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9th CHEMISTRY CONFERENCE

Plovdiv
14-16 October 2011
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BioSupport

WORKSHOP
"Trace Components Analysis in Foods"

Book of abstracts

University of Plovdiv "Paisii Hilendarski"
24, Tsar Assen St., 4000 Plovdiv – Bulgaria

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A G E N D A

Thursday 13 October 2011

Arrival of the foreign participants:

Meeting point at Sofia Airport, transport to Plovdiv and accommodation in the hotels

Friday 14 October 2011

6^{-th} *AUDITORIUM, Rectorate building of the University of Plovdiv*

09:00 –16:00	Exhibition of the 9CC sponsors – advertising materials will be provided

MORNING SESSION

09:00 –13:30	Registration of the participants in 9CC and BioSupport Workshop
10:00 – 11:30	**Assoc. Prof. Iliyan Ivanov- Dean of the Faculty of Chemistry** Conference opening **Assoc. Prof. Zapryan Kozludzhov** **Rector of the University of Plovdiv “Paisii Hilendarski”** Ceremony for awarding Prof. Antonio Canals with the honorary degree of *“Doctor Honoris Causa”* of University of Plovdiv
11:30 – 11:45	**Prof. Ivan Minkov** – BioSupport project Coordinator
12:00 – 13:00	*Official cocktail*

AFTERNOON SESSION

Chairmen **Assoc. Prof. V. Kmetov**		**PLENARY LECTURES - FIRST BLOCK**
14:00 – 14:30	**L1**	**Prof. Antonio Canals** – *University of Alicante* ***Green analytical methodologies: advances in liquid-liquid microextraction and detection methods***
14:30 – 15:00	**L2**	**Prof. Mark Moloney –** *University of Oxford* ***Oxazolomycins and equisetins: natural product lead structures for novel antibiotics***
		Coffee Break
15:30 – 16:00	**L3**	**Prof. Kurt Varmuza –** *Vienna University of Technology* ***Evaluation of empirical models in chemistry***
16:00 – 16:30	**L4**	**Prof. Tsonko Kolev –** *University of Plovdiv* ***New structural motifs of squaric acid derivatives of amino acids, amino acid amides and diamides***
20:00		***9CC Dinner***

Saturday 15 October 2011

MORNING SESSION ***Building of the Union of Scientist in Bulgaria - Plovdiv, 6 Mitropolit Paissii Str.***		
10:00 – 12:30		***POSTER SESSION*** *and* Exhibition of the 9CC sponsors – advertising materials will be provided
AFTERNOON SESSION ***Conference Room , Rectorate building of the University of Plovdiv***		
Chairmen **Assoc. Prof. V. Stefanova**		**PLENARY LECTURES - SECOND BLOCK**
13:30 – 13:45		**Assoc. Prof. V. Kmetov –** *University of Plovdiv* ***Session opening, Presentation of the Food and Bioproducts Analysis Group in the BioSupport***
13:45 – 14:00		**Iliana Vatova –** Manager Analytical Center **KOMICHRIS**
14:00 – 14:30	**L5**	**Prof. Erwin Rosenberg** – Vienna University of Technology ***Taking chromatography to higher dimensions***
14:30 – 15:00	**L6**	**Dr. Christoph Puls** – *Vienna University of Technology* ***Bioavailability of anthropogenic platinum group emissions***
		Coffee Break
15:30 – 16:00	**L7**	**Dr. Lorena Vidal –** *University of Helsinki* ***Imidazolium ionic liquid-functionalized silica as sorbent for solid-phase extraction of organic acids, amines and aldehydes***
16:00 – 16:30	**L8**	**Dr. Dimitar Hristozov** – *U.S. Food and Drug Administration* ***Developing and institutional knowledge-base at U.S. FDA's center for food safety and applied nutrition***

Sunday 16 October 2011

Dep. of Analytical Chemistry and Computer Chemistry, University of Plovdiv

10:00 – 12:00	***Round table of the BioSupport partners***
12:00	***Closing of 9CC and BioSupport Workshop***
	Departure of the foreign participants – transport to Sofia Airport

Plenary

Lectures

LECTURE 1

GREEN ANALYTICAL METHODOLOGIES: ADVANCES IN LIQUID-LIQUID MICROEXTRACTION AND DETECTION METHODS

A. Canals

Department of Analytical Chemistry and Food Sciences, and Institute of Materials, University of Alicante, P.O. Box 99, Alicante, E-03080, Spain
E-mail: a.canals@ua.es

Sample preparation is still critical in analytical laboratories. Although significant and promising advances have been suggested for this step of the Total Analytical Process (TAP) during the last few years, sample preparation is still the “Achilles’ Heel” of TAP and strong efforts and money investments should be made by the researchers. Extraction techniques have a dominant place among the sample preparation methodologies, and more specifically liquid-liquid extraction (LLE) and solid-phase extraction (SPE). Nevertheless, classical LLE and SPE show some important drawbacks.

Miniaturization is an important trend in chemical analysis but so far it has shown more influence on sample preparation than on detection techniques.
Recent contributions of miniaturization on liquid-liquid extraction (i.e., liquid-liquid microextraction, LLME) will be presented. Up to now LLME has been mostly associated with chromatographic techniques, but we need instrumentation and methodologies that can be used directly on the sampling place since in the most of the cases a rapid response could be critical. Therefore, new possibilities of detection will be presented. Finally, some examples of environmental or social applications will be presented and discussed.

Acknowledgements: *The current studies were financially supported by: MEC of Spain Project CTQ2008-06730-C02-01; NSF of Bulgaria – Project DO 02-70 (GAMA) and EC 7FP Project 245588 (BioSupport).*

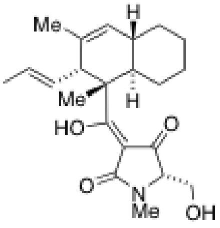
LECTURE 2

OXAZOLOMYCINS AND EQUISETINS: NATURAL PRODUCT LEAD STRUCTURES FOR NOVEL ANTIBIOTICS

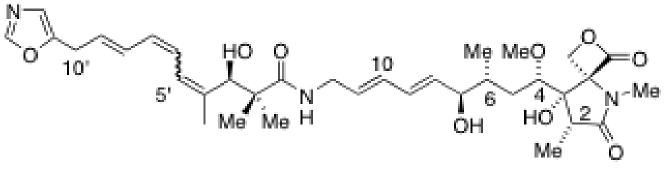
Mark G. Moloney

University of Oxford, Department of Chemistry,
Chemistry Research Laboratory, Mansfield Rd.
E-mail: mark.moloney@chem.ox.ac.uk

The discovery of new antibiotics has become urgent as a result of the emergence of resistance and new pathogenic bacterial strains. However, this need has coincided with unprecedented lowering of levels of productivity in the drug discovery process and consequent reduced investment from large pharma. New strategies for antibacterial drug discovery are required, and a renewed understanding of the value of a natural products' guided approach has emerged. Our focus has been on the use of antibacterial natural products containing pyrrolidine core structures, and using oxazolomycin and equisetin as inspiration, we have developed novel chemistry that uses suitable serine- and threonine-derived oxazolidine templates for highly chemo- and diasteroselective ring closure reactions leading to tetramic acid and pyroglutamate derivatives.[1-6] Moreover, by adopting a strategy of fragment-based synthesis, we have been able to identify several compounds which possess high levels of antibacterial activity, although of interest is that simple unsubstituted pyrrolidines and tetramates appear to be intrinsically devoid of activity.



Equisetin



Oxazolomycin A (4'Z,6'Z,8'E)

This lecture will illustrate the potential of natural products to guide antibacterial drug discovery, the role of synthetic organic chemistry in the construction of libraries which mimic these natural products, and suggest a possible way forward for more efficient drug discovery strategies.

References

1. M. G. Moloney, P. C. Trippier, M. Yaqoob and Z. Wang, *Curr. Drug Discovery Technol.*, 2004, **1**, 181-199.
2. M. Anwar and M. G. Moloney, *Tetrahedron Lett.*, 2007, 48, 7259–7262.
3. M. D. Andrews, A. G. Brewster and M. G. Moloney, *Synlett*, 1996, 612-614.
4. M. D. Andrews, A. G. Brewster, K. M. Crapnell, A. J. Ibbett, T. Jones, M. G. Moloney, C. K. Prout and D. Watkin, *J. Chem. Soc., Perkin Trans. 1*, 1998, 223-235.
5. Z. Y. Wang and M. G. Moloney, *Tetrahedron Lett.*, 2002, **43**, 9629-9632.
6. P. G. Bulger, M. G. Moloney and P. C. Trippier, *Org. Biomol. Chem.*, 2003, **1**, 3726-3737.

LECTURE 3

EVALUATION OF EMPIRICAL MODELS IN CHEMISTRY

K. Varmuza

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Relationships between data sets in chemistry can not always be described by theoretical concepts. Often empirical mathematical models are developed for estimating a desired property (y) from available data (x). Examples are, e.g., modeling the concentration of a substance in a complex mixture by spectral data (IR, NIR), or estimation of substance properties from molecular descriptors (QSAR, QSPR), or classification of the origin of a sample from chemical-analytical data. For such problems multivariate data analysis methods (chemometric methods [1]) are very powerful for the generation of models that relate y with a rather large number of x- data. A short and user-oriented overview will be given about the most common methods for multivariate calibration and classification. Much emphasize will be given on strategies for a proper evaluation of the performance of empirical models if applied to new cases. Appropriate evaluation methods are based on cross validation and bootstrap. The approach “repeated double cross validation” [2] will be discussed with practical examples for calibration and classification; furthermore information will be given about a free and easy use of the method by available software in R [3].

References

[1] K. Varmuza, P. Filzmoser, Introduction to multivariate statistical analysis in chemometrics. CRC Press, Boca Raton, FL, 2009.
[2] P. Filzmoser, B. Liebmann, K. Varmuza, J. Chemom. 23 (2009) 160-171.
[3] R, A language and environment for statistical computing. R Development Core Team, Foundation for Statistical Computing, www.r-project.org, Vienna, Austria, 2011.

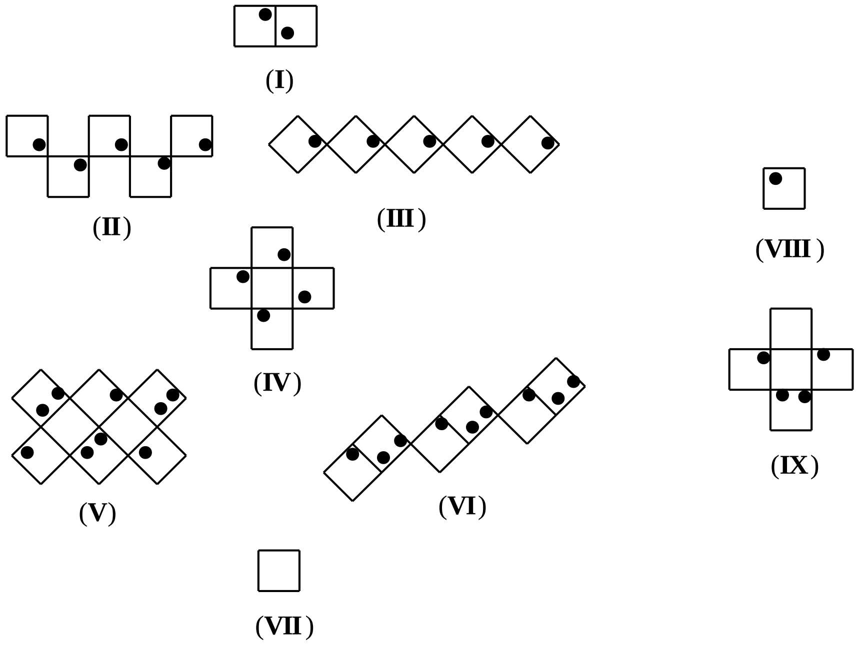
LECTURE 4

NEW STRUCTURAL MOTIFS OF SQUARIC ACID DERIVATIVES OF AMINO ACIDS, AMINO ACID AMIDES AND DIAMIDES

Tsonko Kolev

Plovdiv University "P. Hilendarski", Department of Organic Chemistry, 4000 Plovdiv

Design of new materials with second order nonlinear optical (NLO) properties in the bulk requires a strategy for obtaining noncentrosymmetric crystals and the employment of chiral agents (*e.g.* chiral counter ions) is a powerful technique for obtaining such crystals. Considerable progress has been made in recent years by controlling the assembly of individual molecules in solids, using hydrogen bonding as a powerful non-covalent force for organizing organic molecules. Some new structural motifs of squaric acid derivatives of amino acids, amino acid amides and diamides have been described and presented. The structural motifs are shown in the following schemas.



Squaric acid (H_2Sq) provides an attractive template for generating tightly hydrogen bonded self-assemblies from polarizable cations in general and basic amino acids in particular. The following self-assembly patterns of squaric acid itself and its anions HSq^- and Sq^{2-} have been identified up to know in crystal structures: (HSq^-) α-dimers (**I**), HSq^- α- and β-chains ((**II**) and (**III**), HSq^- anion tetramers (**IV**), $H_2Sq.HSq^-$ double β-chains (**V**) and chains of α-dimers (**VI**), as well as the isolated (Sq^{2-}) dianion (**VII**). It is reasonable to expect that a further systematic variation of the counterion in salts of the HSq^- and/or Sq^{2-} anions should lead to the isolation of additional novel self-assembly motifs and that these could exhibit interesting optical and/or nonlinear optical properties.

LECTURE 5

TAKING CHROMATOGRAPHY TO HIGHER DIMENSIONS

S. Drozdova, A. Nagl, L. Ramopoulou, E. Rosenberg

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The complexity of today's analytical problems poses an enormous challenge to analytical methods and instrumentation. The quest for higher sensitivity, selectivity, and resolution has not only been the motivation to improve analytical instrumentation, but has also led to the development of new analytical concepts.

In chromatography, separation efficiency can be enormously increased if leaving the one-dimensional separation space and going to two-dimensional (2D) separations [1,2]. In the ideal case, the separation efficiency of two-dimensional separations, expressed as the number of peaks that can theoretically be separated (= the peak capacity), is the product of the peak capacities of each separation dimension. It is thus possible even with columns that have relatively limited peak capacity (e.g. 20 to 30 in HPLC) to achieve the separation of several hundred compounds. This contribution will discuss how such two-dimensional separations can be achieved in gas- and liquid chromatography, and how experimental conditions have to be optimized to provide optimum performance.

It will become evident that none of the currently existing 2D-GC- or 2D-HPLC systems is capable of fully exploiting the separation space offered in two-dimensional separations. The practical limitations are in the limited availability of stationary phases that are sufficiently different (orthogonal) for HPLC and GC, and in the mobile phase (in-)compatibility for HPLC. Moreover, achieving the optimum chromatographic performance of such a complex system is not straightforward and requires expert judgment, and in part also an empirical approach since theory is not completely developed to describe two-dimensional separations.

This presentation will discuss the potential and pitfalls of two-dimensional gas- and liquid chromatography, illustrated with examples of complex samples, such as biofluids or environmental samples

Acknowledgements: *The authors thankfully acknowledge the financial support from the Austrian Science Fund – FFG (Project Nr.: 818084/16604) and EC 7FP Project 245588 (BioSupport).*

References

[1] L. Mondello, A.C. Lewis, K.D. Bartle, *Multidimensional Chromatography.* Wiley & Sons, London (2002).
[2] M.-L. Riekkola, Editorial for Special Issue on Multidimensional separations in analytical chemistry. *Anal. Bioanal. Chem.*, 378 (2004) 1935
[3] S.A. Cohen, M.R. Schure (eds.), *Multidimensional Liquid Chromatography.* Wiley & Sons, Hoboken, NJ (2008).

LECTURE 6

BIOAVAILABILITY OF ANTHROPOGENIC PLATINUM GROUP EMISSIONS

C. Puls, E. Herincs, W. Nischkauer, A. Limbeck

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Increasing usage of Platinum group elements (PGE) for medical purposes and as catalyst material in industrial synthesis and especially for pollutant reduction in automotive vehicles has lead to significant emission in the environment. As a consequence, quantification and determination of the environmental fate of PGE has gained in importance, especially concerning traffic-related emission, mobility, accumulation in the biosphere and potential toxicity [1].

Due to the low abundance of PGE in environmental samples, quantification via ICP-MS has to be considered state of the art. Nevertheless, this technique requires elaborate sample preparation techniques to reduce occurring matrix-related interferences and provide pre-concentration of analytes [2]. For removal of organic matrix components different microwave digestion and MW-assisted UV-digestion techniques are employed, whereas ionic interferences are reduced via solid phase extraction using either packed sorbents or functionalized nano-particles, thus enabling accurate and interference-free quantification.

To gain insight into environmental behavior of PGE, different *in vitro* approaches were used to evaluate bioaccessibility of PGE found in urban aerosol samples and uptake of PGE in various types of soil. Greenhouse experiments using hydroponic setups of *Brassica napus* were conducted to evaluate the uptake of dissolved PGE salts into roots and shoots.

Acknowledgements: *The authors thankfully acknowledge the financial support from the Austrian Science Fund - FWF (Project Nr.: P20838-N17) and EC 7FP Project 245588 (BioSupport).*

References:

[4] K. Ravindra, L. Bencs, R. Van Grieken, *Sci. Tot. Environ.* 318 (2004) 1-43
[5] K.H. Ek, G.M. Morrison, S. Rauch *Sci. Tot. Environ.* 334-335 (2004) 21-38.
[6] L. Bencs, K. Ravindra, R. Van Grieken, *Spectrochim. Acta B* 58 (2003) 1723-1755.

LECTURE 7

IMIDAZOLIUM IONIC LIQUID-FUNCTIONALIZED SILICA AS SORBENT FOR SOLID-PHASE EXTRACTION OF ORGANIC ACIDS, AMINES AND ALDEHYDES

L. Vidal[1,2], J. Parshintsev[1], K. Hartonen[1], A. Canals[2], M.-L. Riekkola[1]

[1] Laboratory of Analytical Chemistry, Department of Chemistry, P.O. Box 55, University of Helsinki, Helsinki FI-00014, Finland, lorena.vidal@helsinki.fi
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Ionic liquids, considered "green" chemicals, are widely used in many areas of analytical chemistry due to their unique properties [1]. Recently, ionic liquids have been combined with silica to synthesize new sorbent material. The ionic liquid modified silica materials offer a novel method for examining the intermolecular interaction in retention processes while simultaneously offering the potential to solve some of the most challenging problems confronting analytical separations/extractions. These new sorbents show a dual nature, acting as low-polarity phases with non-polar compounds as well as in the opposite manner for compounds bearing strong proton-donor groups [2,3].

