets helped us to find the reason for tablet bad disintegration and to understand the effect of individual components during disintegration by analyzing the individual slices of the tablet in a specially designed and 3D printed holder.

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DIFFUSE LARGE B-CELL LYMPHOMA SUBTYPES CLASSIFICATION USING VIBRATIONAL SPECTROSCOPY

Martina MEDVEDIKOVA[1,2], Svetlana BRYCHTOVA[3], Alois NEBOJSA[4], Jan PALACKY[1], Vit PROCHAZKA[5], Vlastimil MASEK[1,2]

[1]Department of Pharmacology, Faculty of Medicine and Dentistry, Palacký University Olomouc, Hněvotínská 3, 77900 Olomouc, Czech Republic
[2]Institute of Molecular and Translational Medicine, Faculty of Medicine and Dentistry, Palacký University Olomouc, Hněvotínská 5, 77900 Olomouc, Czech Republic
[3]Department of Clinical and Molecular Pathology, Faculty of Medicine and Dentistry, Palacký University Olomouc, Hněvotínská 3, 77900 Olomouc, Czech Republic
[4]Central European Institute of Technology Nano Research Infrastructure, Brno University of Technology, Purkyňova 123, 612 00 Brno, Czech Republic
[5]Department of Hemato-Oncology, Faculty of Medicine and Dentistry, Palacky University, I. P. Pavlova - 185/6, 77900, Olomouc, Czech Republic.
michalovamartina@email.cz

Diffuse large B-cell lymphoma (DLBCL) is the most common form of non-Hodgkin lymphoma. DLBCL is an aggressive (fast-growing) lymphoma that can arise in lymph nodes or outside of the lymphatic system, in the gastrointestinal tract, testes, thyroid, skin, breast, bone, or brain. There are several subtypes of DLBCL that may affect a patient's prognosis (how well a patient will do with standard treatment) and treatment options. The most significant are named according to their cell of origin and include germinal center B-cell-like (GCB) and activated B-cell-like (ABC). These groups of patients may have different prognosis with treatment. Advances in the development of biologic therapy show that information about what subtype („GCB“ or „ABC“) is involved will be key to choosing the appropriate therapy.

According to our hypothesis, differences in the expression profile of ABC and GCB subtypes also result in a different chemical composition of tumor tissue, and hence a different fingerprint in infrared spectra. The analysis was performed only in a thin cut of a paraffin-embedded tissue sample in 65 patients. Besides the cut for spectroscopic analysis, there is typically another adjacent cut that is treated by the classic hematoxylin and eosin (HE) staining. The thin section is then "scanned" in a suitable raster and obtained by so-called infrared, where each point on the map represents one FTIR spectrum. The maps contained up to hundreds of thousands of spectra and carry a lot of information about the chemical composition of the sample. Based on a comparison with HE, the pathologist could annotate the sample regions that we included in the statistical evaluation, linking the histological and spectral information. Principal component analysis was performed to reveal basic patterns in data. Then, an equal number of spectra from both healthy and diseased patients were selected to train a random forest classifier and the validation performed against the rest of the dataset.

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CHIRAL PLASMONIC NANOASSEMBLIES

Jiří JANOUŠEK,[1,2] Lucie BEDNÁROVÁ,[1] Michal ŠÁMAL,[1] Jitka NEBURKOVÁ,[1] Jan VÁVRA,[1] Jiří RYBÁČEK,[1] Pavel MATĚJKA,[3] Petr CÍGLER,[1] Irena G. STARÁ,[*,1] Ivo STARÝ,[*,1]

[1]Institute of Organic Chemistry and Biochemistry ASCR, Flemingovo n. 2, 166 10 Prague, Czech Republic
[2]Dep. of Analytical Chemistry, Fac. of Chemical Engineering, UCT Prague, Technicka 5, 166 28 Prague, Czech Republic
[3]Dep. of Physical Chemistry, Fac. of Chemical Engineering,UCT Prague, Technicka 5, 166 28 Prague, Czech Republic
bednarova@uochb.cas.cz

Organic field-effect transistors (OFETs) are widely used as logic devices in organic electronics applications because of their low-cost fabrication, energy-efficient production and reliable performance.[1-3] However, in sharp contrast to an enormous attention being paid to OFETs employing organic semiconductors, organic-inorganic hybrid nanomaterials such as metal nanoparticles functionalised with organic ligands have been less studied in this regard. Moreover, no particular interests was given to the OFET device prepared using chiral π-electron containing structures.

Here, we present chiral hybrid nanomaterials based on colloid gold nanoparticles (Au NPs) and colloid silica nanoparticles with gold nanoshell (Silica-Au NPs). These NPs were functionalized with a helicene-like ligand with defined chirality. The obtained assemblies were structurally characterized by microscopic and spectroscopic techniques. Preliminary data indicate induction of plasmonic optical activity by chiral functionalization of gold nanomaterials. The comparable effect was observed for functionalized nanoparticles in solution or deposited on quartz substrate.

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SPECTROSCOPIC STUDY OF TETRATHIAFULVALENE DERIVATIVES IN CHARGE-TRANSFER COMPLEXES

Lucie BEDNÁROVÁ[1], Jan HOLEC[1], Ján TARÁBEK[1], Jiří RYBÁČEK[1], Petr HOLÝ[1], Irena STARÁ[1], Ivo STARÝ[1],

[1]Institute of Organic Chemistry and Biochemistry of the CAS, Flemingovo náměstí 542/2, 166 10 Praha 6, Czech Republic
bednarova@uochb.cas.cz

Tetrathiafulvalene (TTF) and its derivatives have become subjects of great interest in the field of organic semiconductors. Electron-rich TTF core creates charge-transfer (CT) complexes with electron-deficient partners such as tetracyanoquinodimethane (TCNQ) and its derivatives[1,2]. Many studies of semiconducting CT complexes have focused almost exclusively on single crystals. However, in organic semiconductors the CT complexes are often applied in a form of thin films. Langmuir-Blodgett (LB) thin film preparation offers the possibility of controllable molecular packing of CT complexes in thin films which might help to incorporate the CT complexes into practical semiconducting devices.

We have synthesized series of amphiphilic TTF derivatives with different aliphatic and aromatic moieties and studied them by various spectroscopic methods (UV-vis and IR absorption, EPR) in respect to the formation of CT complex with tetrafluorotetracyanoquinodimethane (F_4TCNQ). Herein, we report on an effect of the attached aliphatic and aromatic moieties on character of CT complexes.