In the present work, a functionalized imidazolium ionic liquid on silica gel (60-200 μm) has been used as a sorbent for solid-phase extraction of organic acids, amines and aldehydes, all important compound families in the atmospheric aerosol particles. Cartridges packed with the synthetic material have been successfully applied to the extraction of six organic acids (azelaic, adipic, vanilic sebacic, *cis*-pinonic and pinic), three amines (triethylamine, quinoline and tripropylamine) and two aldehydes (cinnamaldehyde and β-caryophyllene aldehyde). The three groups of analytes have been separated and detected by liquid chromatography-mass spectrometry (LC-MS).

A pH study (2-12) has been done in order to determine the retention mechanism for each group of analytes. Besides, a stability study at pH 2, 8, 10 and 12 for 24 hours has been carried out and, from the results, it can be confirmed that this material is stable at extreme pH values without losing extraction properties.

The modified-material results have been also compared with those obtained with two SPE commercial cartridges, such as a silica-based strong anion exchange (SAX) and a polymer-based mixed-mode anion exchange and reverse-phase (MAX). The results obtained show the potential of the modified material.

Acknowledgements: *The authors would like to thank the Academy of Finland Centre of Excellence program 493 (project no 1141135) for financial support. L.V. also thanks Generalitat Valenciana (Spain) for her post doctoral grant and EC 7FP Project 245588 (BioSupport) for financial support.*

References

[1] P. Sun, D.W. Armstrong, *Anal. Chim. Acta,* 661 (2010) 1-16.
[2] Y. Wang, M. Tan, W. Bi, K.H. Row, *Int. J. Mol. Sci.,* 10 (2009) 2591-2610.
[3] D. Han, K.H. Row, *Molecules,* 15 (2010) 2405-2426.

LECTURE 8

DEVELOPING AND INSTITUTIONAL KNOWLEDGE-BASE AT U.S. FDA'S CENTER FOR FOOD SAFETY AND APPLIED NUTRITION

Dimitar Hristozov[1], Annette McCarthy[1], Chihae Yang[2], Kirk B. Arvidson[1]

[1] U.S. Food and Drug Administration (FDA), Center for Food Safety and Applied Nutrition (CFSAN), Office of Food Additive Safety (OFAS)
E-mail: mitkohr@yahoo.com
[2] The Ohio State University, Columbus, Ohio

The Chemical Evaluation and Risk Estimation System (CERES) project under development in FDA's Center for Food Safety and Applied Nutrition (CFSAN) aims at establishing a sustainable data management and storage system that will provide decision support tools for both pre- and post-market safety assessments of food additives and food contact substances as well as for potential contamination issues. The development of CERES will provide a single unified data repository that compiles all available information on a substance, including: chemical structure and properties, regulation records, toxicity studies, and other biological screening assays. In cases where no information is available for a particular substance, CERES provides tools to identify potential safety concerns by applying mode of action-driven QSAR prediction models as well as to identify and analyze data on structural and biological analogs (read-across). To achieve this goal, CERES requires a solid foundation for handling chemical and toxicity data as well as knowledge (e.g., rules or computational toxicology models) derived from these data. Thus the CERES project not only needs to address a wide variety of issues in database and knowledgebase construction but also in the development of computational methods.

Acknowledgements: *The authors would like to thank molecular Networks GmbH for making their MOSES chemoinformatics platform available as well as their help in developing and supporting the CERES system. We would also like to thank the U.S. EPA NCCT and Leadscope, Inc for making their data entry tools available to the FDA. DH would like to thank EC 7FP Project 245588 (BioSupport) for financial support.*

Poster session

P-1

MECHANOCHEMISTRY IN THE PREPARATION OF NANOCRYSTALLINE OXIDES

M. Fabián[1], A. Kremenovic[2], B. Antic[2], N. Kostova[3], S. Suzuki[4], V. Šepelák[5]

[1]Institute of Geotechnics, Slovak Academy of Sciences, Kosice, Slovakia
[2]Institute of Nuclear Sciences "Vinča", Belgrade, Serbia
[3]Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, Bulgaria
[4]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan
[5]Institute of Nanotechnology, Karlsruhe Institute of Technology, Karlsruhe, Germany
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The properties of nanomaterials are sensitive to microstructural and structural parameters, which in turn strongly depend on the preparation method. There is a challenge to improve physical performance (magnetization, coercivity, conductivity, photoluminescence, etc.) by varying microstructural parameters (such as particle size and shape, strain and their anisotropy) using new or modified synthesis procedures. Among the many types of preparation techniques, the nonconventional mechanochemical synthesis has been recognized as a powerful route to novel, high-performance and low-cost nanomaterials.

This work is focused on the characterization of nanocrystalline oxides prepared by high energy ball milling. Structural and microstructural parameters of as-prepared samples have been investigated by various methods such as X-ray diffraction, nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy and transmission electron microscopy. To analyse the microstructural parameters (crystalline size and strain), the full-profile analysis, Warren-Averbach and simplified integral breadth method were used. The correlation between particular methods used for local structure investigation of nanocrystalline oxides have been discussed.

Acknowledgements: *The present work was supported by the „Japan Society for the Promotion of Science“. Partial support by the Slovak Research and Development Agency (Grant SK-SRB 0019-09), the Scientific Agency of the Ministry of Education of the Slovak Republic and of the Slovak Academy of Sciences (Grant VEGA 2/0139/10) and bilateral project "Multifunctional materials prepared by mechanochemical reactions" between the Slovak Academy of Sciences and the Bulgarian Academy of Sciences is gratefully acknowledged.*

P-2

TERNARY ION-ASSOCIATION COMPLEXES BETWEEN THE INDIUM(III) – 4-(2-PYRIDYLAZO)RESORCINOL ANIONIC CHELATE AND SOME TETRAZOLIUM CATIONS*

Galya Toncheva, Kiril Gavazov, Vanya Lekova, Kirila Stojnova, Atanas Dimitrov

University of Plovdiv, 24 Tsar Asen str., 4000 Plovdiv, Plovdiv, Bulgaria
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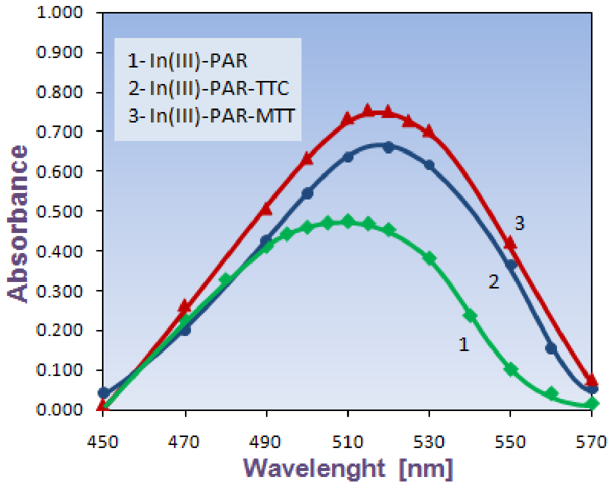
Complex formation and liquid-liquid extraction have been studied in systems containing indium(III), 4-(2-pyridylazo)resorcinol (PAR), tetrazolium salt (TZS), water and chloroform. Two different TZS have been used: 2,3,5-triphenyl-2H-tetrazolium chloride (TTC) and 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide (MTT). The optimum conditions for extraction of In(III) as a ternary complex, $(TT^+)[In(PAR)_2]$ or $(MTT^+)[In(PAR)_2]$, have been found: pH, extraction time, concentration of PAR and concentration of TZS. The constants of extraction (K_{ex}), constants of association (β), constants of distribution (K_D) and recovery factors (R%) have been determined. The apparent molar absorptivities in chloroform have been calculated to be $\varepsilon'_{520}=6.6\times10^4$ L mol^{-1} cm^{-1} and $\varepsilon'_{515}=7.1\times10^4$ L mol^{-1} cm^{-1} for the systems with TTC (**I**) and MTT (**II**), respectively. Beer's law is obeyed for In(III) concentrations up to 3.4 µg mL^{-1} in both the cases. The limits of detection (LOD=0.07 µg mL^{-1} **I** and LOD=0.12 µg mL^{-1} **II**), limits of quantification (LOQ=0.24 µg mL^{-1} **I** and LOQ=0.41 µg mL^{-1} **II**) and Sandell's sensitivities (SS) have been estimated as well.



Keywords: Indium, Liquid-liquid extraction, Spectrophotometry, Triphenyltetrazolium, Thiazolyl Blue Tetrazolium, Azocompound

* The original publication is available at www.springerlink.com
G.K. Toncheva, K.B. Gavazov, V.D. Lekova, K.T. Stojnova, A.N. Dimitrov, *Cent. Eur. J. Chem.*, 9(6), 2011, 1143-1149, DOI: 10.2478/s11532-011-0101-z

Acknowledgements: *The authors are grateful to the Research Fund of the Plovdiv University for the financial support (Grant No NI11-HF-007).*

P-3

COMPLEX FORMATION IN A LIQUID-LIQUID EXTRACTION SYSTEM CONTAINING GALLIUM(III), 4-(2-PYRIDYLAZO)RESORCINOL AND 2,3,5-TRIPHENYL-2H-TETRAZOLIUM CHLORIDE

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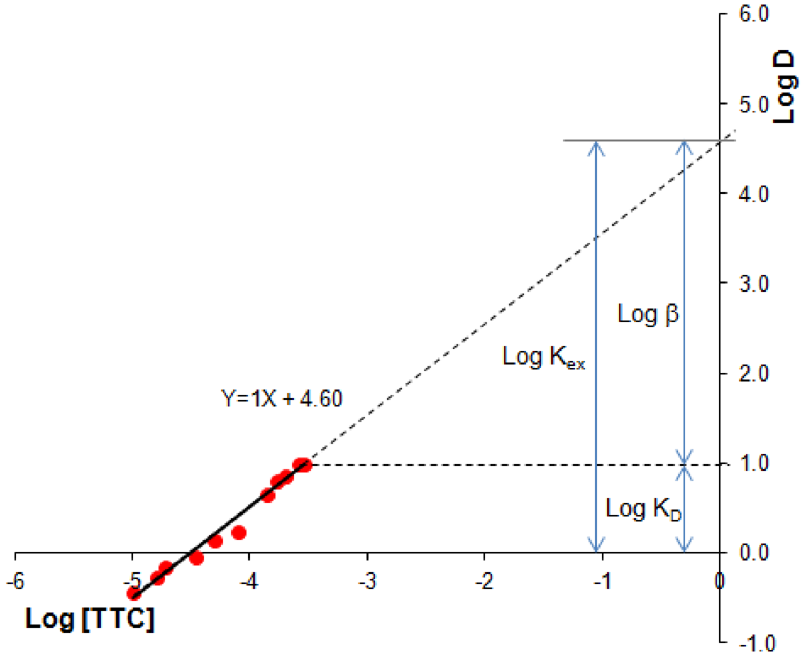
Complex formation and liquid-liquid extraction have been studied in a system containing gallium(III), 4-(2-pyridylazo)resorcinol (PAR), 2,3,5-triphenyl-2H-tetrazolium chloride (TTC), water and chloroform. The optimum conditions for the extraction of Ga(III) as an ion-associate complex $(TT^{+})[Ga(PAR)_2]$ between the gallium(III) – PAR anionic chelate and the cation of TTC have been found: pH, extraction time, concentration of PAR and concentration of TTC. The constant of extraction, constant of association, constant of distribution and recovery factor have been determined. The apparent molar absorptivity in chloroform has been calculated to be $\varepsilon'_{510}=9.5\times10^{4}$ L mol^{-1} cm^{-1}. Beer's law is obeyed for Ga(III) concentrations up to 1.1 µg mL^{-1}. The limits of detection and quantification (LOQ=0.03 µg mL^{-1} and LOQ=0.10 µg mL^{-1}, respectively) have been estimated. The effect of foreign ions and reagents on the exstraction-spectrophotometric determination of Ga(III) has been studied as well.



Keywords: Gallium, Liquid-liquid extraction, Spectrophotometry, Triphenyltetrazolium, Azocompound

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P-4

NEW METAL COMPLEXES OF THE 2-CINNAMOYL-1,3-INDANDIONE

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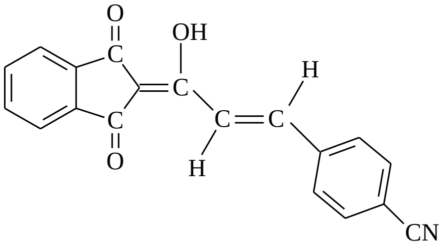
The photophysical properties of 2-substituted 1,3-indandiones are of increasing interest because of the possible phototautomerisaton via Excited State Intramolecular Proton Transfer (ESIPT) process as well as their application as polymer stabilizers and sunscreen agents. Only few data of absorption properties (in solution and solid state) for some 2-cinnamoyl-1,3-indandiones are available. These compounds contain a β–dicarbonyl fragment, which makes them suitable for complexation with metal ions, thus opening up the possibility for practical applications. There are already few spectrophotometric studies on the complexation of some 2-acyl-derivatives of 1,3-indadione, based on which some of them have been suggested as extracting agents for Fe(III) ions.

Subject of the current study is a series of metal complexes of 2-substituted 1,3-indandione as shown in the figure below.



The complexation properties of the compound towards Cu(II), Ni(II), Zn(II), Co(II) and Cd(II) were studied. The isolated complexes were further examined by means of elemental analyses, IR, UV-Vis spectroscopy and EPR spectroscopy for the Cu(II) complexes. The structure of the new obtained complexes is discussed on the basis of the various data.

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P-5

DEVELOPMENT OF AN ULTRASOUND-ASSISTED LIQUID-LIQUID MICROEXTRACTION PROCEDURE FOR STEROID SEX HORMONES BEFORE LIQUID CHROMATOGRAPHIC ANALYSIS

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The endocrine disrupting compounds (EDCs) become an issue of priority concern because their presence in the environmental waters, threat to drinking water, and concern about possible estrogenic and other effects, both to wildlife and humans. Steroid sex hormones which are part of oral contraceptives are one kind of EDCs considered as emerging pollutants for the potential to exert estrogenic effects at low ng/L level. Hence some steroid sex hormones have been included recently in revision of the list of priority substances within the EU water framework directive (2000) and the priority drinking water contaminants within U.S. EPA's final CCL-3 (2009) [1].

A recent trend in sample preparation is solvent microextraction which represents a miniaturization of the traditional liquid-liquid extraction (LLE) procedure whereby the solvent-aqueous volume phase ratio is greatly reduced. The applicability of a new sampling mode, ultrasound-assisted liquid-liquid microextraction (USALLME), has been investigated on this work. Basically, an ultrasonic probe has been used for dispersing a microvolume of octanol in cloudy solution of fine droplets favouring the mass transfer of target analytes to the organic phase [2]. Then a centrifugation step (2 min at 3000 rpm) is performed in order to retrieve the maximum amount of the dispersed octanol phase and recovered with the help of a chromatographic microsyringe for the HPLC analysis. Experimental parameters such as extraction solvent, ionic strength of the solution, acceptor phase volume, sample volume and sonication time have been optimized. The developed method yield high enrichment factors providing an alternative to the EPA method 539 based on traditional SPE and LC-MS-MS.

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References

[1] S.D. Richardson, T.A. Ternes, *Anal. Chem.*, 83 (2011) 4614–4648
[2] A. Papadopoulou, I.P. Roman, A. Canals, K. Tyrovola, E. Psillakis, *Anal. Chim. Acta*, 691 (2011) 56-61.

P-6

VORTEX OR ULTRASOUND ASSISTED IN-SITU DERIVATIZATION AND LIQUID-LIQUID MICROEXTRACTION OF ORGANOTIN COMPOUNDS, FOLLOWED BY GCMS ANALYSIS

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In the past 20 years organotin compounds (OTs) have been widely used as active components in antifouling paints and pesticide formulations, as well as additives for thermal and light stabilization in the plastic industry. The interest in speciation is due to the awareness of their toxicity for mammalian and aquatic organisms. Their high environmental persistence and ability to transfer along the trophic chains depend on the chemical structure. OTs can cause changes in the endocrine system such as the occurrence of imposex in gastropods, which can lead to sterilization and death of the affected organisms [1]. OTs can enter the food chain by accumulation in different marine species and plants.

A vortex-assisted liquid-liquid microextraction (VALLME) [2] and an ultrasound-assisted liquid-liquid microextraction both with in-situ derivatization followed by gas chromatography mass spectrometry have been developed for the simultaneous speciation analysis of nine OTs, including methyl-, butyl-, phenyltin compounds. Two different derivatization reagents were tested: sodium tetraethyl borate and potassium tetrakis(4-chlorophenyl)borate. Potassium tetrakis(4-chlorophenyl) borate was selected as derivatization reagent because both volatile and semivolatile OTs can be analized simultaneously, without the need of two different extraction techniques. The obtained derivative compounds have not been reported before so their spectra were not included in the library of GC-MS instrument up to now. The high boiling points of chloro-phenyl-derivatives of all the OTs studied allow their determination. The detection limit values obtained with chlorophenylation have been improved compared to the ones obtained with ethylation due to the higher bond-dissociation energy of Sn-aryl than those of Sn-alkyl.

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References

[1] R. de Carvalho Oliveira, R. Erthal Santelli, *Talanta*, 82 (2010) 9-24.
[2] A. Papadopoulou, I.P.Roman, A. Canals, K.Tyrovola, E.Psillakis *Anal. Chim Acta*, 691 (2011) 56-61.

P-7

TRACE ELEMENTAL ANALYSIS BY LIQUID-LIQUID MICROEXTRACTION – LASER-INDUCED BREAKDOWN SPECTROMETRY

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During the last years, Laser-Induced Breakdown Spectrometry (LIBS) has shown its huge potential as an effective technique for fast multi-elemental analysis. LIBS analysis only needs optical access to the sample by means of a tightly focused laser beam, which allows just a very small quantity of sample to be analyzed with minimum risk of sample contamination. However, in spite of its numerous advantages, the low sensitivity of LIBS, when compared with other atomic spectrometric techniques (i.e., ICP-MS, ICP-OES or ETA-AAS), constitutes its most important limitation for (ultra)trace elemental analysis.