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INTERACTION OF INTRAMOLECULAR G-QUADRUPLEX DNA STRUCTURES WITH SELECTED ALKALOIDS

Marek VIDO[1], Petra JAROSOVA[1], Petr TABORSKY[1], Ondrej PES[2]

[1]Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
[2]Department of Biochemistry, Faculty of Medicine, Masaryk University, Kamenice 5, 62500 Brno, Czech Republic
408846@mail.muni.cz

G-quadruplex DNA (G4) has been known to be involved in many physiological processes in the cell e.g., in the promoter regions of oncogenes or in the human telomeric region. Because of their supposed role in cancer, G4 are often studied as targets for anti-cancer drugs. Natural and/or synthetic compounds, which are able to selectively bind these structures, have been intensively tested by means of molecular spectrometry, circular dichroism, equilibrium dialysis, and mass spectrometry. Compounds may interact with G4 by several mechanisms with various affinities. An approach to study a great number of potential effective compounds relies on combination of methods when relatively fast; however, imprecise mass spectrometry was used to preselect compounds, which were then subjected to more precise techniques studying G4 in a solution.

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QUATERNARY PROTOBERBERINE ALKALOIDS SELECTIVELY STABILIZE G-QUADRUPLEXES

Petra JAROSOVA[1], Andrea SLANINKOVA[1], Petr TABORSKY[1], Ondrej PES[2]

[1]Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
[2]Department of Biochemistry, Faculty of Medicine, Masaryk University, Kamenice 5, 62500 Brno, Czech Republic
408846@mail.muni.cz

Non-canonical DNA secondary structures have gained interest in recent years. One of these structures is the G-quadruplex (GQ) which is present in several protoncogenic-DNA promoters and thus participates in biological processes such as replication, transcription and translation. Quaternary protoberberine and tetrahydroprotoberberine alkaloids (corysamine, coptisine and stylopine), which are supposed to selectively bind these structures, have been tested. Influence of selected alkaloids on stability of double-stranded DNA and noncanonical form of DNA was observed by determining association constants of alkaloid-DNA complexes using two spectroscopic methods − molecular absorption spectrometry and fluorescence spectrometry. Furthermore, effect of given alkaloids on melting temperature of these DNA structures was determined by using CD spectrometry. Competitive dialysis was performed for affinity comparison of certain alkaloids to different DNA structures including G-quadruplexes. These measurements have confirmed results obtained by CD spectrometry and extended the knowledge, that investigated alkaloids prefer interaction with G-quadruplexes in comparison to dsDNA and ssDNA.

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ENHACEMENT OF SENSITIVITY IN SEPARATION TECHNIQUES WITH FLUORESCENCE DETECTION USING DEUTERATED WATER

Josef KUČERA[1], Ondřej PEŠ[2], Ivona VORÁČOVÁ[3], Petr TÁBORSKÝ[1]

[1]Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
[2]Department of Biochemistry, Faculty of Medicine, Masaryk University, Kamenice 5, 62500 Brno, Czech Republic
[3]Department of Bioanalytical Instrumentation, Institute of Analytical Chemistry, Czech Academy of Sciences, Veveří 967/97, 60200 Brno, Czech Republic
408285mail.muni.cz

Fluorescent molecules with emission maxima above 500 nm are often dynamically quenched by OH oscillators present in water molecules. We have changed H_2O for D_2O to obtain higher fluorescence intensity signal. Our experiments carried out on spectrofluorometer have proved that anthracyclines can achieve about 300 % higher response in D_2O as solvent. The affect can be employed in various analytical methods including HPLC and capillary electrophoresis coupled to fluorescence detection. Fluorescence intensity in D_2O based mobile phase of doxorubicin had increased about 2.87 times. An advantage of capillary electrophoresis compared to HPLC is the lower consumption of background electrolyte due to small volume of capillary. We achieved the separation of daunorubicin and epirubicin using capillary electrophoresis coupled with laser induced fluorescence detection (Ar^+ laser 488 nm). The separation was carried out using borate buffer (105 mM, pH 9.0) prepared in H_2O and D_2O. Estimated LODs in heavy water were significantly lower than those obtained in H_2O.

MONITORING SPECTRAL CHANGES OF NUCLEIC ACID UV ABSORPTION: APPLICATION IN STUDY OF miRNA BINDING

Anežka VACKOVÁ, Kateřina HOFBAUEROVÁ, Josef ŠTĚPÁNEK

Institute of Physics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5,
121 16 Praha 2, Czech Republic
av.zhor@gmail.com

Temperature induced change of UV absorption is widely employed as a basic characterization of the stability of nucleic acid (NA) intermolecular or intramolecular complexes. As a rule, the only recorded parameter is the absorbance at 260 nm, which decreases when the nucleobases are mutually arranged in stacking positions (hypochromic effect). However, it has been found out that the changes of NA structural arrangement are also connected with weak but specific variations of the spectral shape of UV absorption [1]. The temperature effect on UV absorption spectra of NA can be sensitively analyzed and interpreted by using a multivariate analysis. The singular value decomposition [2] applied to a set of UV absorption spectra recorded at various temperatures can reveal up to three kinds of spectral changes even for a simple dissociation of NA duplex. The fit of the temperature profiles of relevant scores (coefficients corresponding to the portion of the particular spectral pattern in the spectra obtained for various temperatures) to a proper thermodynamic model enables determination of the main thermodynamic characteristics of the complex. Our contribution describes the details of this approach on an example of a model study of miRNA binding to its target sequence in mRNA.

MicroRNA (miRNA) are short RNA molecules that mediate post-transcriptional regulation of gene expression by binding to a target mRNA [3]. They usually form imperfect duplexes consisted of short tracks of Watson-Crick base-pairs separated by mismatched pairs, internal loops or bulges. It was just the effect of the bulge, which is the presence of an extra unpaired nucleotide in one strand, on the thermodynamic stability of the complex we have studied in respect of a possible stabilization by an inorganic cation. Temperature dependent UV absorption spectra were recorded and analyzed for aqueous solutions containing mixtures of the segment in question of miRNA *Let-7* with its target sequence *LCS1* at mRNA *lin-41* from *Caenorhabditis Elegans* or with analogs of the *LCS1* segment where the nucleotide in the bulge site was replaced or deleted.

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A COMBINATION OF LIQUID PHASE MICROEXTRACTION AND UV-VIS SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM (VI)

Yaroslav BAZEĽ[1,2], Tetiana RIABUKHINA[2], Daria JANEGOVÁ[1]

[1]*Pavol Jozef Šafárik University in Košice, Šrobárova 2, 04180 Košice, Slovak Republic*
[2]*Uzhhorod National University, Pidhirna str. 46, 88000 Uzhhorod, Ukraine*
yaroslav.bazel@upjs.sk

Chromium (VI) compounds have high mobility at environmental objects, but they show carcinogenic, mutagenic and embryotoxic effect. That's why the monitoring of the quantity of Cr(VI) is an object of special interest. The electrochemical, atomic absorption, chromatographic and spectrophotometric methods of determining Cr(VI) with different selectivity, sensitivity and precision are in use to solve various tasks. Modern trends in the development of analytical chemistry such as automation, miniaturization, on-line analysis, the use of "green" technologies put forward new requirements to methods of determination of Cr(VI). A combination of spectrophotometric methods and microextraction comply with these requirements. The purpose of this work is to study the possibility of indirect spectrophotometric determination of Cr(VI) with combination of liquid phase microextraction based on oxidation of iodide by dichromate ions with further detection of forming triiodide ions which form ion associates (IA) with cations of polymethine dyes.