A common way to improve limits of detection is analyte preconcentration. To this end, several novel liquid-liquid microextraction techniques, such as cloud point extraction (CPE), single-drop microextraction (SDME) or dispersive liquid-liquid microextraction (DLLME) are nowadays extensively used for analyte preconcentration by using negligible volume of extractants, often hazardous and expensive.

Analyte preconcentration by liquid-liquid microextraction techniques results in a micro-volume of extractant to be analyzed, which can be easily performed by LIBS technique owing to its ability to interrogate extremely low quantities of material. However, direct LIBS analysis of liquids presents several drawbacks when compared with solid samples analysis, mainly due to problems associated with sample splashing or short plasma life-time.

In this work, the combination of LIBS with liquid-liquid microextraction techniques as a simple and fast method for trace elemental analysis is shown. To this end, a new LIBS methodology to analyze droplets of extractants generated from microextraction metodologies is presented. The experimental LIBS procedure consists on the generation of a laser-induced plasma by laser irradiation of microdroplets deposited on a solid sample support. The use of solids substrates minimizes the drawbacks associated with the analysis of liquids and enhances LIBS sensitivity. The proposed methodology was applied to the elemental analysis of micro-droplets having different extractant concentration and nature. The influence of the micro-sample matrix and the solid support material on LIBS analytical capability is presented and discussed.

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P-8

ELEMENTAL SPECIATION BY CAPILLARY ELECTROPHORESIS WITH INDUCTIVELY COUPLED PLASMA SPECTROMETRY: ENHANCEMENT BY FLOW FOCUSING® NEBULIZATION

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Capillary Electrophoresis (CE) is a powerful tool in elemental speciation because of its high separation capabilities and extremely low reagent/sample consumption. The latter, however, presents an important drawback when CE is coupled to Inductively Coupled Plasma (ICP) based atomic spectrometry due to liquid flow incompatibility (typically one order of magnitude lower for CE). Different solutions of this problem have been proposed and some of them have been commercialized. But despite of the advances, the analyte quantity introduced in the plasma after CE separation is still much lower than the ones from other separation techniques (chromatography, on-line solid phase extraction, etc.). Therefore, the detection limits obtained with the CE-ICP combination tend to be higher, which combined with its long analysis times, makes it unattractive for routine elemental speciation analyses.

In this work, a novel system for electrophoretic separation and ICP sample introduction is presented. In contrast to the typical CE that relies on electroosmosis to generate carrier/sample flow, the proposed system uses pneumatically generated liquid flow for carrier transport and sample injection. The main innovation is that the system incorporates a dedicated Flow-Focusing® based nebulizer as aerosol generation unit. These allows a significant increase in the liquid flow and the sample volume injected, aiming to achieve lower detection limits and analysis times while maintaining the use of aqueous solutions and very low sample consumption rates.

To prove its viability, the new system has been coupled to an ICP-optical emission spectrometer and an ICP-mass spectrometer for Cr(III) and Cr(VI) separation. System and operation parameters (i.e., capillary length, nebulizer geometry, carrier flow, carrier ionic strength, separation potential and sample injection volume) have been studied, and the analytical figures of merit obtained are presented. The developed instrumental system permits Cr speciation in less than one minute.

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P-9

APPLICATION OF BARE AND SILICA-COATED $MnFe_2O_4$ MAGNETIC NANOPARTICLES AS A SORBENT FOR SOLID PHASE EXTRACTION AND ICP-OES TRACE ELEMENTS DETERMINATION

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A new solid phase extraction (SPE) method based on $MnFe_2O_4$ magnetic nanosized sorbent material (MnNPs) is presented. Nanoparticles were synthesized by co-precipitation. A silica coated nanoparticles (SMnNPs) were obtained by a procedure[1] developed for $CoFe_2O_4$. Coated and bare sorbents were tested for SPE of ammonium pyrrolidine dithiocarbamate (APDC) complexes of V, Co, Cr, Ni, Cu, Zn, Pb and Cd.

The elution of elements was achieved by treatment with 7 mol.l^{-1} nitric acid at 25^{o}C for 10 min. The procedure was compared with a complete digestion for 4h (only for the MnNPs) with respect to the recovery and specific matrix effects in ICP-OES.

The high acid concentration leads to suppression of emission signals in the range - 25% (Cr, Co) to - 37% (Cd, Pb). Dilution prior instrumental analysis to 1.4 mol.l^{-1} nitric acid reduced the matrix effect by a factor of 3 to 5, but at the expense of the enrichment factor decrease. There were no spectral interferences observed for the SMnNPs eluates. In contrast in the case of bare MnNPs the obtained emission spectrum was significantly complicated due to Fe and Mn dissolved. Hence special attention should be paid to the line selection and spectral interferences.

In this study, at least two emission lines for each analyte were monitored. A spectral peak maximum was recomended for analytical data handling and necessary background corrections were suggested. The elution of non-modified MnNPs was preferred instead of total digestion to reduce the matrix effects.

Using SMnNPs quantitative recoveries were obtained for Co, Cu and Ni, while for other elements R% were in range 60% - 85%. For all analytes R%≥90% were achieved with the exception of Cd (R=72%) applying bare MnNPs.

At the optimized SPE conditions an enrichment factor of 10 was obtained. The proposed SPE-ICP-OES method allows detection limits decrease by factors 2-7 (SMnNPs) and 3-8 (MnNPs), in comparison to direct ICP-OES determination.

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Reference

[1] I. P. Román, A. Chisvert and A. Canals, *J. Chromatogr. A*, 1218, (2011) 2467-2475

P-10

SYNTHESIS AND APPLICABILITY OF GOLD NANOPARTICLES AS SORBENTS FOR TRACE ELEMENTS SOLID PHASE EXTRACTION COMBINED WITH ICP-MS ANALYSIS

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This research is focused on the suitable methods for synthesis of gold nanoparticles (AuNPs) and investigation of their applicability as sorbents for preliminary separation and pre-concentration of trace elements in solid phase extraction (SPE) followed by ICP-MS as a method for final detection. The synthesis was based on homogeneous reduction of $[AuCl_4]^-$ in water phase with three reducing agents: sodium citrate, hydrazinium sulphate and L-cysteine. Two kind of gold nanoparticles without surface layer as well as ones with surface layer were investigated as potential sorbents for SPE.

For studying of SPE, the measurement conditions for ICP-MS were optimized: spectral interferences were avoided via selection of suitable analyte isotope and/or collision cell application, while the method of internal standardization was applied for correction of non-spectral matrix effect and instrumental drift.

A survey was made on the influence of sample pH on the retention degree of 22 elements on the AuNPs surface. On this basis, the observed elements were divided into groups of similarity and for each group the optimum pH value, providing the highest analyte retention was suggested.

The best sorption efficiency for the majority of studied analytes were achieved with L-cysteine modified AuNPs, while the nanoparticles produced by reduction with hydrazinium sulphate showed better selectivity.

AuNPs with retained elements were completely separated from the initial sample solution via centrifugation. The elution was carried out with dilute nitric acid and corresponding analyte recoveries were calculated.

Quantitative comparison of the two main stages of phase distribution process – retention of analytes (assessed by degree of extraction on AuNPs) and restoration in the final solution for measurement (assessed by recovery), was made. These results were used to outline the research issues for further development of the study: 1) for the elements: Ag, Cd, Sn, Pb, Ga, Bi, Co, Pd, Cr, Hg, Ni, Pt, Be and Mn quantitative retention on AuNPs was achieved, but for some of them the elution with dilute nitric acid was incomplete; 2) for Cu, V, As, Rh, Tl, U, Se and Te the retention was only partial, hence the conditions influencing on the sorption process should be further optimized.

The results of this study proved that gold nanoparticles have a potential as a sorbent for solid phase extraction of trace elements in combination with ICP-MS analysis. By varying of the nanoparticles synthesis procedure and pH of the sample solution, during extraction, the effectiveness of analyte separation from the matrix and the target group of elements could be controlled.

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P-11

SIMULTANEOUS DETERMINATION OF P, S, K, OTHER ESSENTIAL AND TRACE ELEMENTS IN PLANT AND SOIL SAMPLES BY ICP-MS

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An ICP-MS method for simultaneous determination of S, P, K in plant and soil samples, appropriate for environmental screening analyses was developed. The digestion efficiency of 3 oxidative mixtures (HNO_3+H_2O_2; HNO_3+H_2O_2 + HF; HNO_3+HCl) and two dissolution procedures (microwave and hot plate) were studied. Very high background signals registered for all analyte isotopes have been reduced using helium as collision gas and less interfered ^{34}S, ^{39}K were proposed for measurement. The instrumental detection limits were used as a target function for optimization of the collision gas flow rate. The achieved detection limits for S, P were decreased two times, and the reduction of background signal for K led to ~3 times lower detection limit in comparison with the standard "No Gas" mode.

For correction of non spectral interferences, 4 potential internal standards were tested - Be, B, Rh and Cl. It was found that the best internal standard for S, P, K was Be, while Rh could be used only for K. The method of internal standard was found to be effective for correction of variable matrix effects and compensation of the sensitivity drift during long serial analyses of different plant and soil matrices.

The accuracy of the proposed method was demonstrated by analysis of 6 certified reference materials (CRM) for soils and 2 for plants - moss and poplar leaves and branches.

Under the optimized conditions for determination of S, P, K the method can be successfully expanded, allowing simultaneous determination of other 21 essential and trace elements in various plant and soil samples for ecological studies.

The developed method was applied for analysis of 90 real samples representing 4 different types of plants, studied as potential bioindicators.

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P-12

APPLICATION OF CLOUD POINT EXTRACTION FOR COMPLEX INVESTIGATION OF ORGANIC POLLUTANTS AND TRACE ELEMENTS IN CANNED FISH

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The application of non-hazardous reagents, energy efficiency and system miniaturization as principles of green chemistry [1] were used for development of environmentally benign cloud point extraction procedures for concentration of polycyclic aromatic hydrocarbons (PAHs) and inorganic species in canned fish.

Benzo(a)pyrene (BaP) was chosen as a representative of the PAHs. Water solution of Triton X-114 (2% w/w) was applied for both: to transfer the analyte from the sample matrix to a surfactant solution and to concentrate BaP by cloud point extraction (CPE). UV/VIS was used for detection at four wavelengths (348 nm, 367 nm, 386 nm, 403 nm). The CPE efficiency was studied by analyte spiking to the fish sample. A reproducible recovery of 45% and a preconcentration factor of six were achieved. These results were considered as promising and further studies will be carried out to combine the CPE procedure with GC-MS or HPLC for joint determination of several PAHs.

A microwave-assisted cloud point extraction (MW-CPE) [2] using Triton X-100 as surfactant and ammonium pyrrolidine dithiocarbamate as ligand was also tested for the mutual separation/concentration of V, Cr, Fe, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Te, Tl, Pb, Bi and U prior to ICP-MS analysis of canned fish. Reproducible spike recoveries from the sample matrix were obtained for Cr (79%), Fe (96%), Co (81%), Ni (84%), Cu (76%), Zn (74%), Cd (65%), Pb (69%) and Bi (80%) under the listed experimental conditions: i) extraction system - 40 ml, 7.5 pH, 0.5% w/v Triton X-100, 2500 : 1 molar ligand excess, 20 min incubation time and ii) dissolution of the surfactant-rich phase with 3 $\mathrm{mol.l^{-1}}$ HNO_3 to 10 g. The evolved MW-CPE-ICP-MS method was used for trace element analysis in fish samples obtaining the following detection limits (in ng/g): Cr (42), Fe (325), Co (2), Ni (28), Cu (6), Zn (18), Cd (3), Pb (11) and Bi (1). Method validation was made by direct ICP-MS analysis of the canned fish in which the non-spectral matrix effects were accounted by the method of standard addition while the spectral ones by application of octopole reaction cell using collision gas helium.

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References

[1] L. H. Keith, L. U. Gron, J. L. Young, *Chem. Rev.*, 107 (2007) 2695-2708
[2] K. Simitchiev , V. Stefanova , V. Kmetov , G. Andreev , N. Kovachev, A. Canals, *J. Anal. At. Spectrom.*, 23 (2008) 717-726.

P-13

DETERMINATION OF EXPLOSIVES IN WATER SAMPLES BY ULTRASOUND-ASSISTED DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOLLOWED BY GAS CHROMATOGRAPHY MASS SPECTROMETRY

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Over the past few years the interest on nitroaromatic explosives (NE) analysis has increased due to military activities, but specially for the continuous upsurge in terrorist activity. This has generated tremendous demand for innovative analytical tools capable of detecting these compounds. Extraction is often recommended before detection due to its low concentration or complicated matrices in the real samples. Conventional liquid-liquid extraction (LLE) and solid phase extraction (SPE) are the most commonly used methods of sample pretreatment for isolation and/or enrichment of nitroaromatic explosives. However, these techniques present many disadvantages, such as they use of large amounts of potentially toxic and normally expensive organic solvents, are time-consuming and so on. Therefore, efforts have been placed on the miniaturization of the SPE and LLE procedures to remove these disadvantages. Recently, a novel liquid-liquid microextraction technique, dispersive liquid-liquid microextraction (DLLME), was introduced by Rezaei et al.. This novel technique has the advantages of simplicity, rapidity, low sample volume, low cost, high recovery, and a high enrichment factor. However, the necessity of using a disperser solvent to disrupt the extractant phase on many microdroplets presents some drawbacks. One is the use of higher organic solvent quality, and other is the decreasing of the partition coefficient of analytes into the extractant solvent.

Sonochemistry is a growing topic in science and technology. Ultrasound energy can be used to produce very fine emulsions from immiscible liquids, which result in very large interfacial contact areas between the liquids and a corresponding dramatic increase in the mass transfer between two immiscible phases.Therefore, the main aim of this work was to develop a new, simple, rapid, inexpensive, sensitive, and efficient ultrasound-assisted dispersive liquid-liquid microextraction (DUSA-DLLME) method for extraction of NE’s (nitrobenzene, 2-nitrotoluene, 2,6-dinitrotoluene, trinitrotoluene and 2-ADNT) from aqueous matrices. Separation and detection were carried out on gas chromatography-mass spectrometry (GC-MS). In this method an ultrasonic probe (i.e., sonotrode) was used, directly introduced into the sample, disrupting the extractant phase on many microdroplets, and therefore, increasing the efficiency of energy transmission and avoiding the use of a disperser solvent. The method was optimized by experimental design, validated and applied to “real world” water samples.

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P-14

Cu(II)-IMPRINTED COPOLYMER GELS FOR SELECTIVE SEPARATION OF COPPER IONS FROM ENVIRONMENTAL SAMPLES

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Molecular and ion imprinted polymers (MIPs and IIPs) are synthetic polymeric materials with specific recognition sites complementary in shape, size and functional groups to the template molecule (ion), involving an interaction mechanism based on molecular recognition. Their stability, ease of preparation and low cost for most of the target analytes make them attractive for numerous applications in separation sciences, catalysis, molecular sensing, and drug delivery.

Cu(II) imprinted copolymers (Cu(II)-IIPs) using a Cu(II)-4-(2-pyridylazo)resorcinol (Cu-PAR) complex,or PAR only as the templates are prepared by non-covalent imprinting approach. The functional monomers used include the acidic and hydrogen binding methacrylic acid (MAA), the weakly basic 4-vinylpyridine (4-VP) or a combination of them.The chemical structure and morphology of the Cu(II)-imprinted microbeads were analyzed using elemental analysis, FTIR, and SEM. The separation and preconcentration characteristics of the IIPs for copper ions have been investigated by batch procedure. The optimal pH value for the quantitative preconcentration is 7, and full desorption is achieved by 2 M HNO_3 for 15 min. The maximum adsorption capacity and the relative selectivity coefficients of imprinted beads for Cu(II)/Cd(II), Cu(II)/Ni(II) and Cu(II)/Pb(II) were also calculated. The prepared with 4-VP and Cu-PAR complex copolymer gel has highest capacity than the copolymer gels prepared using the combination of MAA and 4-VP or MAA only and the non imprinted copolymers. It shows a metal ion affinity in the competitive conditions of Cu(II)>Ni(II)>Cd(II)>Pb(II). This new sorbent can be used as an effective solid-phase extraction material for the highly selective preconcentration and separation of Cu(II) in environmental samples.

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P-15

NEW SORBENTS FOR MERCURY SPECIATION

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The determination of mercury species in environmental samples is very important analytical task because all of them are toxic. Due to their trace amount and the influences of coexisting substances in real samples, the selective preconcentration and separation of mercury species are of great significance prior to analysis. The solid-phase extraction methods using ion-imprinted polymers (IIP-SPE) are the most popular methods for this aim.

In this study are presented the preparation and characterization of Hg(II) ion-imprinted polymer layer-coated silica gel particles (Hg(II)-IIP) toward analysis of trace inorganic mercury in water samples. To induce the selective occurrence of surface polymerization, the polymerizable double bonds were first grafted at the surface of silica gel particles by the silylation. Afterwards, the Hg(II) templates were imprinted into the polymer-coating layer through the non-covalent interaction between functional monomer and Hg(II) complex with 1-pyrrolidinedithiocarboxylic acid (Hg-PDC), 1-(2-thiazolylazo)-2-naphthol (Hg-TAN) and dithizone (Hg-DTZ), respectively. After removal of templates, recognition sites of Hg(II) were exposed in the polymer layers. The separation and preconcentration characteristics of the Hg(II)-IIPs for inorganic mercury were investigated by batch procedure. The optimal pH values for the quantitative sorption were determined. The adsorbed Hg(II) was easily eluted by 0.1 M thiourea in 0.1 M HCl. The selectivity of the Hg(II)-IIPs toward inorganic mercury (Hg(II)) ion was confirmed through comparison of the competitive adsorptions of $CH_3Hg(I)$, Cd(II), Co(II), Cu(II), Ni(II), Pb(II), Zn(II)) and high values of the selectivity and distribution coefficients were calculated. There is also evidence indicating that the Hg(II)-IIPs compared with non-imprinted sorbent show a higher selectivity and affinity to Hg(II). The new Hg(II)-IIPs were tested and applied for the speciation of Hg in surface waters.