The optimum conditions for redox reaction between dichromates with iodide ions have been investigated. Astrazone diamond red 4G (ADR) and Astraphloxine FF (AF) were used as dyes. The formation of ion associates passes in acidic medium (0.2 mol×L^{-1} H_2SO_4) in the presence of excess of reagents (3.0×10^{-4} mol×L^{-1} KI, 1.6×10^{-4} mol×L^{-1} ADR or AF), microextraction is carried out with isoamylacetate (ADR) or CCl_4 (AF). Various techniques of microextraction of IA of Cr(VI) have been studied and the Vortex is shown to be the most effective (the extraction equilibrium is set to 10 seconds, the recovery rate of the IA is 93.7% - AF and 95.1% - ADR at a ratio of volumes of water and organic phase 5:1). It can be concluded that the combination of liquid phase microextraction and UV-VIS spectrophotometric determination of Chromium (VI) is effective, and it was determined the analytical characteristics of the proposed analytical forms:

Cr(VI)-I$^-$-ADR. λ=530 nm, the limit of detection is 0.015 μg×L^{-1}, a linear dynamic range is 0.050 – 4.2 μg×L^{-1}, with correlation coefficient of 0.9983.

Cr(VI)-I$^-$-AF. λ=560 nm, the limit of detection is 0.010 μg×L^{-1}, a linear dynamic range is 0.035 – 4.2 μg×L^{-1}, with correlation coefficient of 0.9968.

A new rapid, sensitive and selective method of determination of Cr(VI) has been developed and tested on certificated reference materials, natural and drinking water samples.

Acknowledgements
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HPLC-UV ANALYSIS OF SELECTED ESTROGENS.

Katarína REIFFOVÁ, Ľudmila TOKARČÍKOVÁ, Yaroslav BAZEĽ

Department of Analytical Chemistry, Faculty of Science, Pavol Jozef Šafárik University,
Moyzesova 11, 040 01 Košice, Slovak Republic
yaroslav.bazel@upjs.sk

This work was focused on the simultaneous analysis of the selected estrogens: estradiol (E2), estriol (E3), estrone (E1) and ethinylestradiol (EE2). The methanol-water and acetonitrile-water mobile phases in different volume ratios were used and optimized for this purpose. The mobile phase acetonitrile-water (45:55, v/v) with flow rate 0.9 mL min^{-1} provided the best separation of the analytes (Fig. 1) and was used for analysis of real urine sample spiked with standards of estrogens.

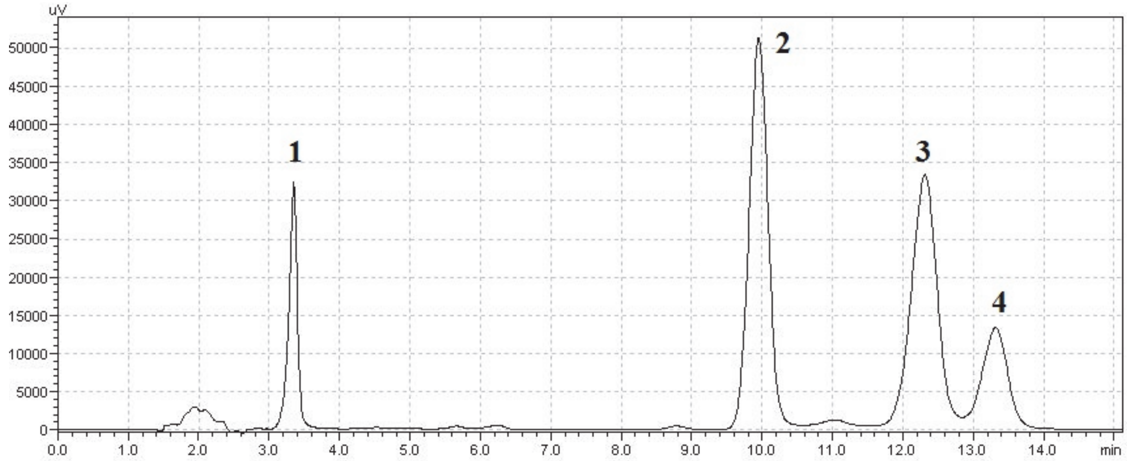

Fig. 1 HPLC-UV Chromatogram of selected estrogens, MF: acetonitrile-water (45:55, v/v), flow rate 0.9 mL min^{-1} , estriol (1), estradiol (2), etinylestradiol (3), estrone (4)

In addition to the basic retention parameters, the stability of the prepared standard solutions as well as the effect of the urine matrix on the retention time of the standards was monitored. Chromatographic analysis was performed on Shimadzu LC 20 Prominence (Kyoto, Japan) equipped with two LC-10AS pumps, Degasys DG-2410 degasser, CTO-10A oven and SPD-10A UV detector. Chromatographic column Nucleosil C-18 (250 x 4 mm; 5 µm) from Macherey-Nagel (Germany) was used at temperature of 26 °C. The UV detector was set to the wavelength 280 nm.

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DETERMINATION OF PHENOLIC ACIDS IN WHITE WINE BY HPLC WITH FLUORESCENCE DETECTOR

Jarmila SVANCAROVA LASTINCOVA[1]

[1]Department of vine and wine, Central Controlling and Testing Institute in Agriculture,
Matuskova 21, 833 16 Bratislava, Slovak Republic
Jarmila.lastincova@uksup.sk

Because different grape varieties ripen at different times the final quality of wine aroma influenced by phenolic acids is evident. The wide spread of organic compounds are presented in the white wines aroma. Some volatile compounds present in Slovakian white wines with protected designation of origin /PDO/ wintage year 2016 were examined (see table 1). Direct estimation of these compounds has sometimes several methodological problems. In this work direct estimation of phenolic acids was performed by HPLC analysis with the fluorescence detector in the four white grape varieties (Pálava, Gewurztraminer, Pinot gris and Rheinriesling). The identities of the different chromatographic peaks for gallic, vanillic, caffeic and para-coumaric acids were determined and confirmed by comparing their spectral characteristics to standards. The detection limits were calculated of each calibration graph and were 0,9-1,6µg.l^{-1}. The fluorescence detector was operated at λ_{ex} = 278 nm and λ_{em} = 360 nm (gallic and vanillic acids) or λ_{ex} = 278 nm and λ_{em} = 454 nm (caffeic and p-coumaric acids). The mobile phase for gradient elution was mixture of methanol/water/formic acid, the temperature was kept at 40°C and the sample injection was 20µl. With fluorescence detection linear calibration range was 5-500µg/l. Detection limits were calculated as three times the standard deviation of the background noise.

Table 1. Determination of phenolic acids in the dry white wines vintage 2016

	Rulandské šedé	*Tramín červený*	*Pálava*	*Rizling rýnsky*
Gallic (mg/l)	4.2±0.5	1.8±0.3	2.8±0.2	5.6±0.4
Vanillic (mg/l)	1.2±0.2	1.6±0.2	1.2±0.2	1.8±0.2
Caffeic (mg/l)	1.3±0.2	2.3±0.2	3.1±0.3	2.5±0.3
p-coumaric mg/l	0.8±0.1	1.2±0.3	0.4±0.1	1.6±0.3
Sugar (g/l)	1.6±0.16	6.6±0.6	3.7±0.4	1.9±0.19
Alcohol %	12.37±0.12	12.90±0.12	12.86±0.12	12.38±0.12

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DROP SENSING PLATFORMS FOR DETECTION OF BROMINE UNDER HEADSPACE LIQUID-PHASE MICROEXTRACTION CONFIGURATION: A COMPARISON OF ORGANIC AND NANOSTRUCTURED RECEPTORS

Adrián, GARCÍA-FIGUEROA; Francisco, PENA-PEREIRA; Isela LAVILLA; Carlos BENDICHO

Analytical and Food Chemistry Department, Faculty of Chemistry, University of Vigo, Campus as Lagoas-Marcosende s/n, 36310 Vigo, Spain
adriangf@uvigo.es

This work reports on a comparison between two different applications of chemical bromine generation in combination with Headspace Single-Drop Microextraction (HS-SDME) for bromide and total bromine determination. On the one hand, the exposure of fluorescein aqueous microdrop to headspace and further measurement of microdrop with microvolume fluorospectrometry provides an excellent sensing approach with high sensitivity for bromide determination in water samples. It is based on decrease in the analytical signal due to the formation of tetrabromofluorescein (eosin) [1]. By comparison, the exposure of an aqueous microdrop containing gold nanoparticles (AuNPs) allows total bromine determination in polymers containing brominated flame retardants (BFRs) through a ratiometric analysis by microvolume spectrophotometry [2]. The interaction of AuNPs with bromine causes a decrease in the plasmonic band intensity at λ=521 nm as well as the emergence of an additional band at λ=245 nm, a relationship between absorption at both wavelengths and bromine concentration being observed. Under optimal conditions both sensing approaches display excellent limits of detection (LOD), *i.e.* 1.4 µg L^{-1} and 8.8 µg L^{-1} Br, respectively. The limits of quantification (LOQ) were 4.4 µg L^{-1} and 56.7 µg L^{-1} Br, respectively. HS-SDME microvolume fluorospectrometry was successfully applied to environmental waters and validated against the certified reference material BCR-661 (ground water, Br^- low level). HS-SDME microvolume spectrophotometry was successfully applied to total bromine determination in E-waste polymers after conversion of brominated flame retardants into bromide with alkaline fusion and it was validated against two reference material (BCR-681 trace elements in polyethylene and ERM®-EC680 low-density polyethylene).

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DETERMINATION OF LANSOPRAZOLE AND ITS METABOLITES IN HUMAN SERUM FOR PHENOTYPIZATION OF CYP2C19 AND CYP3A4

Jan JUŘICA[1,2], Sabína SEDLAČKOVÁ[2], Katarína KOSTOLANSKÁ[3], Ondřej PEŠ[3]

[1]*Department of Pharmacology, Faculty of Medicine, Kamenice 5, 625 00 Brno, Czech Republic*
[2]*Dept. of Biochemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic*
[3]*Dept. of Biochemistry, Faculty of Medicine, Masaryk University, Brno, Czech Republic, Kamenice 5, 625 00 Brno, Czech Republic*
jurica@med.muni.cz

Lansoprazole is a proton pump inhibitor, used in treatment of duodenal ulcers, reflux oesophagitis, Zollinger-Ellison syndrome and *H. pylori* eradication. It is metabolized via CYP3A4 and CYP2C19 enzymes. CYP2C19 is responsible for low capacity and highly selective 5-hydroxylation and CYP3A4 for high capacity sulfoxidation. Therefore, we have considered lansoprazole as a low-dose probe for determination of their metabolic activity.

The aim of this work was to develop a simple and sensitive method for the determination of lansoprazole (L), lansoprazole sulfone (LS) and 5-hydroxylansoprazole (OH-L) and to validate the method in terms of basic validation parameters and in in real samples of the patients.

The HPLC system was a Shimadzu LC-10ADvp system equipped DAD detector SPD-M10Avp. The separation was achieved on an Ascentis Express column (3.0 mm × 100 mm, 3µm) with a binary mobile phase (A= 0.1 % CH_3COOH, 0.1% NH_4OH and B= acetonitrile), 0.6 mL/min flow with gradient in composition: A: 75 to 60 % from 0 to the 6th min, then remained at 40 % for 1 minute and subsequently returned to initial conditions till 10th min. Omeprazole was used as an internal standard to ensure precision and accuracy of the method and analytes were extracted using a single-step liquid-liquid extraction The limits of quantitation were of 52, 17 and 89 ng/ml for L, OH-L and LS, respectively. Both intra-day and inter-day repeatability measured at three concentration levels were in acceptable range ($\leq$ 13.4 and 15.72 %, respectively) for all analytes. The real serum sample contained 556 µg/mL of L, 35 µg/mL of OH-L and 129 µg/mL of LS. Method was also transferred without any modification of separation conditions to LC MS, which was carried out on an a Dionex Ultimate 3000RS module coupled to a Bruker EVOQ Qube triple quadrupole mass spectrometer operated in ESI+ mode. The analytical sensitivity was improved and the samples with lower than 30 mg dose of lansoprazole could have been analyzed as well.

We have developed a simple yet useful HPLC-UV method for the determination of lansoprazole and its metabolites in human serum for CYP2C19 and CYP3A4 phenotyping.

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STABILITY STUDIES OF RIFAMPICIN AND GENTAMICIN BY USING SIMPLE HPLC-UV AND HPLC-FLD METHODS

Dagmar ČOŽÍKOVÁ, Jaromír KULHÁNEK, Ivana KULHAVÁ, Martina HERMANNOVÁ, Daniel ŠVADLÁK, Petra FALTUSOVÁ, and Vladimír VELEBNÝ

Contipro a.s., Dolní Dobrouč 401, 561 51 Dolní Dobrouč, Czech Republic
dagmar.cozikova@contipro.com

Several chromatographic methods for the separation and quantitation of rifampicin and gentamicin have been developed, including reversed-phase liquid chromatography (RPLC) employing detection modes such as UV [1] or fluorescence [2], supercritical fluid chromatography and more recently mass spectrometry [3]. HPLC has been shown to be one of the most suitable technique for the measuring of both antibiotics in human plasma and tissues. However, certain drawbacks could be listed against the mentioned techniques: a poor long-term stability, a time-consuming sample treatment, and the most important, generation of non-controlled impurities and degradation products which could not be detected.