P-16

ICP-MS and ETAAS/CVAAS/HGAAS in the determination of As, Cd, Hg, Pb and Se in fish tissue solubilizat/slurry

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Determination of As, Cd, Hg, Pb and Se in fish tissue is within routine analytical procedures performed in laboratories controlling food and environmental samples. Standard procedure consists of MW sample digestion mostly by a mixture of HNO_3 and H_2O_2 followed by ETAAS/HGAAS or ICP-MS measurement. Calibration procedure depends on matrix interferences observed and typically calibration graph prepared with aqueous standards is preferred. Critical points are connected with very low natural content of Cd and Pb, high volatility of Hg species and noncomplete digestion of As-betaine (HGAAS). Direct instrumental measurement after sample solubiliztion using agents like tetramethylammonium hydroxide (TMAH) or formic acid are preferable analytical procedures however several important steps should be optimized: (i) fast and complete sample solubilization which ensures quantitative recoveries for all studied elements, (ii) careful optimization of instrumental parameters which ensures minimal matrix interferences. In the present study parameters for both procedures: MW digestion of fish tissue and low temperature MW assisted sample solubilization with relatively small amount of TMAH (25 % v/v H_2O) 1µl per mg sample were defined. Optimal parameters for next measurement by most suitable instrumental method are proposed. The most reliable method for calibration taking into account matrix interferences observed is recommended. Results obtained for certified reference materials were discussed from the view point of trace elements recoveries, analytical procedures duration, determination limits achieved, precision and accuracy. The most useful combination for each studied analyte is proposed.

P-17

INVESTIGATIONS OF FAME COMPOSITIONS IN BIODIESEL FUELS BY GAS CHROMATOGRAPHY

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Biodiesel fuels are an alternative source of energy and in the present world energetic context, they continues to stimulate interest in their producing and quality determining.

Biodiesel fuels are produced:

- From trans-estherification of vegetable or animal fats to yield fatty acid methyl esters (FAME) and glycerol (first-generation biofuel);
- Biochemical or thermochemical conversion of lignocellulosic biomass (second-generation biofuels).

The contents of FAME in first-generation biofuel were determined using gas chromatographic (GC) technique, applying an internal standard methyl heptadecanoate. GC was performed with Agilent Technologies 7890A gas chromatograph equipped with a flame – ionization detector and a HP – INNOWAX column.

This work includes our investigations on the composition of biodiesel fuels to monitor FAME distribution and biodiesel origin.

Quantitative results for FAME distribution of biodiesel fuel from different origin show that vegetable oils typically contain high levels of unsaturated fatty acids. There is a difference between the levels of mono- and polysaturated fatty acids. Rapeseed and peanut oils contain higher concentrations of C18:1 (58-61%). Soybean, corn and sunflower oils contain higher concentrations of C18:2 (49-61%). The animal oils contain higher concentrations of C18:1 (20-40%), but lower compared with vegetable oils. On the other hand animal oils contain higher C16:0 (16-35%).

Methyl esters of saturated acids in vegetable oils change within 7 and 17%, and in animal oils from 17 to 57%.The content of methyl esters of polyunsaturated acids in vegetable oils varies from 16 to 60%, and in animal oils from 2 to 13%.

The fact that FAME distribution reflects the origin of biodiesel, suggest to us to determine the most characteristic values from chromatograms and apply them on unknown biodiesel fuels as "pattern recognition". Samples for origin distinguishing are given.

P-18

APPLICATION OF CLASSICAL METHODS FOR ISOLATION OF RUTIN FROM ORIENTAL TOBACCOS

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Major commercial sources of rutin include Sophora japonica, Eucalyptus spp., Fagopyrum sculentum and Ruta graveolens. However, the necessity of identifying a better cheaper commercial source of rutin is still valid. Tobacco is a rich source of this medicinally important flavonoid. Especially the Oriental tobaccos grown in Bulgaria contain large amount of rutin, approximately 1% and potentially can be used commercially to obtain a product rich of this natural antioxidant. In this study the classical methods of extraction and isolation of rutin from Oriental tobaccos were investigated. By using analytical HPLC, the amounts of rutin present in the tobacco levels and extracts were determined. The largest amount of rutin was obtained by water extraction with heat reflux and liquid-liquid extraction with ethyl acetate. The results of the quantitative determinations by HPLC of rutin show the amounts of 0.93% or 9.3 mg/g rutin in tobacco leaves and 0.7 mg/g in the obtained extract.

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References

[1] S. Dagnon, A. Edreva, *Beitr. Tabakforsch. Int.,* 20 (2003) 355-359.
[2] F. Fathiazad, A. Delazar, R. Amiri, S. D. Sarker, *Iranian Journal of Pharmaceutical Research* 3 (2006) 222-227.
[3] H. Wang, M. Zhao, B. Yang, Y. Jiang, G. Rao, *Food Chemistry,* 107 (2008) 1399–1406.

P-19

SPECTROSCOPIC, CHROMATOGRAPHIC AND MORPHOLOGICAL STUDY OF PHOTOPOLYMERIZED DENTAL COMPOSITES

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The objective of the present study was to characterize the morphology, determine the degree of conversion of light polymerized resin-based dental composites and quantify the leachable portion of unreacted monomers in water solution. Two microhybrid composites - Charisma (Heraeus Kulzer, Germany) and Filtek Z250 (3M, USA), color A2, one microfilled composite - Durafil VS and one condensable composite - Solitaire2 (Heraeus Kulzer, Germany)) were polymerized with LED light curing unit. The surface morphology of the composite films and their cross-sections were determined using scanning electron microscopy (SEM). The degree of polymerization was evaluated by Fourier transform infrared spectroscopy (FTIR). The leaching of unpolymerized monomers from photocurable composites was measured by High- performance liquid chromatography (HPLC). It was found that the degree of polymerization was highest for Filtek Z250 (58%) and lowest for Durafill VS(42%). HPLC results showed elution of basic monomers of their organic matrix. These results are consistent with the SEM observation. A relatively smooth surface and homogeneous cross-section structure with irregular shaped zirconia-silica particles was observed in the microfilled composite Filtek Z250, while the other microfilled composite Durafill VS is characterized by significant roughness probably due to the large aggregates made of silica microfillers embedded in a prepolymerized organic matrix.

P-20

EXTRACTION OF ISOPRENOIDS FROM PSYCHROPHILIC YEASTS BIOMASS

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A method for the extraction of β-carotene, coenzyme Q_{10} and ergosterol from biomass of psychrophilic yeast strains was described. The investigation substances were derived from the *Sporobolomyces salmonicolor* AL_1 and *Cryptococcus laurentii* AS_{58} biomass with n-hexan:acetone at a ratio of 1:1 at room temperature after two repeated extraction. This combination of solvents was better for simultaneously extraction of mentioned substances than each of n-hexan, acetone, CH_2Cl_2, CH_3OH, i-PrOH and EtOH.

P-21

DETERMINATION OF HERBICIDE FLUMIOXAZINE IN CHERRIES USING HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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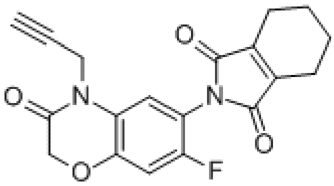
A selective, highly and accurate liquid chromatography method (HPLC/UV-Vis) for determination of flumioxazin residues in cherries, to ensure reliable control over the purity of fresh products reach consumers was attached. The appropriate conditions for efficient extraction of herbicide residues and separation of interfering substances analysis was studied.



flumioxazin

Our investigation showed, that the level of herbicide residues in fresh fruit is within prescribed limits after three years treatments of fruit trees with herbicide PLEDGE 50 WP (active substance – 50% flumioxazin). The characteristics of the method (sensitivity, accuracy and repeatability) showed that it is appropriate for monitoring residues of flumioxazin in fresh fruits. The same can be applied to residue analysis and related compounds.

P-22

SPECTROPHOTOMETRIC METHOD FOR DETERMINATION OF FRUCTANS IN FOOD PRODUCTS

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A simple, rapid and sensitive spectrophotometric method was developed for determination of fructans (inulin and oligofructoses) in food products (candies, bread containing *Jerusalem artichoke* flour and jogurts). The proposed method is based on the familiar Seliwanoff test for ketoses. The presence of monosaccharides glucose and galactose did not show any interference in the analysis. The best operating conditions for development and measurement of a colored compound formed by interaction of fructose with resorcinol and thiourea in the hydrochloric acid medium was heating the samples for 8 minutes at 80 °C. The producing red colored product is measured spectrophotometrically at 480 nm and the color is stable more than 1 hour. Beer`s law was obeyed in concentration range of fructose 0,05-2 mg/ml (R^2=0,997). The proposed method was tested and validated for various parameters according to the ICH (International Conference on Harmonization) guidelines. The results demonstrated that the method is accurate, reproducible, cheap and less time consuming.

P-23

RELATIONSHIP BETWEEN MOLYBDENUM AND NITRATE NITROGEN IN PLANTS AND THEIR YIELD

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Molybdenum is a micronutrient required by plants in very small amounts.

The essential nature of molybdenum as a plant nutrient is based solely on its role in the NO_3^- reduction process via nitrate reductase. Molybdenum and nitrate are both required for the induction of nitrate reductase in plants, and the enzyme is either absent, or its activity is reduced, if either nutrient is deficient. In this respect a certain subordination is traced between the content of molybdenum and nitrate nitrogen in the fruit of marrows in leaf fertilization and mixed (soil and leaf) fertilization.

Molybdenum has a great significance for the circum rotation of nitrogen and its assimilation by plants. Molybdenum secures the assimilation of nitrate nitrogen sources by plants. The experimental data show that in leaf fertilization the nitrate nitrogen is assimilated at the greatest extent 250 mg/kg in the content of molybdenum 3.94 mg/kg in the fruit of marrows. In soil and leaf fertilization the highest content of molybdenum 4.35 mg/kg responds to the biggest content of nitrate nitrogen 250 mg/kg assimilated by plants.

A certain subordination is traced between the content of nitrogen in the leaf fertilizers Humustim, Fitona and Hortigrow and the assimilation of molybdenum by plants. The highest content of molybdenum 3.99 mg/kg is determined in leaf feeding up with Fitona (comprising 7.2 % N). In mixed fertilization (soil and leaf) the highest content of molybdenum 4.35 mg/kg is determined in fertilization with $N_{16}P_{16}K_{16}$ + Humustim (comprising 3 % N).

Molybdenum is one of the main nutritious elements for vegetable crops. That is the reason for molybdenum to be a factor with influence on yield itself. In this respect the subordination is traced between the content of molybdenum in the fruit of marrows and the rendered yield.

In leaf fertilization yield decreases with the increase of the amount of accumulated molybdenum by plants. The highest yield 3917 kg/dka is obtained in the content of molybdenum 3.42 mg/kg in the fruit of marrows.

In soil and leaf fertilization the positive influence of molybdenum is determined upon the yield of marrows. The highest yield 4945 kg/dka is rendered in the content of molybdenum 4.35 mg/kg in the fruit of marrows.

P-24

INFLUENCE OF MANGANESE UPON THE CONTENT OF CARBOHYDRATES IN THE FRUIT OF MARROWS AND THEIR YIELD

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The determination of manganese essentiality in plant growth focused the attention of plant nutritionists on this nutrient, and led the way for further studies. Manganese has a catalytic role in plants, and combinations with proteins are essential to higher plant life. In this connection the content of manganese is determined in the fruit of marrows in leaf fertilization with Fitona, Hortigrow and Humustim, as well as in mixed (soil and leaf) fertilization.

Manganese is determined with a new developed method with Blue tetrazolium chloride as a chromogenic reagent. The BTC method can be successfully applied to the determination of manganese in plant samples.

The subordination is investigated between the content of manganese and total carbohydrates in the fruit of marrows. In soil and leaf fertilization the content of total carbohydrates in the fruit increases with an increase of the concentration of manganese in the same fruit. The content of total carbohydrates varies in the interval 1.34 % - 2.39 % in mixed (soil and leaf) fertilization.

The experimental data show that the content of manganese in the fruit of marrows is highest in leaf fertilization with Hortigrow 9.70 mg/kg Mn and mixed fertilization with Hortigrow 10.10 mg/kg Mn. This is may be due to the fact that in the content of the leaf fertilizer Hortigrow can be found 0.01 % Mn.

In leaf fertilization the content of total carbohydrates varies in the interval 0.78 % - 0.92 % and is lower than that in mixed fertilization. The highest content of total carbohydrates 0.92 % in leaf fertilization is determined in a content of Mn 8.69 mg/kg in the fruit of marrows.

Manganese is an important nutritious element for plants that has an influence on the quality of yield and production. The experiment showed that yield decreases with an increase of the amount of accumulated manganese in the fruit of marrows. This subordination can be seen in the different ways of fertilization. The highest yield 4945 kg/dka is rendered in the content of Mn 8.85 mg/kg in the fruit.

P-25

GAS CHROMATOGRAPHIC RETENTION MODELING BY QSRR APPROACH FOR SATURATED ESTERS SEPARATED UPON STATIONARY PHASES WITH DIFFERENT POLARITIES

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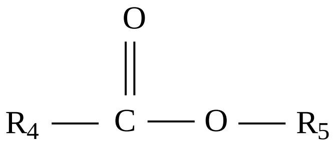
The Quantitative Structure-Retention Relationship (QSRR) approach was applied to model the gas-chromatographic retention of 100 saturated esters, separated upon the five columns with different polarities - the nonpolar phases SE-30, DC-710, OV-7 and the polar phases XE-60 and OV-225. The experimental retention data were taken from literature.



$$R_4 - \overset{\overset{O}{\|}}{C} - O - R_5$$

R_4 = H, alk, i-alk
R_5= alk, i-alk

The multiparameter linear regressions (MLR) were derived in a form of equation:

$$RI = a_0 + dD + \sum p_i P_i$$

where **RI** is the *Kovats* Retention Index; **D** – a global structure molecular index to quantify the nonspecific chromatographic interactions (physico-chemical, topological and quantum molecular indices); $\mathbf{P_i}$ – a specific molecular descriptor to quantify the polar intermolecular interactions of the solute with the stationary phase (dipole moment, the net atomic charges of the atoms in the solute molecules, indicative structure descriptors, which reflect the presence or the absence of the substitution $\mathbf{R_4}$ and $\mathbf{R_5}$); $\mathbf{a_o}$, **d** and $\mathbf{p_i}$ are the regression coefficients, depending on the properties of the stationary phases.
The best statistics was achieved for the regression case:

$$RI = a_0 + d_i D_i + p_i R_i \quad ,$$

were $R_{ij} = R_{4j}$ or R_{5j} ; j = 1,2,3 reflects the type of the carbon atom (primary, secondary, tertiary and quaternary).

The statistical precision of the various QSRRs derived with different global descriptors for the five phases was compared as a measure for their ability to reflect the intermolecular interactions between the solutes and the stationary phases.

A comparison of the parametric values of the regression coefficients among the similar QSRR models for different stationary phases exhibits the specific features of solute-stationary phase interactions in each case. The statistical significances of the QSRR models derived by using these indices were compared and assessed. The QSRRs derived for the five stationary phases were of adequate statistical quality (r > 0.99) and predictive ability.

P-26

AUTOMATIC GENERATION OF TAUTOMERS

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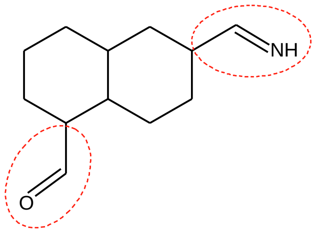
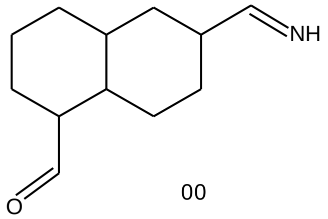
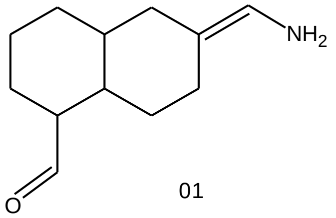
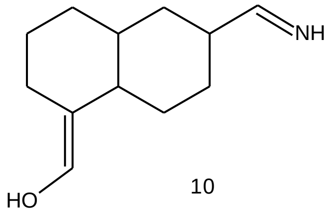
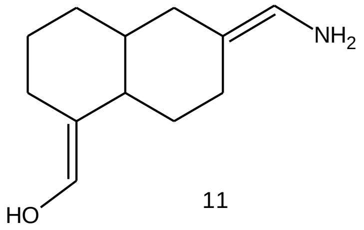
A software module for automatic generation of tautomers is introduced. The software is implemented on top of Chemistry Development Kit (CDK) Library. The program enumerates all possible tautomeric forms of a given molecule. All places for double bond/hydrogen atom shift are identified and combined via exhaustive combinatorial algorithm. Different tautomerism cases are described as rules represented in the form H-X-Y=Z ↔ X=Y-Z-H, where the two states are coded as SMILES strings and the H atom positions are denoted as well. For a particular target molecule, each rule is applied by means of exhaustive substructure searching of the rule fragments against the target structure. As a result all possible locations for a shift are recognized. The tautomeric forms in this sense could be described as binary numbers where each digit represents the "shift" state of each recognized location.



 00	 01
 10	 11

P-27

EXCITED-STATE REACTION PATHS OF CYTOSINE AND ISOCYTOSINE: C=O ELONGATION

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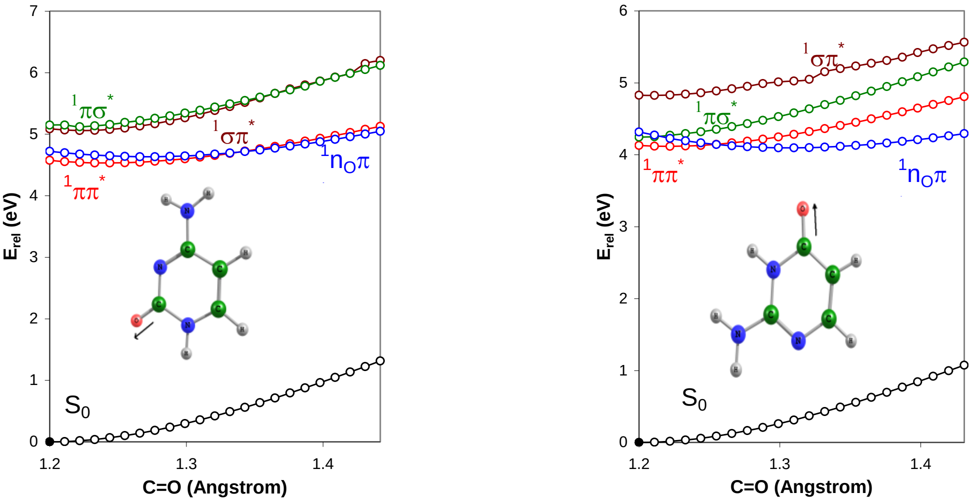
We investigated the excited-state reaction paths for the C=O elongation in the most stable oxo-amino tautomers of cytosine and isocytosine. They were studied at the B3LYP (TD) level of theory and aug-cc-pVDZ basis functions. As expected for this kind of reactions, no S_0-S_1 conical intersections were found for both compounds. We explained the ps-relaxation of cytosine with the population of the $^1n_O\pi^*$ excited state via conical intersection $^1n_O\pi^*/^1\pi\pi^*$ and subsequent fluorescence to the S_0 state at C=O = 1.443 Å. This finding is in excellent agreement with the experimental fluorescence maximum of cytosine registered at 325 nm [1]. In isocytosine we found a channel for the population of the $^1\pi\sigma^*$ excited state, which would contribute to the photochemical dissociation of the compound. This is the first step for the formation of the hydroxo tautomer of isocytosine. In other words, cytosine is photostable, while isocytosine shows tautomeric conversions upon UV irradiation.



(a) *(b)*

Excited-state reaction paths of (a) cytosine and (b) isocytosine for the C=O elongation

References

[1] A. Sharonov, T. Gustavsson, V. Carre, E. Renault, D. Markovitsi, *Chem. Phys. Lett.*, 380 (2003) 173-180.

P-28

SEARCH IN RAMAN SPECTRAL LIBRARIES OF ORGANIC COMPOUNDS

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The infrared (IR) and Raman spectra reflect in a great extent the compound's structure, therefore both techniques are well suited for the process of structure elucidation. Similar to the IR spectrum, the Raman spectrum is based on molecule fundamental vibrations and their overtones, thus providing a detailed spectral "fingerprint" of the compound under study. As an analytical technique, Raman spectroscopy offers many advantages over IR spectroscopy: the most important of them are the following: (1) little or no sample preparation is required; (2) water as a liquid is a weak scatterer and no special accessories are needed for measuring aqueous solutions; (3) water vapors and carbon dioxide are very weak scatterers – sample compartment's purging is unnecessary; (4) Raman bands of symmetric vibrations which are weak in an infrared spectrum are very strong.

In this work, the created Raman spectral libraries of more than 300 entries and performance of the search software IRIS [1] are described. 200 of the spectra were measured in our lab on RAM II (Bruker Optics) with a focused laser beam between 10 and 900 mW power of Nd:YAG laser (1064 nm) from 4000 cm^{-1} to 51 cm^{-1} at resolution 2 cm^{-1} with 25 scans. They are spectra of common organic compounds (solvents, reagents and products of reactions, and some natural compounds). The second library is composed of more than 100 spectra of natural organic compounds that are present in plants. These spectra of natural compound standards were measured by Dr. Baranska in Julius Kühn-Institut, Federal Research Centre for Cultivated Plants, Germany, on RFS 100/S instrument (Bruker Optics) with the same laser and power.

Several algorithms for the comparison of Raman spectra are implemented in IRIS, as well as, a procedure for the analysis of Raman spectra of mixtures through a search in a Raman spectral library. All 30 "unknown" test compounds were successfully identified by library search of their Raman spectra. Even Raman spectra with low signal-to-noise ratio measured on a microscope (RamanScope, Bruker Optics) could be identified by the search procedure. Additionally, the identification of the components of 10 binary mixtures proved to be very successful.

The library search software IRIS and the two Raman spectral libraries can be free downloaded from http://irra.uni-plovdiv.bg/.

References

[1] K. Varmuza, P.N. Penchev, H. Scsibrany, J. Chem. Inf. Comput. Sci. **38** (1998) 420.

Acknowledgements

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P-29

PHOSPHORYLATED ALLENES – SUITABLE PRECURSORS IN ORGANIC SYNTHESES

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This article deals with the methods for the syntheses of titled compounds, and their application in organic syntheses.

Contents:

***Keywords**: 1,2-Alkadienephosphonates • 1,2-Alkatrienephosphonates • Electrophilic addition reactions, Nucleophilic addition reactions, Cycloaddition reactions, Cycloizomerization reactions*

P-30

THE NUCLEOPHILIC SUBSTITUTION REACTION OF SULFINIC ACIDS WITH HALONITROALKANES

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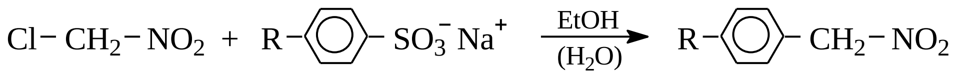
Arylsulfonylnitromethanes were obtained by a nucleophilic substitution reaction.



1 2 3

The suggested method of obtaining arylsulfonylnitromethanes has some important advantages over the methods known so far: it is a relatively short, one stage process; no by-products are obtained, so there is no need of further procedures to separate the main products from the reaction mixture, the final compounds possess a good degree of purity.

Studies on the chemical behaviour of α-nitrosulfones show that they readily take part in reactions of nucleophilic addition. As a result, α-nitrosulfones, nitroacetonitriles, and bis (phenylsulfonyl)methane are obtained.

These synthesized compounds have been characterized by microanalytical and spectral methods.

P-31

OPTIMIZATION OF THE OPTICAL AND NLO PROPERTIES OF NEW MEROCYANINE DYE E-4(2-HYDROXYNAPHTHALEN-1-YL)VINYL)-1-METHYL-QUINOLINIUM IODIDE AND ITS DEPROTONATED FORM

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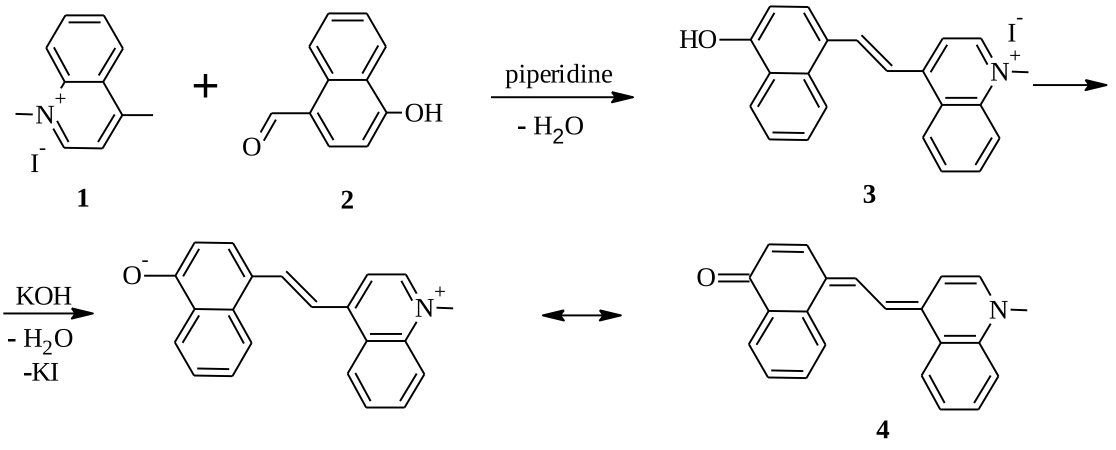
Organic dyes, such as styrylquinolinium salts are novel materials with excellent properties for photonic applications.

One new styrylquinolinium dye (**3**) and its quionoide form (**4**) have been synthesized in good yields (Scheme 1). Detailed spectroscopic and structural elucidation of the compounds (**3**) and (**4**) have been carried out by means of conventional solid-state IR- and Raman spectroscopy, UV-Vis spectroscopy, ^{1}H- and ^{13}C NMR methods. Quantum chemical DFT calculations have been performed to predict both structure and spectroscopic properties of the studied compounds.



Scheme 1

The theoretical electron charge redistribution was studied in the compound (**3**) and corresponding quinoide form (**4**). The possible redistribution of the electronic density in these compounds as typical push-pull systems is dependant on the solvent polarity. As far as the electron transition is concerned, intramolecular charge transfer (CT) leads to a significant difference between the dipole moment in the ground and exited states, *i.e*. it determines their significant solvatochromism, or NLO properties in solution. The observed negative solvatochromic effect in these compounds has been explained by both intra- and intermolecular CT.

P-32

SPECTRAL AND STRUCTURAL ELUCIDATION OF 4-{(*E*)-2-[4-(DIMETHYLAMINO)NAPHTHALEN-1-YL]ETHENYL}-1-METHYLQUINOLINIUM IODIDE MONOHYDRATE

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In the present investigation, one new merocyanine dye, 4-{(*E*)-2-[4-(dimethylamino) naphthalen-1-yl]ethenyl}-1-methylquinolinium iodide monohydrate has been synthesized by Knoevenagel condensation of 4-N,N-dimethylaminonaphtaldehyde and the respective quaternary lepidinium salt in good yield.

Detailed spectroscopic and structural elucidation of the compound has been carried out by means of single crystal X-ray diffraction, conventional solid-state IR- and Raman spectroscopy, UV-Vis spectroscopy, ^{1}H- and ^{13}C NMR methods. Quantum chemical DFT calculations have been performed to predict both structure and spectroscopic properties of the studied compound.

The dye crystallized in the monoclinic space system and $P2_1/n$ space group (Fig. 1). The unit cell contains 4 molecules of the dyes, participating in the intermolecular interaction with the I^- anion and water molecule.

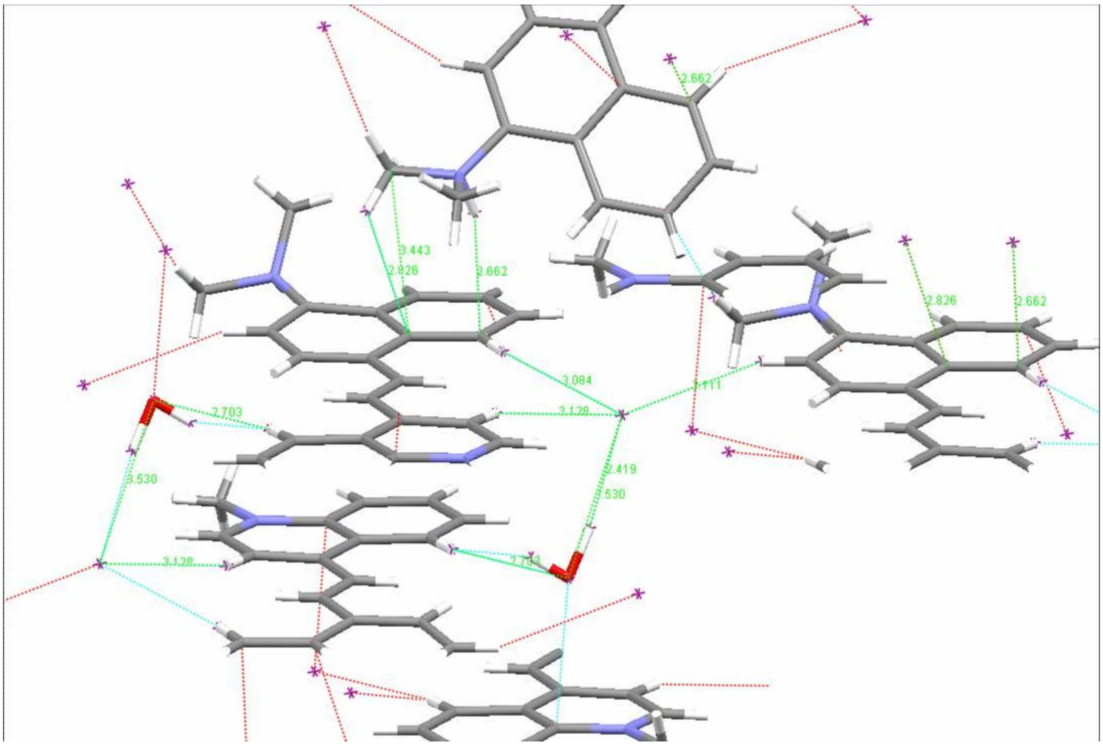

Fig. 1. Crystal structure of investigated compound

P-33

SELECTIVE ACETOXYLATION OF CYCLODODECENE BY DIOXYGEN CATALYZED BY PALLADIUM(II) ACETATE, HYDROQUINONE AND IRON(II) PHTALOCYANINE

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Selective palladium-catalyzed aerobic oxidation of cyclododecene with the aid of a metal macrocycle-quinone system was conducted. This involves a multistep electron transfer with three catalysts (Palladium(II) acetate, hydroquinone and iron(II) phtalocyanine). The triple catalytic system was applied to acetoxylation of cyclododecene to cyclododec-2-en-1-yl acetates in high selectivity (93.4%) and a convertion of cyclododecene up to 93-98% were obtained.

P-34

SYNTHESIS AND ANTIBACTERIAL EVALUATIONS OF SOME NOVEL DERIVATIVES OF BENZIMIDAZOLE

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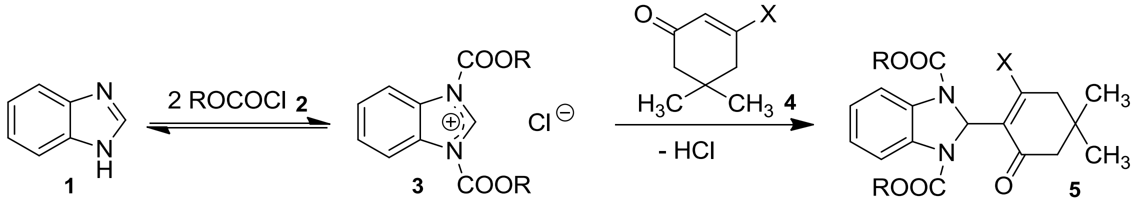
N-Acyliminium reagents derived from benzimidazole have been successfully used in reactions with active methylene nucleophiles. A series of cyclic enaminoketones and dimedone were selectively amidoalkylated. In all of the examples the reaction took place regioselectively at the α-carbon atom of the enaminone, as indicated by the disappearance of the characteristic vinyl signal in the 1H NMR spectra. No reaction at N or O was detected.

As a result of that, the scope of application of the intermolecular reaction of α-amidoalkilation has been successfully expanded. The new 2-substituted derivatives of 2,3-dihydrobenzimidazole are interesting both from synthetic point of view and as potential bioactive compounds.



R = Me, Et; X = OH, NHR_1

R_1 = Me, Et, Pr, Ph, Bz, $C_6H_5CH_2CH_2$, 4-$ClC_6H_4CH_2CH_2$, 3,4-$(MeO)_2C_6H_3CH_2CH_2$

All compounds were assayed for antibacterial activity using standardized tests (DM and DDM) against: *Escherichia coli* ATCC 25922; *Enterobacter aerogenes* ATCC 25029; *Salmonella abony* ATCC 6017; *Pseudomonas aeruginosa* ATCC 27853; *Enterococcus faecalis* ATCC 29212; *Staphylococcus aureus* ATCC 33592 (MRSA); and *Candida albicans* ATCC 10231. Six compounds displayed antibacterial activity against two strains microorganisms. For some of the compounds was registered bacteriostatic effect against *Enterobacter aerogenes* and antimicotyc activity against *Candida albicans.*

P-35

APPLICATION OF THE BISCHLER-NAPIERALSKI REACTION FOR THE SYNTHESIS OF 1-BIPHENYL-1,2,3,4-TETRAHYDROISOQUINOLINES

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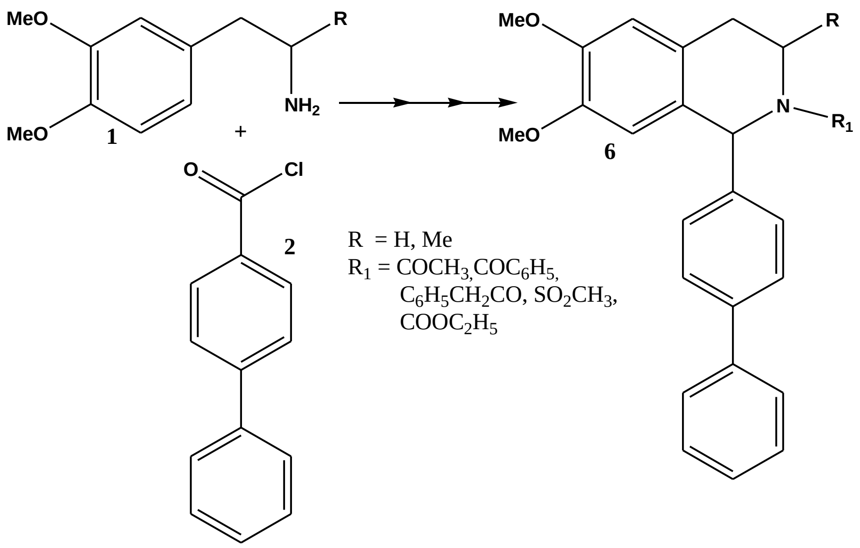
Dihydroorotate dehydrogenase (DHODH) is enzyme, identified in the Plasmodium falciparum. Two well-described inhibitors of human dihydroorotate dehydrogenase (hDHODH) are Leflunomide and Brequinar, which are currently used to treat malaria, rheumatoid arthritis, and analogs are in clinic to treat graft versus host disease and multiple sclerosis. In view of varied biological activities, there is a strong interest in the development of synthetic methodologies giving access to novel isoquinoline alkaloids, as potential DHODH inhibitors. We applied for this purpose the classical Bischler-Napieralski reaction.