The aim of our work was to develop a rapid and simple analytical method which allows a stability studies of antibiotics in aqueous solutions. To confirm the stability, following parameters such as temperature (-20°C, 5°C, 25°C and 37°C), light-dark sensitivity, and pH (3.5, 5.0 and 7.5) were monitored.

Rifampicin detection was based on absorption of light at the wavelength around 345 nm (HPLC-UV) while gentamicin was determined by employing fluorescent detection (HPLC-FDL). The optimized HPLC-FLD method allow to well separate gentamicins C1, C1a, C2a and C2 and other minor components. Gentamicin was found to be more stable than rifampicin. Evidently, the stability of rifampicin decreased with increasing temperature in time. Besides, a negative effect of low and high pH was also established. Lower stability of rifampicin was observed due to the measuring of generated rifampicin quinone. Rifampicin and the side reaction product rifampicin quinone were identified by using LC-MS.

Defining the parameters by which the stability of antibiotics is influenced will enable us to better understand mechanism of its action in human body, and furthermore to find out its potential broad application in pharmaceutics.

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GC-MS DETERMINATION OF THE RESIDUAL MALONDIALDEHYDE IN HYALURONIC ACID GRAFTED BY LINOLENIC ACID

Jaromír KULHÁNEK[1], Gloria-Huerta ANGELES[1], Martina BRANDEJSOVÁ[1], Vladimír VELEBNÝ[1]

[1]Contipro a. s., Dolní Dobrouč 401, 561 02 Dolní Dobrouč, Czech Republic
Jaromir.Kulhanek@contipro.com

In this study, an analytical method for determination of malondialdehyde, a toxic product of peroxidation of sodium linoleyl hyaluronate (αLNA-HA), is described. The hyaluronic acid derivative containing a fatty acid having three double bonds revealed an unexpected cytotoxicity after oven drying and storage at 40 °C. Therefore, the presence of malondialdehyde (MDA) was determined, because MDA is the principal and most studied toxic product of polyunsaturated fatty acid peroxidation. [1,2]

For determination of MDA in αLNA-HA a GC-MS method was optimized. MDA was reacted with 1-phenyl-hydrazine, reaction product was extracted into n-hexane and analyzed on HP-5 column. Quantification was achieved by measuring the ion current at the typical (MW 144 fragment), in comparison with those of an internal standard. The calibration curve of the MDA derivative was linear in the range used 0,05 – 2 µg/ml and recoveries from spiked matrices was between 88,4 to 105,5 % from four different samples. The optimized method was used to monitor stability of the αLNA-HA derivatives.

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ONLINE SOLID-PHASE EXTRACTION LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY OF HAIR CORTISOL USING A SURROGATE ANALYTE

Katarina KOSTOLANSKA, Lucie NOVOTNA, Eva TABORSKA, Ondrej PES

Department of Biochemistry, Faculty of Medicine, Masaryk University, Kamenice 5, 62500 Brno, Czech Republic
katarinakostolanska@centrum.sk

Cortisol is a glucocorticoid hormone, which plays an important role in stressful situations when stressors activate the hypothalamic-pituitary-adrenocortical (HPA) system. Cortisol has been routinely analyzed in the laboratory from saliva, serum/plasma, and/or urine. However, the HPA axis represents a highly dynamic system influenced by several factors and expose circadian rhythmicity. When analyzed in hair, it can allow the unique possibility to assess the long-term systemic levels and obtain a retrospective index of long-term hormone secretion. Based on an average hair growth rate of 1 cm per month, it is possible to distribute the hair along the length of individual segments and determine the concentration of cortisol reflecting secretion in the monitored period.

Online SPE LC-MS with $^{13}C_3$-cortisol as a surrogate analyte was developed, validated and applied for obtaining hair cortisol levels of 114 healthy volunteers. The first 3 cm from a posterior vertex position were analyzed as three individual segments resulting in 310 hair cortisol levels, which were used, after log transformation, to predict a range of values observed in future. The median value of hair cortisol was 4.76 pg/mg. The employed method allowed simple processing, high throughput and may be readily expanded to analyze additional steroid compounds in hair.

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ELECTRON AFFINITY OF POLYCRYSTALLINE DIAMOND FILMS

O. ROMANYUK[1], I. BARTOŠ[1], I. GORDEEV[1], A. ARTEMENKO[1], M. VARGA[1],
T. IŽAK[1], M. MARTON[2], P. JIŘÍČEK[1], A. KROMKA[1]

[1]Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 00 Prague, Czech Republic
[2]Institute of Electronics and Photonic, Faculty of electrical engineering and information technology, Slovak University of Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia
romanyuk@fzu.cz

The electron affinity in semiconductors is defined as an energy distance from the conduction band minimum (CBM) to the vacuum level. When the vacuum level is below the CBM, the electron affinity is negative (NEA). Amongst variety materials, mono- and poly-crystalline diamond thin films and diamond nanoparticles terminated with hydrogen exhibit the NEA [1], which makes them a promising material for electronic applications such as cold photocathode devices or flat panel displays.

In the present work, a combination of X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) have been utilized to determine the electron affinity of undoped and B-doped polycrystalline diamond films with differently modified surface (i.e. as-grown, H-terminated and O-terminated). The undoped and B-doped diamond films were grown on Si substrates by chemical vapour deposition (CVD) methods. The surface hydrogenation was carried out in linear antenna micro-wave (MW) plasma system and surface oxidation in the radio frequency (rf) plasma reactor Diener (FEMTO).

We revealed that both types of as-grown polycrystalline diamond films exhibit a true NEA (-0.9 ÷ -1.1 eV). After their surface hydrogenation in rf plasma, the NEA magnitude of H-terminated samples decreased to -0.5 eV. This effect is a complex issue which can be attributed to the depolarization effect of surface dipoles and to the increased density of sub-surface defects induced during the rf plasma modification. Despite of this reduction, a true NEA is still preserved. The oxidized polycrystalline diamond surfaces always exhibited the positive electron affinity of 1.9 eV and 0.5 eV for undoped and B-doped diamond samples.