R = H, Me
R_1 = $COCH_3$, COC_6H_5, $C_6H_5CH_2CO$, SO_2CH_3, $COOC_2H_5$

We synthesized amides of 1-biphenyl-1,2,3,4-tetrahydroisoquinoline **6** from starting amides of 3,4-dimetoxy-2-phenylethylamine (homoveratrylamine) **1** with biphenyl-4-carbonyl chloride **2** through the classical Bischler-Napieralski reaction with phosphorus oxychloride as cyclisation agent. This reaction obtained 3,4-dihydroisoquinolines with more than 80% yield. We found that corresponding 3,4-dihydroisoquinolines were reduced under mild reaction conditions to the corresponding 1,2,3,4-tetrahydroisoquinolines. For the last step we prepared easily required amides with good yields.

Some of the newly synthesized compounds were submitted to India for testing of their antimalarial activity.

P-36

KINETICS OF LIPID OXIDATION IN PRESENCE OF SOME NEW BIOLOGICALLY ACTIVE COMPOUNDS - INDIVIDUAL AND IN MIXTURES WITH ALPHA-TOCOPHEROL

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The aim of this study is to shed some light on the mechanism of action of some new biologically active biphenylic compounds (AH) synthesized recently and their corresponding monomers to inhibit lipid oxidation process (i.e. to react as antioxidants). Chain-breaking antioxidant activities of individual compounds were determined from the kinetic curves of lipid autoxidation. The effects of compounds concentration (0.1-1.0mM), the temperature (37°C and 80°C) and the reaction time were tested by monitoring the kinetics of lipid (kinetically pure triacylglycerols of sunflower oil) and determination of the primary oxidation products – lipid hydroperoxides. All dimmers are with higher activities than the corresponding monomers. All equimolar binary mixtures with alpha-tocopherol (TOH) and triple mixtures with TOH and ascorbic acid (AscH) demonstrated much higher oxidation stability of lipid substrate. However, a synergism (i.e. the summary induction period, IP_{Σ} , is higher than of the sum of induction periods of the individual components, $IP_{\Sigma}>\Sigma IP_i$) of the most binary mixtures was observed only for the lower concentration (0.1mM) of compounds. Strong synergism (for some of dimmers even higher than 60%) was found for the triple mixtures, due to the possible regeneration of TOH in reactions: a) with ascorbic acid ($TO^{\bullet}+AscH \rightarrow TOH + Asc^{\bullet}$) and b) with studied biphenyls ($TO^{\bullet} +AH\rightarrow TOH +A^{\bullet}$), as well as c) in cross-disproportionation reactions between tocopheryl radical and phenoxyl radicals ($TO^{\bullet}+A^{\bullet}\rightarrow TOH+A$). On the basis of a comparable kinetic analysis with standard antioxidants the differences of antioxidant activities of compounds is discussed and a reaction mechanism is proposed. The geometries of dimmers and their corresponding monomers and possible phenoxyl radicals as well as bi-radicals were optimized using density functional theory. For description of the scavenging activity bond dissociation enthalpies (BDE), HOMO and LUMO energies and spin densities in presence of acetone solvent were also employed.

P-37

RADICAL SCAVENGING ACTIVITY OF SOME NEW BIPHENYLIC COMPOUNDS AND THEIR CORRESPONDING MONOMERS

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New biologically active biphenylic compounds synthesized recently and their corresponding monomers were tested experimentally for their capacity to scavenge free radicals (i.e. diphenylpicrylhydrazyl radical, DPPH$^{\bullet}$). Two different approaches were applied: a) TLC DPPH rapid test and b) kinetics of DPPH absorbance decay at room (25^{o}C) and physiological (37°C) temperatures. The effects of compounds' concentration (1 and 10mM), reaction time (0-20 min) and DPPH solvent (methanol and acetone) were tested. Only individual compounds with free OH groups were found to be active as DPPH$^{\bullet}$ scavengers. However, biphenyls with $(OCH_3)_2$ substituents instead of $(OH)_2$ showed a higher biological activity. The reaction time with DPPH$^{\bullet}$ and compounds' concentrations influenced deeply the radical scavenging evaluation. Quantitatively the radical scavenging activity towards DPPH free radical was calculated as %RSA=$(\mathrm{Abs}_{(0)}–\mathrm{Abs}_{(t)}/\mathrm{Abs}_{(0)})$x100, % by monitoring the kinetics of DPPH absorbance decrease at different times (t). The highest values of radical scavenging activity (%RSA) and largest rate constants for reaction with DPPH$^{\bullet}$ at different temperatures (25^{o}C and 37^{o}C) and at two ratios of [AH]/[DPPH] = 0.23 and 0.40 in acetone solution, were obtained for compounds with a double bond in the side chains. We separated compounds into 3 main groups: Group A – with strong activity (%RSA > 40%); Group B – with moderate activity (15<%RSA< 40%); and Group C – with weak activity (%RSA< 15%). The total stoichiometry n_{tot} $\{n_{tot}=(\mathrm{Abs}_0-\mathrm{Abs}_t)/\varepsilon[\mathrm{AH}]\}$, i.e. the number of free radicals scavenged by one molecule of AH, was calculated for t=20 min. In our experiments ε = 12 000 $M^{-1}cm^{-1}$ is the molar absorption coefficient of DPPH$^{\bullet}$ in acetone solution, [AH] = 2.7 10^{-5}M and 3.9 10^{-5} M, resp. Differences of radical scavenging activity of tested compounds is compared with those of known antioxidants and the reaction mechanism is proposed. Correlations between the experimental and theoretical data were presented on the base of quantum chemical calculations by applying density functional theory.

P-38

MULTIFUNCTIONAL MECHANOCHEMICALLY SYNTHESIZED α-Fe_2O_3-ZnO MIXED OXIDES

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Fe_2O_3-ZnO mixed oxides with the different molar ratios have been synthesized using the mechanochemical method. This method was found to be inexpensive, environment friendly, convenient and efficient, compared with the other methods of preparation. The structural analysis of the prepared samples was carried out by X-ray diffraction. Undoped ZnO was found to be pure wurtzite phase. The data obtained by XRD and Mössbauer spectroscopy indicate the changes in the structure of the mixed oxides occurring upon varying iron-to-zinc ratio. The effect of surfactant on the properties of mechanochemically activated α-Fe_2O_3-ZnO mixed oxides was studied. The reactivity of α-Fe_2O_3-ZnO mixed oxides as catalysts was investigated using the decomposition of isopropanol as model reaction. Their catalytic activity decreases with the annealing temperature due to the corresponding increase in the particle size.

The photocatalytic activity of α-Fe_2O_3-ZnO mixed oxides, using ethylene as a model air pollutant, has been tested in a gas-phase flat-bed continuous flow photocatalytic reactor. The conversion degree of ethylene was taken as a measure of the photocatalytic activity of the sample. The performance of the α-Fe_2O_3-ZnO photocatalytic material was compared with previous results, obtained with the standard reference photocatalyst TiO_2 Degussa P25. The second is superior in case of using UV light, while the composite α-Fe_2O_3-ZnO material displays some activity with visible light, where Degussa shows zero activity. The obtained results can be explained with the fact that the band gap of α-Fe_2O_3-ZnO is narrow (2.2 eV, corresponding to λ=564 nm, i.e. activation by visible light), while the wide band gap of anatase TiO_2 (3.2 eV, corresponding to λ=388 nm) shows that it can be excited only by UV light. This explanation displays the zero activity of TiO_2 with visible light and the moderate activity of α-Fe_2O_3-ZnO under visible light irradiation. To the contrary: under UV light irradiation TiO_2 has higher photonic efficiency than α-Fe_2O_3-ZnO composite material. At one and the same illumination intensity the UV-C lamps are more efficient that the black light blue lamps (UV-A light) probably because of the higher photon energy. A kinetic model is proposed for ethylene complete oxidation rate, based on Langmuir-Hinshelwwod mechanism.

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PHOTOCATALYTIC TESTING OF MECHANOCHEMICALLY-SYNTHESIZED CADMIUM SELENIDE

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Spectroscopic and optical properties of highly luminescent II-VI semiconductor CdSe nanocrystals have been extensively studied due to their application in electrical and opto-electrical devices. CdSe nanocrystals are preparing by chemical wet process mainly. However, mechanochemical synthesis in planetary ball mill produces surface clean semiconductor nanoparticles without the influence of organic ligands coming from chemical process and such nanoparticles can be investigated as photocatalyst.

The aim of the present investigation was to test the photocatalytic activity of mechanochemically synthesized CdSe semiconductor with UV-C (monochromatic λ=254 nm) light and to compare this activity with the activity of the standard reference photocatalyst TiO_2 Degussa P25 (75% anatase + 25% rutile, average anatase particle size 25 nm). The second aim of the study was to test the photocatalytic activity of CdSe with visible light. The photocatalytic activity of the samples was tested in a batch reactor with Chromium Acidic Black Diazo Dye (Colour Index Acid Black 194), which is used for colouring textiles. It appears in waste waters from textile factories and the new environmental regulations have forbidden discharging it into the water ways it strictly.

The relatively low conversion degrees over CdSe, compared to the TiO_2 Degussa P25, can be explained by the low specific surface area of the CdSe sample. In order to increase the conversion degree sonication pretreatment of the CdSe is required as it falls at the bottom of the reactor as sediment, probably due to formation of agglomerates of large size. The sonication, prior to the photocatalytic activity test improves considerably the performance of the CdSe semiconductor. The result with model waste water is encouraging and the investigation could be extended to monitor the performance of CdSe for contaminated air purification in a gas-phase flat-sheet continuous flow steady state photocatalytic reactor. In view of the band gap of CdSe (ΔE = 1.7 eV corresponding to band gap absorption edge wavelength of 730 nm) the investigation can be extended also in the direction of photocatalytic performance of CdSe with visible light to test the photonic efficiency (quantum yield) of this nanosized semiconductor material.

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P-40

ROLE OF PREPARATION METHOD ON CATALYTIC ACTIVITY OF Ag/CeO_2 FOR OXIDATION OF CO, CH_3OH AND $(CH_3)_2O$

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The removal of volatile organic compounds (VOCs) emitted from industrial and domestic processes have drawn a lot of attention due to increasing social and political concern in environment. A cheap and efficient way of VOCs removing is their complete catalytic oxidation to harmless products such as H_2O and CO_2. Supported Pt and Pd are well established as efficient catalysts for VOCs combustion. However, due to the high cost and limited reserve of such noble metals, the quest for cheaper and more environmentally friendly catalytic materials are of an ever-increasing importance for tomorrow's applications.

The aim of present study was to examine the catalytic activity of Ag/CeO_2 catalysts for abatement of air pollutants – CH_3OH, $(CH_3)_2O$ and CO in waste gases from formaldehyde production. HRTEM, X-ray diffraction, FTIR of CO at LNT and RT, XPS and H_2-TPR were employed to obtain information about the effect of different synthesis procedures on the surface and on the bulk structure of the catalysts and to explain the differences observed in their catalytic activity.

Ag/ceria (3 wt. % Ag) catalysts were prepared by two different methods (deposition-precipitation and modified deposition-precipitation). Deposition-precipitation (DP) took place by precipitation of a desired amount of $AgNO_3$ (at pH 9.0) with K_2CO_3 on ceria previously prepared and suspended in water by ultrasound. The MDP involved precipitation of $AgNO_3$ on cerium (III) hydroxide freshly precipitated and aged 1 hour at 60 ^oC. In both cases, the resulting precipitates were aged 1 h at 60 ^oC, then filtered and washed until no NO_3^- could be detected. Further, the precipitates were dried in vacuum at 80 ^oC and calcined in air at 400 ^oC for 2 hours.

Ag/CeO_2 sample prepared by DP demonstrated higher CO and CH_3OH oxidation activity. The most pronounced effect of the different synthesis procedures was registered in the CO oxidation reaction. Temperature of 50% CO conversion over DP-prepared sample was 100 ^oC, whilst over MDP-prepared it was 160 ^oC. As concerns CH_3OH oxidation, at 100 ^oC was attained 90 and 15 % conversion over DP- and MDP-prepared Ag/CeO_2, respectively. Very similar was catalytic performance of both samples for $(CH_3)_2O$ oxidation.

FTIR spectra of CO adsorbed on oxidized and reduced catalysts and XPS measurements evidence that the concentrations of Ag on the surface of the catalyst prepared by DP is higher than that observed on the catalyst prepared by MDP. The higher Ce^{3+} surface concentration over reduced DP-prepared catalyst supports suggestion that nanosized metallic particles in close contact with oxygen defects on ceria are responsible for better catalytic performance of this catalyst.

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PHOTOCATALYTIC ACTIVITY OF SPRAYED TiO_2 FILMS DEPOSITED ON DIFFERENT SUBSTRATES

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Thin photocatalytically active TiO_2 films are successfully prepared on glass and alumina foil substrates by spray pyrolysis method.

The films are characterized by means of X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), Thermal Analyses (TG-DTA).

The XRD spectra of TiO_2 thin films, treated at 400◦C showed formation of nanosize anatase phase.

The investigations of chemical composition by XPS shows the presence of Na and Si in TiO_2 films, deposited on glass substrates, annealed at 400◦C. This could be explained by interaction of glass substrate with the films.

The as-obtained TiO_2 films were studied with respect to the photo-initiated bleaching of Reactive Black 5 (RB5) under UV illumination. It was investigated the influence of the substrate, spray solution composition and pH of the dye solution on the decolorization of the RB5 dye.

It was found that the films deposited on alumina foil revealed a better photocatalytic activity than those on glass substrate, due to the roughness of the alumina substrate.

The use of the solvent with high boiling point leads to a formation of films with higher activity than the films, obtained from solutions with polymer modifier.

The highest rate of decolorization was obtained at low pH of the dye solution.

Acknowledgement: The authors thank to the Bulgarian Ministry of Science and Education for the financial support by project DDVU 02-36/10.

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DECOLORIZATION OF REACTIVE BLACK 5 DYE ON TiO_2 HYBRID FILMS DEPOSITED BY SOL GEL METHOD

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Photocatalytically active hybrid TiO_2 films were successfully prepared by sol gel method.

The suspensions, which consist of titanium alkoxide solution, enriched with Degussa P25 powder were spin coated on glass substrates. The deposits were treated using microwave (TiO_2-MW) and conventional oven (TiO_2-C), as well as the combination of both methods (TiO_2-MWT).

The phase composition and crystallite size of the films were characterized by means of X-ray diffraction (XRD). The morphology and chemical composition were studied by Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS).

The XRD spectra of TiO_2 thin films, annealed at 400◦C showed formation of nanosize anatase phase.

The decolorization of Reactive Black 5 dye, used in the textile industry was investigated at low pH.

The mode of treatment of the films has significant influence on their photocatalytic properties.

The films, obtained by microwave-assisted drying, following by conventional treatment (TiO_2-MWT) have a rate of the RB5 degradation compatible with those of TiO_2-C films. TiO_2-MW films showed the lowest rate of decolorization, probably due to the low crystallinity and incomplete destruction of the precursor.

The TiO_2 thin hybrid films prepared by us are promising as efficient photocatalyst for degradation of Reactive Black 5 azo dye.

Acknowledgement: The authors thank to the Bulgarian Ministry of Science and Education for the financial support by project DDVU 02-36/10.

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REMOVAL OF CATIONIC DYES FROM AQUEOUS SOLUTIONS BY ADSORPTION ONTO BENTONITE AND USED COFFEE GROUNDS: EQUILIBRIUM AND KINETIC STUDIES

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Water quality is regarded as one of the most significant problems related to environmental protection. Organic dyes, being constituents of wastewaters from textile, pharmaceutical, food-stuff, cosmetic, paper, leather industries are among the compounds causing water pollution. The discharge of untreated dye effluents, due to their toxic and esthetic impacts on receiving waters, is becoming a major concern. Therefore, the removal of these colored compounds from wastewater is an important target from the environmental point of view. The physical adsorption at solid-liquid interface is regarded as one of the most efficient and economic method for decreasing the concentration of soluble dyes in effluents.

This study aims to evaluate the adsorption properties and potential applications of abundant, cheap and environmentally friendly materials - bentonite and used coffee grounds for removal of methylene blue (MB) and Rhodamine B (RhB) dyes from aqueous solutions.

Results obtained reveal that selected materials are suitable for efficient removal of MB and RhB from aqueous solutions under certain conditions. Bentonite demonstrated better adsorption properties – complete MB uptake and about 90% degree of decolorization of RhB solution was observed within 30 minutes for 0.2 g/l adsorbent content at ambient conditions. As concerns coffee grounds, larger amount of adsorbent and longer contact time is required to attain similar removal degree, especially for RhB dye.

Adsorption equilibrium data correlated with the Langmuir isotherm model. The calculated monolayer adsorption capacities of bentonite for MB and RhB are much higher than that for coffee grounds. The adsorption kinetics of both dyes on adsorbents studied follows the pseudo second-order model of McKay & Ho. Rate constant of the adsorption process was found to decrease with increasing initial dye concentration. It was also established that intraparticle diffusion played a significant role. The adsorption was highly dependent on various operating parameters. Sonication accelerated the dye removal process but did not affect the adsorption capacity. The extent of MB removal by used coffee grounds increased from 58 % to 94 % with increase in pH from 4 to 10, whilst the adsorption onto bentonite was almost not pH-dependent. In contrast, the amount of adsorbed RhB dye onto bentonite decreased by 19% and about 2 times when coffee grounds was used as adsorbent in basic solutions. The calculated thermodynamic parameters indicated that the adsorption of MB and RhB onto bentonite and coffee grounds is spontaneous and exothermic.

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TERMOCHEMICAL AND KINETIC PROPERTIES OF Bi-Ni-Sn SYSTEM

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Joining of diverse modules is indispensable procedure in the electronics production. Since long time Sn-Pb alloys have been predominantly used for this purpose. Nonetheless, Pb-containing solders are under way to be phased out of use due to environmental risks. Intensive studies of prospective multicomponent lead-free systems were undertaken but the replacement of the whole variety of Sn–Pb based solders turned out to become a very complicated task. In this view alloys containing tin plus some low-melting metals (e.g. Bi, Zn, Sb) are considered prospective for the replacement of the lead bearing solders. Besides, nickel substrates are largely applied in electronic devices. Although investigations of the Ni-Bi-Sn system and the kinetics of the corresponding interfacial reactions have already been done further efforts are necessary in order to achieve a full description of the pertinent ternary phase diagram. The present work continues this trend being aimed to obtain phase transitions temperatures and identify microstructures of the pertinent alloys as well as growth kinetics study of the diffusion layer formed between solid Ni and liquid Bi-Sn alloy.