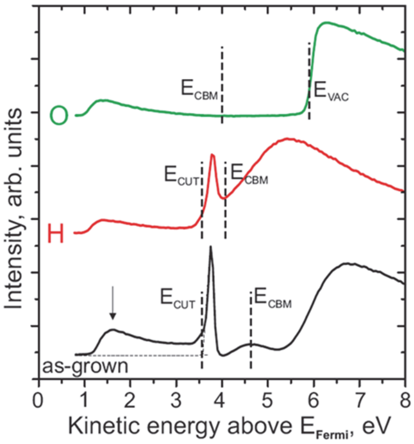

Figure 1 – UPS spectra close to spectra cutoff [2], E_{CUT}, measured with sample bias voltage of -4 V (spectra were calibrated on sample bias). The sharp peak below the E_{CBM} represents the NEA for as-grown and H-terminated samples.

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DEVELOPMENT OF NEW PREPARATION PROCEDURES AND THE USAGE OF PLASMONIC RECYCLABLE NANOMATERIALS FOR ENHANCED MOLECULAR SPECTROSCOPIC TECHNIQUES

Richard ZAKL[1] Pavel MATĚJKA[2]

[1]*Department of Physical Chemistry, Faculty of Chemical Engineering, University of Chemistry and Technology, Technická 5, 166 28 Prague 6, Czech Republic*
richardzakl@seznam.cz

During recent years various Raman and infrared spectroscopic techniques have become ordinary analytical methods. Using plasmonic nanoparticles prepared from various coinage metals (Au, Ag, Cu) we can significantly improve a detection limit ideally to a single molecular level. Surface enhancement, in particular, depends on various parameters of the nanoparticle/nanostructure such as size, shape, roughness or metallic composition. Currently, the usual synthetic methods used for the preparation of nanoparticles with desired properties exhibit no potential of reusability or recyclability. The goal of our development is focused chiefly on a new type of nanomaterials the can be used multiple times, that means that they are either reusable or recyclable.

The aim of this partial contribution is the preparation of nanostructural composite material consisting of a thin layer of titanium dioxide prepared by the dip-coating method and gold nanoparticles prepared using Turkevich reduction method and immobilized on the surface using APTMS (amino-propyl trimethoxy silane). The Au nanoparticles should enhance spectra signal while the titanium dioxide layer should catalyze the decomposition of the analyte molecules after spectral usage to renew the surface of Au nanoparticles. Prepared composites were examined by UV-VIS spectroscopy and SEM technique. SERS properties were tested after modification by model analytes (methyl-orange and methylene blue dyes) using the acquisition of Raman spectra in the visible region. Photocatalytic activity was tested by UV lamp illumination and, consequently, a decrease of SERS signal was observed in correlation with UV illumination time period. The multivariate chemometric methods were used for data evaluation to confirm the decomposition of the previous analyte and to describe the time dependence of the photocatalytic process.

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THE DEVELOPMENT OF SURFACE- AND TIP-ENHANCED VIBRATIONAL SPECTROSCOPIC METHODOLOGIES FOR STUDIES OF POLLEN GRAINS

Pavla ŠIMŮNKOVÁ[1], Pavel MATĚJKA[1]

[1]Department of Physical Chemistry, Faculty of Chemical Engineering, University of Chemistry and Technology, Technická 5, 166 28 Prague 6, Czech Republic
pavla.simunkova@vscht.cz

Pollen grains are constituted by the exine from the outer side. This part of the pollen grain consists from sporopollenin which is a polymeric compound protecting the intine (i.e. the inner part of the grain) from thermal shocks and influences of different chemicals (such as acids and bases). The exact composition of the exine is not completely known; nevertheless, we know it is composed mainly of fatty acids, carotenoids, and various phenolic substances.

Every kind of pollen exhibit different topographic and chemical characteristics. Thanks to exine resistance, it can persist unaltered and stable, although the intine can be somewhat affected. Considering this property of exine, it can be used for targeted drug delivery and/or targeted transportation of selected substances in organisms. For proper design of the drug delivery system, the interaction between the individual active pharmaceutical ingredients and the exine needs to be examined in details.

The non-invasive microscopic and spectroscopic techniques will be used in this project such as Surface Enhanced Raman spectroscopy (SERS), Scanning Near-Field Optical Microscopy (SNOM/NSOM), Atomic Force Microscopy (AFM), Infrared Microscopy, which can clarify individually distinct morphological and chemical properties of the pollen grain surface and further the inner interphase. AFM imaging is a powerful technique for displaying 3D form of a shape of the pollen's surface at the really high resolution and in the meantime, SNOM can overcome the diffraction limit and can create high-resolution images in the range of nanometers too. The sample preparation is almost none, the sample needs to be properly fixed to allow the probe tip to scan the surface, but in the case of SNOM the technique to fix the powder pollen grains needs to be developed due to the problem of glue evaporation from the stationary layer and further destruction of the probe tip on the cantilever.

The modification of the exine surface with plasmonic metal nanoparticles is developed both to employ the surface-enhanced spectroscopic techniques and to exploit the possibilities of chemical modification of metallic nanoparticles. Preliminary infrared microscopic data, AFM images, and Raman spectral data will be compared and shortly discussed.

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Maryam	Aghaei	maryam.aghaei@uantwerpen.be
Günter	Allmaier	guenter.allmaier@tuwien.ac.at
Vladimír	Baumruk	baumruk@karlov.mff.cuni.cz
Yaroslav	Bazel'	yaroslav.bazel@upjs.sk
Lucie	Bednárová	bednarova@uochb.cas.cz
Miroslava	Bittová	spmirka@seznam.cz
Ivana	Bonková	ivana.bonkova@gmail.com
Josef	Čáslavský	caslavsky@fch.vut.cz
Tomáš	Černohorský	tomas.cernohorsky@upce.cz
Dagmar	Čožíková	dagmar.cozikova@contipro.com
Margaretha	de Loos-Vollebregt	margaretha.deloos@ugent.be
Marcela	Dendisová	marcela.dendisova@vscht.cz
Anton	Dik	anthonydik@protonmail.com
Veronika	Dillingerová	nikadilli@gmail.com
Alessandro	D'Ulivo	dulivo@pi.iccom.cnr.it
Magda	Dvořáková	mdvorakova38@gmail.com
Radovan	Fiala	radovan.fiala@ceitec.muni.cz
Pavlína	Fialová	fialova@svuom.cz
Joachim	Franzke	franzke@isas.de
Adrián	García-Figueroa	adriangf@uvigo.es
Filip	Gregar	filda.gregar@gmail.com
Ingrid	Hagarová	ingrid.hagarova@uniba.sk
Jitka	Hegrová	jitka.hegrova@cdv.cz
Tereza	Helešicová	helesict@vscht.cz
Michaela	Hložková	hlozkova.michaela@mail.muni.cz
Martin	Hof	hof@jh-inst.cas.cz
Markéta	Holá	mhola@sci.muni.cz
Dominika	Holková	dominika.holkova@stuba.sk
Jakub	Hraníček	jakub.hranicek@natur.cuni.cz
Aleš	Hrdlička	ales2003h@centrum.cz
Norbert	Jakubowski	norbert.jakubowski@bam.de
Petra	Jarošová	petra.jarosova1@gmail.com
Adéla	Jeništová	adela.jenistova@vscht.cz
Jan	Juřica	jurica@med.muni.cz
Jozef	Kaiser	kaiser@fme.vutbr.cz
Martin	Kalbáč	kalbac@jh-inst.cas.cz
Jana	Kalbáčová Vejpravová	jana@mag.mff.cuni.cz
Antonín	Kaňa	kanaa@vscht.cz
Viktor	Kanický	viktork@chemi.muni.cz
Ladislav	Kavan	kavan@jh-inst.cas.cz
Miroslav	Kloz	Miroslav.Kloz@eli-beams.eu
Josef	Komárek	komarek@chemi.muni.cz
Katarína	Kostolanská	katarinamayl@gmail.com
Jan	Kratzer	jkratzer@biomed.cas.cz
Anna	Krejčová	anna.krejcova@upce.cz

Josef	Kučera	408285@mail.muni.cz
Václav	Kulas	Vaclav.Kulas@preciosa.com
Jaromír	Kulhánek	Jaromir.Kulhanek@contipro.com
Martin	Loula	martin.loula@vscht.cz
Přemysl	Lubal	lubal@chemi.muni.cz
Karolína	Machalová Šišková	karolina.machalova@upol.cz
Jana	Machotová	Jana.Machotova@continental-corporation.com
Stanislava	Matějková	matejkova@uochb.cas.cz
Tomáš	Matoušek	matousek@biomed.cas.cz
Irena	Matulková	matulkov@natur.cuni.cz
Michaela	Matulová	matulov.michaela@gmail.com
Peter	Matúš	peter.matus@uniba.sk
Martina	Medvedíková	michalovamartina@email.cz
Marcel Bruno	Miglierini	marcel.miglierini@stuba.sk
Jana	Miglierini	jana.miglierini@gmail.com
Martin	Michl	martin.michl@fjfi.cvut.cz
Peter	Mojzeš	mojzes@karlov.mff.cuni.cz
Stanislav	Musil	stanomusil@biomed.cas.cz
Ivan	Němec	agnemec@natur.cuni.cz
Karel	Novotný	codl@sci.muni.cz
Lukáš	Pašteka	pashty89@gmail.com
Jan	Patočka	jan.patocka@student.upce.cz
Ondřej	Peš	ondramayl@gmail.com
Inga	Petry-Podgórska	podgorska@iach.cz
Filip	Polák	filip.a.polak@gmail.com
Ivana	Poláková	ivana.polakova@preciosa.com
Jürgen	Popp	juergen.popp@leibniz-ipht.de
Pavel	Pořízka	pavel.porizka@ceitec.vutbr.cz
Eva	Pospíšilová	379264@mail.muni.cz
Jan	Preisler	preisler@chemi.muni.cz
Marek	Procházka	prochaz@karlov.mff.cuni.cz
Dagmar	Remeteiová	dagmar.remeteiova@tuke.sk
Oleksandr	Romanyuk	romanyuk@fzu.cz
Pavel	Roubíček	roubicek@cluz.cz
Silvia	Ružičková	silvia.ruzickova@tuke.sk
Jozef	Sitek	jozef.sitek@stuba.sk
Vladimír	Sklenář	vladimir.sklenar@ceitec.muni.cz
Jana	Smolejová	jana.smolejova@natur.cuni.cz
Milan	Svoboda	svoboda750@biomed.cas.cz
Jiřina	Sysalová	Jirina.Sysalova@vscht.cz
Martin	Šebesta	martin.sebesta@gmail.com
Tereza	Šídová	tesi1247@upce.cz
Alena	Šimáková	asimakova@svuol.cz
Pavla	Šimůnková	pavla.simunkova@outlook.com
Ivana	Šloufová	sloufovi@natur.cuni.cz

Josef	Štěpánek	stepjos@karlov.mff.cuni.cz
Helena	Štěpánková	stepanko@nbox.troja.mff.cuni.cz
Jarmila	Švancarová Laštincová	jarmila.lastincova@uksup.sk
Kateřina	Švecová	katerina.svecova@ukzuz.cz
Marie	Švecová	svecovam@vscht.cz
Jaroslav	Švehla	svehla.jaroslav@gmail.com
Petr	Táborský	taborak@email.cz
Ján	Tóth	jantoth92@gmail.com
Michaela	Tvrdoňová	358018@mail.muni.cz
Martin	Urík	urik@fns.uniba.sk
Anežka	Vacková	av.zhor@gmail.com
Tomáš	Vaculovič	vaca@mail.muni.cz
Jan	Valenta	jan.valenta@mff.cuni.cz
Václav	Valeš	vaclav.vales@jh-inst.cas.cz
Dominik	Vaněk	dominikc.v@gmail.com
Elena	Vaníčková	elena.vanickova@gmail.com
Blanka	Vlčková	vlc@natur.cuni.cz
Magda	Vosmanská	Magda.Vosmanska@vscht.cz
Zdeněk	Weiss	weissz@fzu.cz
Richard	Zakl	richardzakl@seznam.cz
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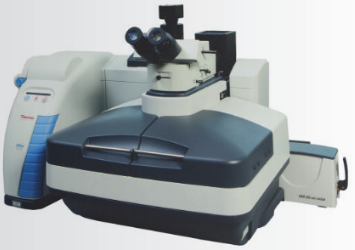


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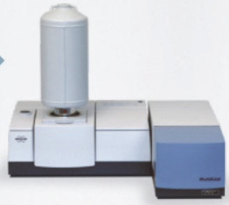