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THERMODYNAMIC DESCRIPTIONS OF Cu-Pb-X SYSTEMS

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Copper and nickel are among the most often used metals for metallization in electronic devices and are expected to take part of new multicomponent solders. The accessibility of thermodynamic descriptions allows also calculating some physical properties (e.g. surface tension, viscosity) and predicting the solidification kinetics of the corresponding alloys.Thermodynamic descriptions of three ternary Cu-Pb-X systems were done. The adjustable parameters of the sub-systems, are taken from earlier assessments and those of the ternary systems are optimized using ternary experimental data.

(A, Cu-Pb-Sn) By limiting the validity of the description to the Cu-Pb side and excluding the presence of two “less significant phases”, $Cu_{10}Sn_3$ (ζ) and Cu_6Sn_5 (η), six phases, i.e., liquid, fcc, bcc, gamma (γ), $Cu_{41}Sn_{11}$ (δ) and Cu_3Sn (ε), were considered. Ternary interactions were not taken into account for a significant number of phases (i.e. the latter three phases either for the excluded compounds). This might imply that the suggested thermodynamic estimation would be valid in a wider composition range that is claimed.

(B, Cu-Pb-Zn) The results are quite similar to those presented in the earlier Cu-Pb-Zn description except that the present calculations give a smaller liquid miscibility gap in the copper-rich part of the system and more realistic lead solubilities in the fcc and bcc phases of Cu-Zn brasses.

(C, Cu-Pb-Ni) Only two phases, i.e., liquid and fcc, were considered. In the optimization, the unary and binary thermodynamic data of the systems were taken from recent optimizations. The general solution model was used to assess ternary integral molar Gibbs excess energies of the liquid phase. The latter disagree clearly with the values obtained by the ternary system optimizations.

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THERMODYNAMIC DESCRIPTION OF THE Cu-Mg-Sn SYSTEM AT THE Cu-Mg SIDE

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This study continues the recently started work for the development of a thermodynamic database for technically important copper alloys [1,2]. Thermodynamic description of the ternary Cu-Mg-Sn system at its Cu-Mg side is presented. The thermodynamic parameters of the binary sub-systems, Cu-Mg, Cu-Sn and Mg-Sn, are taken from the earlier assessments [3-5] (modifying the Mg-Sn description slightly) and those of the Cu-Mg-Sn system are optimized in this study using the experimental thermodynamic and phase equilibrium data. The solution phases of the systems are described with the substitutional solution model and the intermetallic Cu_2Mg compound (Laves C15), treated as simple semi-stoichiometric phases of the $(A,B)_pC_q$ type, is described with the two-sublattice model. The present ternary description is valid for tin contents up to 45 wt% (x_{Sn}≈0.30).

References

1. J. Miettinen, Thermodynamic description of the Cu-Ni-Si system in the copper-rich corner above 700°C, *CALPHAD,* 29 (2005) 212–22.
2. J. Miettinen, Thermodynamic description of the Cu-Mg-Ni and Cu-Mg-Zn systems, *CALPHAD* 32 (2008) 389–98.
3. C. Coughanowr, I. Ansara, R. Luoma, M. Hämäläinen, H.L. Lukas, Assessment of the Cu-Mg system, *Z. Metallkd.,* 82 (1991) 574–82.
4. J. Miettinen, Thermodynamic description of the Cu-Al-Sn system in the copper-rich corner, *Metall. Mater. Trans.* 33*A* (2002) 1639–48.
5. S. Morioka, M. Hasebe, Thermodynamic constraints to describe Gibbs energies for binary alloys*, J. Phase Equilibria, 20* (1999) 244–57.

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GALVANOSTATIC ELECTROEXTRACTION OF Cu IN THE PRESENCE OF Zn OR Fe IONS

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By means of galvanostatic deposition the best experimental conditions were selected for copper electroextraction from electrolytes containing zinc or iron ions. Depending on the ratio between Cu^{2+} and Zn^{2+} ions in the electrolytes conditions can be created favoring deposition of both pure Cu and Zn phases, as well as alloy Cu-Zn phase with different composition. The coathings produced from electrolytes containing 1 g dm^{-3} Cu^{2+} and 50 g dm^{-3} Zn^{2+} (without or with 130 g dm^{-3} H_2SO_4) are composed predominantly of Zn (80-90%). The coatings are black, smooth and powdery. Pure Cu coatings are produced by deposition at 1 A dm^{-2} in electrolytes containing 10 g dm^{-3} Cu^{2+} and 50 g dm^{-3} Zn^{2+} (without or with 130 g dm^{-3} H_2SO_4). Alloyed Cu-Zn coathings are produced at 5 A dm^{-2} current density with Zn content from 4.9% to 22.3%. The coatings deposited at 1 A dm^{-2} are orange in color, smooth and semi-bright, and those obtained at 5 A dm^{-2} are dark-red, spongy and brittle. To produce fine-grain, dense and smooth coatings of pure Cu the concentration of Cu^{2+} ions in the electrolyte should be higher than 10 g dm^{-3} and the current density should not exceed 1 A dm^{-2}. The current efficiency of copper electrodeposition at 2 A dm^{-2} in electrolytes containing 10 g dm^{-3} Cu^{2+} (without or with 130 g dm^{-3}) declines abruptly with increase in the Fe^{2+} concentration. The coatings are dark red in colour, brittle and powdery. The current efficiency of deposition in electrolytes containing 50 g dm^{-3} Cu^{2+} and 60 or 130 g dm^{-3} H_2SO_4 is above 95% and decreases slightly with increase in the Fe^{2+} concentration. Their surface morphology does not change much with the increase in the Fe^{2+} concentration. The coatings are light red in colour, smooth and semi-bright in appearance. The microprobe analysis indicates that the obtained coatings are of pure copper in all cases.

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KINETICS OF INSULIN CRYSTAL NUCLEATION, ENERGY BARRIER AND NUCLEUS SIZE

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Number density of insulin crystals versus nucleation time dependences were measured simultaneously, during the same experiment, at four typical places: in solution bulk, at the glass support, at air/solution interface and at solution/glass/air boundary. Stationary nucleation rates were determined from the linear parts of the corresponding plots, and energy barriers for nucleus formation and nucleus sizes were estimated. A key finding of the present investigation was that, surprisingly, the lowest energy barrier (3.8×10^{-13}erg), and correspondingly the smallest nucleus size (six insulin molecules), were calculated not for some kind of heterogeneous substrate, but for insulin crystals nucleated in the solution bulk; in both cases, the critical nuclei were formed from preliminary built Zn-insulin hexamers. The interpretation of the results is that no true homogeneous but rather heterogeneous (surface) insulin crystal nucleation is taking place also in the bulk solution. The nuclei form on some foreign particles of biological origin that are present in every protein solution.

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INVESTIGATION OF INSULIN CRYSTALLIZATION AND DISSOLUTION OF CRYSTALS IN PHYSIOLOGICALLY MIMICKED ENVIRONMENT

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Systematic investigation was performed on *in vitro* crystallization of commercial porcine insulin at conditions mimicking the *in vivo* environment. High supersaturation (0.47) was used for the crystallization studies in an attempt to match insulin concentration in natural β-cells [1]. Furthermore, physiologically relevant NaCl concentrations and temperature of 36ºC were used for the obtaining of rhombohedral insulin crystals. Crystal systems were then subjected to dissolution with some model flood solutions and finally with blood plasma. The effects of pH, solution composition and flow rate were investigated in an attempt to elucidate most important factors for *in vivo* crystals’ dissolution. Populations of tiny crystals were obtained through immediate nucleation and very short periods for crystal growth during insulin crystallization studies. In that way we managed to model fast storage of insulin in crystalline state in the granules of β-cells [2]. The dissolution studies were performed at flow rates closely related to the erythrocyte flow rates at common blood capillaries. Although we observed a dependence of crystals’ dissolution rate on flood solution flow rate, we proved that the effects of pH and solution composition are much stronger and generally working in a synergistic way. The blood plasma, used as a flood solution, had the greatest impact (quite reasonable result as insulin is supposed to perform readily its function upon release in the bloodstream).

Similar investigation was started to check the importance of polymorphic insulin modifications for some medical insulin formulations.

References

[1]. S. L. Howell, Diabetologia 26 (1984) 319-327.
[2]. Dimitra K. Georgiou and Peter G. Vekilov, PNAS 103 (2006) 1681-1686.

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BLOCKING OF THE HARMFUL EFFECT OF BISMUTH IONS DURING THE ELECTROEXTRACTION OF ZINC FROM SULPHATE ELECTROLYTES

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Binary and ternary (Pb-Bi and Pb-Ag-Bi) cast and rolled alloys have been investigated. These alloys are intended for use as anodes in the electroextraction (electrowinning) of zinc from sulphate electrolytes. Characterization of the alloys has been performed by means of quantitative inductively coupled plasma atomic emission spectroscopy (ICP-AES). This analytical technique has also been employed to determine the quantity of dissolved bismuth in the sulphate electrolytes. The electrochemical behaviour of the investigated alloys has been evaluated by galvanostatic tests and their surface morphology has been examined by scanning electron microscopy. It has been established that addition of inhibitors and complex forming agents leads to an increase of the current efficiency of zinc electrowinning and blocks significantly the harmful effect of bismuth ions on the reaction of zinc deposition.

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ELECTROCHEMISTRY OF MYOGLOBIN SELF-ASSEMBLED ON GOLD-PLATED GRAPHITE

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Redox protein myoglobin was immobilized on gold-plated graphite through self-assembly process. Its redox behavior was probed with linear sweep, cyclic and square-wave voltammetry. The experimental results suggest irreversible binding of the protein to the gold layer due to the interaction of sulfur-containing amino-acid cysteine from the protein shelf with gold: $2HS\text{-}R + 2Au \rightarrow 2Au\text{-}S\text{-}R + H_2$. In addition to that, two separate peaks appear on the cathodic part of the cyclic voltammetric curve one of which with a formal potential of -350 mV (vs. Ag/AgCl, 3M KCl) being assigned to the redox transformation of heme-prosthetic group. The efficiency of the electron exchange between the chemisorbed myoglobin was found to be much bigger as compared to the one of physically adsorbed myoglobin. It was hypothesized that upon chemisorption, most of the myoglobin molecules bind to the gold layer in an orientation superior for direct electron communication with the underlying electrode surface.

The immobilized protein was found capable to electrocatalytically reduce H_2O_2 and Cl_3CCOOH at working potentials of -350 and -700 mV (vs. Ag/AgCl, 3M KCl) respectively, in neutral aqueous solutions at room temperature. The kinetic pattern implies the process is limited by the rate of the very enzymatic reaction in both cases. It obeys the equation of Hill for hydrogen peroxide as substrate, while for substrate trichloroacetic acid the formal kinetics of Michaelis –Menten describes the process. It should be pointed out that the electroreduction of Cl_3CCOOH was found to occur at much lower overpotentials compared to bare graphite electrode.

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ULTRAFAST SYNTHESIS OF TITANIUM OXIDE THIN FILMS BY PULSED FIBER LASER ABLATION

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Titanium Oxide (TiO_x) thin films were obtained by Pulsed Laser Deposition (PLD) technique from a pure 99,99% Ti target at room temperature and low vacuum medium 2 Pa. Itterbium (Yb^+) nanoseconds pulsed fiber laser were used and investigated as new ablation source. Dense and smooth thin films with thickness from 163 nm up to 313 nm and area 7,5 cm^2 were deposited onto glass substrates at high grow rate up to 1nm/s and at laser fluence 10 J/cm^2.The coating synthesis were studied for two working fiber laser modes, at high repetition rate 20 kHz and by modulation at 1 kHz. Specific morphology and chemical composition of those TiO_x thin films were evaluated using Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX) data. The morphology of thin films and deposition rate strongly depended from working fiber laser modes at the same target – substrate distance and vacuum conditions. Very smooth surfaces, without droplets and cracks, showed TiO_x thin films deposited at lower deposition rate. The use of a Q- switched nanosecond fiber laser as novel ablating source for PLD method were investigated. The industrial scaling for this technique for deposition at high grow rate TiO_x thin films and others complex and functional metal oxide coatings will be discussed.

Keywords: TiO_x thin films, PLD, Pulsed Yb^+ Fiber Laser, SEM, EDX

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MORPHOLOGY AND COMPOSITION OF MAGNESIUM OXIDE THIN FILMS DEPOSITED BY NANOSECOND FIBER LASER ABLATION

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Magnesium oxide (MgO_x) thin films have applications as buffer layers by reason of their chemically stability in microelectronics, in waveguides structures as optical confinement because of relatively low refractive index in optoelectronics and in biotechnology as biodegradable and biocompatible barrier implant coatings. Thin MgO_x films were prepared onto glass substrates by laser ablation using a magnesium target with purity 99,5% at room temperature and low vacuum environment (2Pa). Pulsed fiber Itterbium (Yb^+) laser (λ = 1060 nm, τ = 100 ns, repetition rate of laser pulses up to 200 kHz, maximum average power 20W) were used as ablation source at laser peak power density 3,5 10^8 W/cm^2. Homogeneous and dense thin films with thickness from 267 nm up to 310 nm and area 7,5 cm^2 were obtained at grow rate up to 2,06 nm/s. The films deposited by this novel variation of conventional Pulsed Laser Deposition (PLD) technique were examined by Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX). The EDX spectroscopy analysis revealed the chemical films composition in dependence of the target purity thoroughly. Using the laser with relatively high repetition rate and high pulse energy as ablation source, the coatings grow rate could be significantly improved and could be opened new potential industrial applications for PLD method.

Keywords: MgO_x thin films, PLD, Pulsed Yb^+ Fiber Laser, SEM, EDX

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SYNTHESIS OF FERRITES FROM THE SYSTEM MeO – Fe_2O_3 AND STUDY THEIR SOLUBILITY IN SULFURIC ACID SULUTIONS AFTER PRELIMENARY TREATMENT

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Ferrites from the MeO – Fe_2O_3 system, where Me – Zn, Cd, were synthesized using a ceramic technology. Their composition, structure and properties were studied by chemical and X-ray diffraction analysis and Mössbauer spectroscopy. They are mono phase samples and have properties very close to the ones obtaining during zinc sulfide concentrates roasting in fluidized bed furnace.

The solubility of the ferrites in diluted sulfuric acid solutions (7, 10.5 и 14 vol.%) was studied using microwave heating. The obtained results were compared with the results from the experiments using conventional heating.

The experimental results show that the Zn and Cd degrees of solubility using microwave heating are higher than the ones obtained by other conditions of leaching.

On the basis of the data obtained a conclusion can be made that $CdFe_2O_4$ is lower stable than $ZnFe_2O_4$ using the both ways of heating.

The solubility of ferrite of the $Zn_{0,5}Cd_{0,5}Fe_2O_4$ type as well as of samples of zinc cake where the zinc is mainly as $ZnFe_2O_4$ is investigated using a method of mechanical activation and following acid and high-temperature leaching. For this purpose the energy of mechanical milling techniques was used. It was established that crystal structure changes have occurred in the studied samples. The results obtained show that the degree of Zn and Cd solubility from ferrites and zinc cake after mechanical treatment increase significantly comparing with the obtained data for the initial non-treated samples.

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RECOVERY OPTIONS WASTE TONER AND CARTRIDGES

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The increasing consumption of electrical products and electronics as a result of technological innovation and market expansion has led to the generation of significant quantities of electronic waste in the world (mainly in Europe, USA and Australia).In the past few years alone, these waste materials were estimated at 20-30 mil t / y. A significant portion of this figure is composed of waste toner and cartridges. Complicated chemical composition, development of new technologies and pressure by environmental organizations incentivized the search for solutions for treatment and recovery of waste toner and cartridges with minimal environmental impact [1, 2, 3].

The present investigation involves determining the ash content and calorific value of waste and toner cartridges. Non-magnetic, magnetic and mixed waste toner and waste cartridges and packaging printers have been analyzed. Mixtures of non-magnetic and magnetic toner in different proportions were examined for better comparability of results.

The ash content was determined by burning at 850 ^{0}C to constant weight. The caloric effect was analyzed with automatic isoperibolic calorimeter KL - 10 calibrated with benzoic acid. Values obtained for ash content varied between 3.4% and 45.5%, and values obtained for calorific value varied between 30,7 MJ / kg and 22,33 MJ / kg for non-magnetic and magnetic toner, respectively. Results of the analysis were compared with those for conventional fossil fuels and biomass.

Odors and harmful gases, emitted during combustion, reduce the possibilities for utilization of these waste products. Eventual combustion of waste should be carried out under appropriate conditions in convenient reactors and should be accompanied by purification of exhaust gases. The separated heat could be used to produce process steam or electricity.

The possibility of using toner waste as an additive for specialty inks and paints is of interest, which is the subject of our further research.

References

[1] Y. Yildirim et al., *Resources, Conservation and Recycling*, 42 (2004) 295–308.
[2] B.H. Robinson, *Science of the Total Environment*, 408 (2009) 183–191.
[3] J. Ruan et al., *Journal of Hazardous Materials*, 185 (2011) 696–702.

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RISK ASSESSMENT OF CYCLODODEC-2-EN-1-YL ETHERS

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Environmental pollutants are continuously being emitted from anthropogenic activities in large amounts. They move throughout the ecosystem by a variety of processes and are eventually degraded or accumulated somewhere in the environment. The chemical diversity of pollutants and the variations in behaviour, both with respect to transport, degradation, accumulation (fate) and toxicity (effects) has introduced the field of risk assessment. As a consequence, this has become an essential and necessary discipline in the legislation for controlling the use and release of chemical substances to ensure that they pose negligible risk to the health of humans, wildlife, and the larger ecosystem of which we are only a small part. To assess the potential risk of chemicals on humans and ecosystems, it is essential to develop a quantitative description of the pathways of contaminant transport and the resulting exposure combined with an estimate of the potential effects on the exposed organisms. New chemicals are continuously being introduced to the environment either directly (primary emission) or indirectly as an unintended result of the use. Assessment of all these chemicals based on experimental studies requires tremendous efforts and costs, and such a task is presently beyond existing human, technical, and economic resources. Therefore risk assessment needs to be based on an interdisciplinary approach involving monitoring of exposure concentrations in the natural environment, laboratory scale fate and effect studies and predictive models designed to establish a quantitative link between sources, exposure levels, and risk of effects of potential hazardous pollutants. The aim of this is to predict risk assessment of some new chemicals (cyclododec-2-en-1-yl ethers) in the environment.