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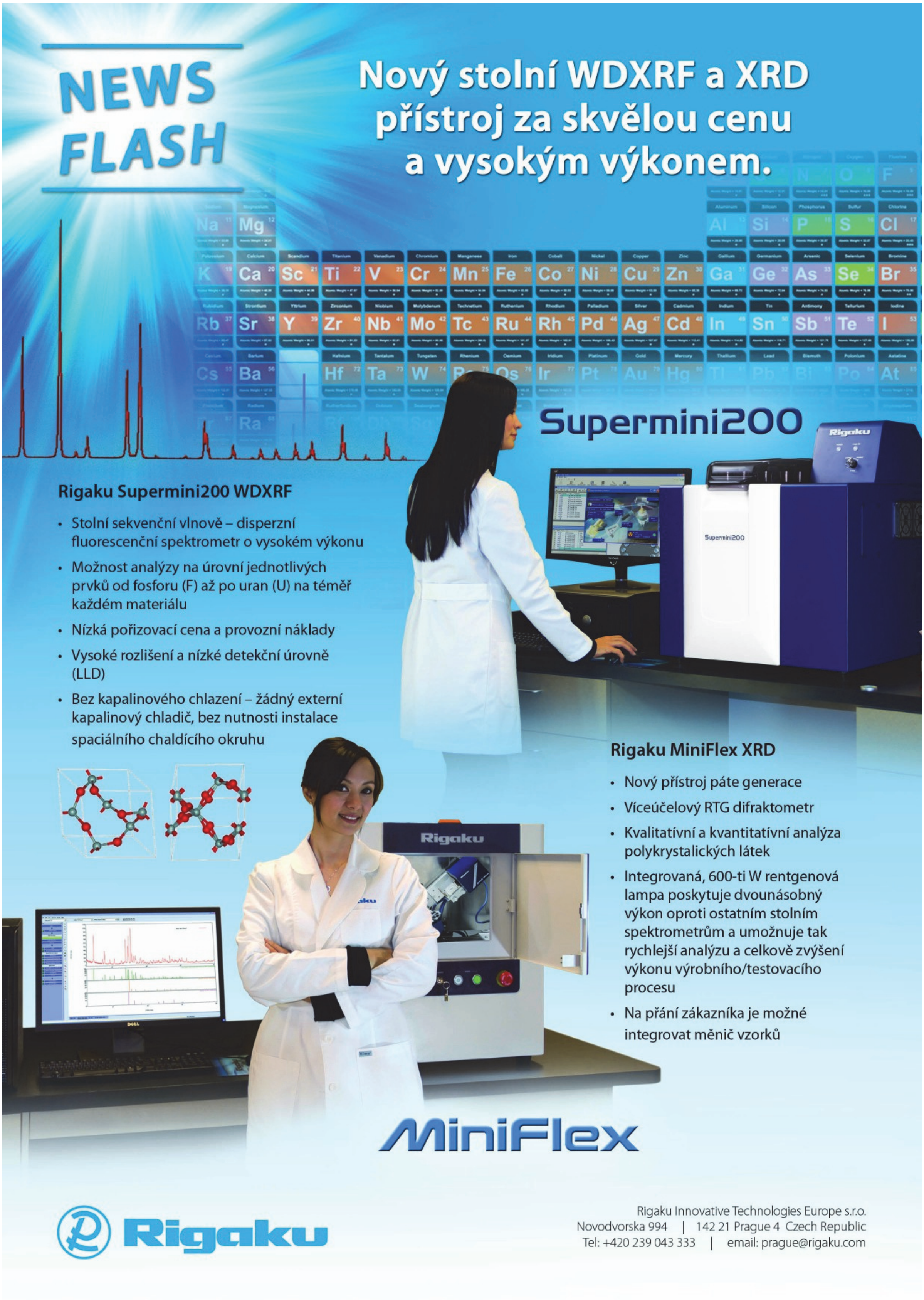
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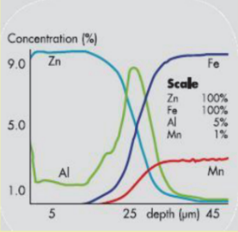
Concentration (%)
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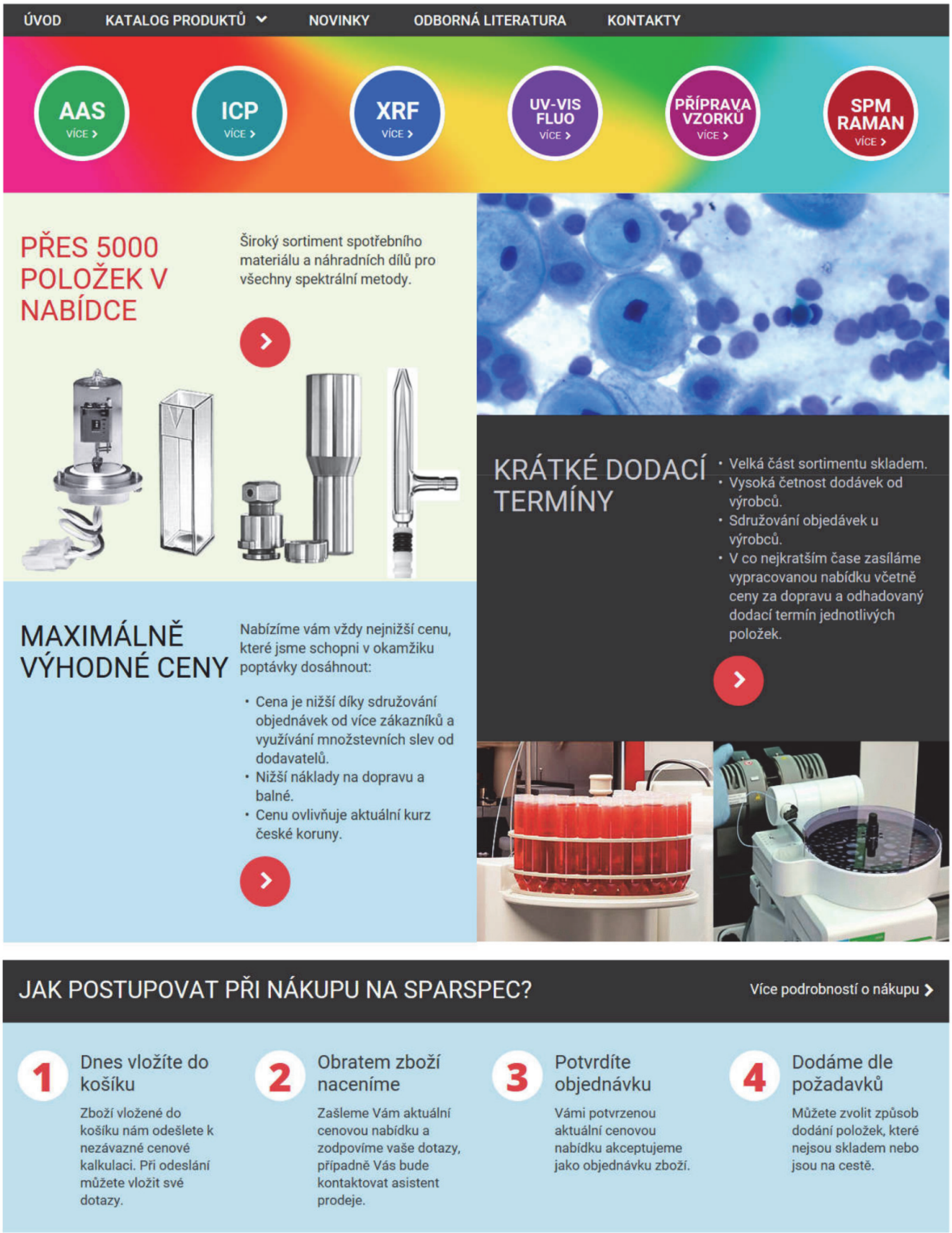
5.0
1.0
Zn
Fe
Al
Mn
Scale
Zn 100%
Fe 100%
Al 5%
Mn 1%
5
25
depth (µm)
45



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