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ANTIOXIDANT CAPACITY OF BILBERRY FRUITS

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Total polyphenolic and anthocyanin contents and antioxidant capacity (DPPH- and FRAP-assay) of methanolic extracts from bilberry (*Vaccinium myrtillus* L.) fruits were studied depending on the origin (the region of Troyan/Velingrad) of the plant material. Total polyphenols correlated well (R = 0.98-0.99) with the antioxidant capacity of the analysed samples. The anthocyanin content of the extracts contributed significantly to their antioxidant capacity, which was higher for the fruits from the region of Velingrad.

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STABILIZATION OF FLAXSEED OIL

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This study focuses on the oxidative stability of flaxseed oil. Experimental studies showed that the crude flaxseed oil is prone to rapid oxidation (6 h at 100ºC by Rancimat method) and hence needs to be stabilized. The addition of different synthetic and plant-derived antioxidants to the oil samples was found to affect drastically its oxidative stability, the most pronounced effect being observed with ascorbyl palmitate. It was noticed that the oil sample containing 0.2% of the ascorbate derivative enhances more than 8 times its oxidative stability (more than 48 h at 100ºC by Rancimat method).

An electrochemical method for quantitative assay of water insoluble ascorbyl palmitate was developed. Preliminary results suggest that the compound of interest could be analyzed electrochemically in water-ethanol mixtures under experimental conditions allowing highly sensitive determination of the ascorbyl palmitate alcoholic extracts with concentrations close to these expected in real samples.

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COMPOSITION OF CYPRESS SEEDS OIL

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The lipid composition of cypress (*Cupressus*) seeds was investigated. The seeds contain 27.3% glyceride oil. The total content of phospholipids was 0.9%. Sterols general amounts 2.2% were found. In the tocopherol fraction (328 mg/kg) γ-tocopherol predominated (91.3%). Fatty acid composition of triacylglycerols was identified. In the triacylglycerols the main component are oleic, linoleic, linolenic and palmitic acids.

Keywords: Cypress seeds, glyceride oil, fatty acids, phospholipids, sterols, tocopherols

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SEASONAL CHANGES ON VITAMINS AND FATTY ACIDS COMPOSITION OF BIGHEAD CARP FILLETS

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Aquaculture in Bulgaria is mainly fresh water. One of the most farming warm-water fishes in our country are carps family (about 50% of total aquaculture production). After common carp, the bighead carp *(Hypophthalmichthys nobilis)* is another highly breaded member of this family – in freshwater farms and dam lakes [1]. Fish tissue fats are rich source of fat soluble vitamins and both saturated and unsaturated fatty acids. These nutrients are very important for human health and might be obtained from the diet. There is limited information in the scientifically literature about the nutritive composition on bighead carp edible tissue.

The aim of this study was to determine and compare fat soluble vitamins content and fatty acids composition in bighead carp raw fillets in two seasons – spring and autumn.

All-trans-retinol, cholecalciferol and α-tocopherol were analyzed simultaneously using HPLC system (Thermo Scientific Spectra SYSTEM) equipped with analytical column ODS2 Hypersil™ 250 x 4,6 mm, 5u. Retinol and cholecalciferol were monitored by UV detection and α-tocopherol was detected by fluorescence. The sample preparation procedure includes saponification and liquid-liquid extraction of the unsaponifiable matter [2]. Total lipids were extracted according to Bligh and Dyer method [3]. Analysis of fatty acid methyl esters was performed by gas chromatography system with MS detection.

Palmitic, palmitoleic, stearic, linolenic, arahidonic and docosahexaenoic fatty acids and cholecalciferol and α-tocopherol were found in substantial amounts in the lipid fraction for the two seasons.

The total lipids, sum of SFA and MUFA, and sum of n6 fatty acids are increased in autumn samples. On the other hand the bighead carp fillet from spring is richer on PUFAs, n3 fatty acids and three analyzed fat soluble vitamins.

References

[1] National Strategic Plan for Fisheries and Aquaculture, 2007 – 2013. Ministry of Agriculture and Forestry, National Agency for Fisheries and Aquaculture, Bulgaria.
[2] Dobreva D.A., Galunska B., Stancheva M., 2011. Liquid chromatography method for the simultaneous quantification of fat soluble vitamins in fish tissue. Scripta Scientifica Medica, Varna Medical University, 43, 1, 276-279.
[3] Bligh E., Dyer W.J., 1959. A rapid method of total lipid extraction and purification, *Canadian J of Biochem and Physiolog,* 37, 913–917.

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ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS IN FRESHWATER FISH

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Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) were determined in muscle tissue of three freshwater fish species: common carp *(Cyprinus carpio)*, grass carp *(Ctenopharyngodon idella)* and bighead carp *(Hypophthalmichthys nobilis).* Fish samples were collected in 2010 from the Pyasachnik Dam Lake. The OCPs and PCBs were analysed in order to evaluate the status and potential sources of pollution in area of the lake. The species were selected because of their importance to local human fish consumption.

The fifteen congeners of PCBs, p,p'-DDT and its two main metabolites p,p'-DDE and p,p'-DDD were determined by capillary gas chromatography system with MS detection. DDTs were the predominant organohalogenated contaminants in all species, with the p,p'- DDE contributing to more than 70% to the total DDTs. All samples of muscle tissue examined contained detectable levels of p,p'-DDE and p,p'- DDD. The residues of p,p'- DDT were not detected in all samples. The sum of the individual PCB congeners was determined lower than those found in similar fish species from other aquatic ecosystems.

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RAPID GROWTH DIAMOND-LIKE-CARBON FILMS BY YTTERBIUM NANOSECOND FIBER LASER

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Pulsed Laser Deposition of high quality Diamond-Like- Carbon films has been demonstrated from Yb$^+$ nanosecond fiber laser operating with 1,06 μm radiation, an average power 20W, pulse duration 100 ns and repetition frequency 20 kHz at room temperature and vacuum 4.10^{-5} mbar. Maximum deposition rates from 1,5 nm/s were obtained at fluencies between 8 J/cm^2 and 12 J/cm^2 .The chemical bonding structure and surface morphology of DLC films deposited on to metal and dielectric substrates were characterized by Raman spectroscopy, optical microscopy and Scanning Electron Microscopy. The effect of substrates on DLC films structures were studied. The films deposited on to dielectric substrates were characterized as typical tetrahedral (ta-C) DLC with high sp^3 content. DLC coatings on to metal substrate were typical a-C amorphous carbon films with mixing sp^2/sp^3 bonds. Uniform and dense films were obtained on substrate area of 10 cm^2 without any special scanner device. A promising pulsed laser technique for industrial applications using Q-switched nanosecond fiber laser has been demonstrated.

Keywords: DLC films, PLD, Fiber Laser, SEM, Raman spectroscopy

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METABOLIC CHANGES AS ADAPTIVE PLANT RESPONSE TO THE POLARIZATION CONDITIONS OF DIRECT PHOTOSYNTHETIC PLANT FUEL CELL

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Duckweeds (*Lemnaoideae)* are autotrophic aquatic plants which dominate a pond's surface and inherently absorb sunlight. Recently we proved that 3 duckweed species- *Lemna minuta, Lemna valdiviana and Wolfia globosa* are appropriate for utilization in a newly developed Direct Photosynthetic Plant Fuel Cell (DPPFC). The conversion of sunlight into carbohydrates by photosynthesis can be conjugated with electricity generation through this technology. In this study we demonstrate the duckweed plant biofuel cells' performance by investigation of their electrochemical behavior. The highest fuel cell power density of 140 mW/m^2 and short circuit current density of 1.2 A/m^2 were achieved with *Lemna valdiviana*. The same duckweeds exhibit also the best performance during long-term experiments at constant load resistance. The electrons' flow to the anode is accomplished by electrochemically active compounds produced and excreted by plants cells in the anolyte in consequence of the polarization conditions in the biofuel cell. The biochemical analyses showed that the protein content in the chlorophyll and mitochondria enriched fractions of the analyzed duckweeds species increased double under DPPFC-conditions. In parallel, the quantity of inorganic phosphate decreased probably due to an enhanced respiration and ATP production. The polarization conditions shifted the carbohydrate production towards starch accumulation. The adaptive mechanisms in the plants are expressed in different activity of important enzymes like α-amylase and phytase.

Acknowledgment: *This study was funded by the program "New power sources and energy-saving technologies" of the National Science Fund of Bulgaria through contract D002-163/2008.*

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NEW ELECTRDEPOSITED CATALYSTS FOR SODIUM BOROHYDRIDE HYDROLYSIS AND ELECTROOXIDATION

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Alkaline borohydrides are hydrogen-rich compounds, which are intensively studied as safety hydrogen storage materials. Based on catalyzed borohydride hydrolysis, various hydrogen-on-demand (HOD) generators have been recently developed as a promising way to overcome disadvantages with existing hydrogen storage and transportation methods. Moreover, alkaline borohydrides can be directly used as a fuel in power sources referred as direct borohydride fuel cells (DBFCs). In the present study, CoNiMoW nanocomposites were investigated as potential catalysts for sodium borohydride hydrolysis and electrooxidation. The nanocomposites were electrodeposited on nickel foam (RECEMAT, RCM-Ni-2733.03) under different galvanostatic conditions (1A, 2A, 3A, 4.8A) and characterized by means of SEM and XRD. The catalytic properties of produced materials towards borohydride hydrolysis reaction were examined by volumetric measurement of evolved hydrogen at the temperature range from 288 to 315 K. The results from these kinetic studies show that the rate of hydrogen evolution increases when CoNiMoW composites electrodeposited at lower currents are applied as catalysts. The estimated close values of activation energy indicate that the process takes place via identical mechanism on all examined catalysts. The same materials were applied as anodes in DBFC with air-cathodes. As a tendency, higher generated power was obtained with nanocomposite anodes, produced at lower currents. Proportional increase of the power was achieved with stacks of two or more DBFCs, connected in series. Significant improvement of generated current and power was attained by applying two gas-diffusion cathodes, which indicates that the oxygen reduction reaction is the rate-limiting step of the overall process. Based on the results from both electrochemical and catalytic studies it can be concluded that the electrodeposited CoNiMoW composites are suitable for development of hybrid systems combining DBFC and HOD generator.

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9th Chemistry Conference and Workshop BioSupport
Plovdiv 14-16 October 2011

Фирма Т.Е.А.М. ООД е основана в началото на 1992 год. Фирмата е оторизиран дистрибутор и сервизен център на **Agilent Technologies** за хроматографска, масспектрална, ICP-MS, NMR аналитична апаратура на територията на България, както и представител на **Foster&Freeman** за широка гама от доказателствена техника

Т.Е.А.М. ООД е посветила дейността си на продажби, гаранционна и извънгаранционна поддръжка, технически и методологически консултации, профилактика, верифициране и проверка на аналитични системи съобразно съответните стандарти, както и на организиране на семинари и обучения в различни градове на страната.

Фирмата има утвърдени пазарни позиции в областта на аналитичната апаратура за химическата и фармацевтичната промишленост, нефтохимията, металургията, хранително-вкусовата промишленост, токсикологията, опазването на околната среда, здравеопазването и др.

Основните видове аналитични продукти, които предлагаме, са:

- Системи за газова хроматография (GC);
- Системи за течна хроматография (LC);
- Индустриален клас високоефективна течна хроматография (HPLC, UPLC);
- Масспектрометрични детектори за GC (Q, QQQ);
- Масспектрометрични детектори за HPLC (Q, QQQ, IT, TOF, QTOF, Chip);
- Детектори за HPLC (UV-VIS, DAD, FLD, RID, ELSD);
- Индуктивно-свързана плазма – масспектрометрия (ICP/MS);
- Комбинирани техники на разделяне и детектиране:
  - GC/MS, HPLC/MS, CE/MS;
- Техники за подготовка и автоматично инжектиране на пробите:
  - Purge and Trap, Headspace, Autosampler;
- Хроматографски колони, консумативи, стандарти за инструментален анализ и пробоподготовка.
- Видеоспектрални системи за сравняване и проверка на банкноти, паспорти, визи както и за рутинна проверка на съмнителни документи;
- Криминалистични светлинни източници, уреди за анализ на веществени доказателства по индекс на пречупване, елементен анализ с лазерна аблация, раманови микроскопи за анализ на мастила, тонери и др., системи за проявяване, заснемане и сравняване на пръстови отпечатъци.

На нашия уеб-сайт www.team-cag.com можете да намерите не само най-новата информация за иновациите в областта на предлаганата аналитична апаратура, но и най-съвременните приложения в различните области на промишлеността, научните и медицинските изследвания.

От месец юни 1998 г. работим в съответствие със стандарта ISO 9001. Новият ни сертификат по последната ревизия на стандарта ISO 9001:2008 е издаден от ÖQS, австрийска организация за сертифициране, верифициране и оценка, член на IQN (Международната Мрежа за Сертифициране).

Референции:

Сред най-големите ни клиенти са:

Министерство на Околната среда и водите; Изпълнителна агенция по околната среда - София и Регионални лаборатории; Изпълнителна Агенция по Лекарствата (ИАЛ); Регионални здравни инспекции; Лаборатория за допинг контрол – София; Българска Академия на Науките; МВР - София и 25 ОДП в страната; Гранична полиция; Национална мрежа от митнически лаборатории – София, Пловдив, Русе; Централна лаборатория по ветеринарно-санитарна експертиза и екология (ЦЛВСЕЕ); Национален диагностичен научноизследователски ветеринарномедицински институт (НДНИВМИ) – София; Централна лаборатория за контрол на пестициди, нитрати, тежки метали и торове; Национален център по метрология; Медицинска Академия – София, Пловдив, Варна; Медицински Университет – София, Пловдив и Варна; Актавис АД; Софарма АД; Биовет АД; Лукойл - Нефтохим Бургас АД; СЖС България ЕООД; Астера АД; Арома АД; Българска роза АД; Летище София и др.

NEOCHIM PLC

HISTORY

Neochim PLC is the successor of the Chemical Plant in the town of Dimitrovgrad in Bulgaria which started its production activities on 5th of November 1951. In the beginning nitrogen and phosphate fertilizers were produced. Later on, expansions, reconstructions and modernizations of the production facilities were carried out. In 1987 a new complex for the production of ammonia, nitric acid and ammonium nitrate was commissioned. In the period 1992-93 the plants producing sulfuric and phosphoric acid, aniline and nitrobenzene were shut down.

Neochim PLC is a leading company in the production and trade of fertilizers in Bulgaria. It is also the only producer of ammonium nitrate NEOFERT, formalin, fertilizers blend, sodium nitrate, urea-formaldehyde resins etc. The ammonium nitrate Neofert is the most popular and the most demanded product at the Bulgarian market. Our products are used in agriculture, food industry, medicine etc. On the local market all products of Neochim PLC are distributed by the trading company Eurofert PLC.

High quality production, well-developed distribution network and excellent trade relations with business partners contribute to stable positioning on the local market as well as on the international markets in Western Europe, the Balkan Peninsula.

LOCATION

Neochim PLC is situated near the town of Dimitrovgrad. The plant's infrastructure is distributed on two plots with a total area of 2 300 decares, situated on both banks of the Maritsa river, outside the town limits. It is located 200 km southeast of Sofia, in a region with well-developed railway junction and near to Pan - European transport corridors No 4, 9 and 10.

PURPOSE

Production and trade of inorganic and organic chemical products.

MANAGEMENT STRUCTURE AND STAFF

Neochim PLC is a joint-stock company with a single-stage structure of management, managed by a Board of Directors.

The organizational and executive activities are concentrated in departments, each administered by a Director, directly subordinate to the Chief Executive Director and two Executive Directors.
The company employs nearly 1200 people.

STRUCTURE OF THE PRODUCTION FACILITIES

The production facilities are structured in the following groups:

- Nitrogen - Fertilizer Complex
- Organic Production
- Repair and Mechanical works
- Railway Station

ADVANTAGES

- Modern equipment
- High quality products
- Well-developed distribution network, combined with storage facilities.
- Highly motivated and trained personnel
- Good and well established maintenance practice
- Environment friendly production

CAPACITIES

Operational nameplate capacities for major production units are:

Ammonia	450 000 mt/yr.
Nitric Acid	480 000 mt/yr.
Ammonium nitrate NEOFERT ®	710 000 mt/yr.
Sodium Nitrate	9 300 mt/yr.
Formalin	30 000 mt/yr.
Urea-Formaldehyde Resins	20 800 mt/yr.
Ammonium Bicarbonate	6 000 mt/yr.

Neochim PLC is the only company in Bulgaria producing formalin (formaldehyde solution), urea-formaldehyde resins, sodium nitrate, ammonium bicarbonate, laughing gas (nitrous oxide), etc.

MARKETS

The products of Neochim PLC are well received on the international markets. The company has commercial relations with partners from USA, Brazil, Great Britain, France, Italy, Greece, Turkey, Poland, Romania, etc. 40 to 60% of the earnings are formed by exports.

The market advantages of Neochim PLC are:

- excellent process technologies and modern equipment;
- offering high quality products;
- stable positioning on international markets in Western Europe, the Balkan Peninsula, Latin America and the USA;

- well-developed distribution network and warehouse facilities on the Bulgarian market;
- excellent trade relations with its business partners.

CAREER DEVELOPMENT

Neochim PLC gives an opportunity to young people for professional realization and gathering precious experience by participation in the two programmes for practice and scholarship. If you are a student, you can apply for the programme for trainees or for the scholarship programme during the period of your education.

The trainee programme:

- at least one month
- work in real working conditions
- receive free lunch
- free hostel
- receive a certificate in the end of the practice
- you can apply for it year-round

The scholarship programme:

- if you are a bachelor student
- if your grades are over “Good 4” you can receive up to two minimum salaries for the country depending on the grades for the last year - “Excellent 6” – two minimum salaries; “Very good 5” – one and a half minimum salary; “Good 4” - one minimum salary for the country.
- during the preparation of diploma work you receive professional help from specialists working in Neochim PLC
- opportunity for practice in Neochim PLC

In order to apply for these two programmes you should study one of the following subjects:

1. chemical technologies
2. industrial chemistry
3. automated production
4. electrical engineering
5. energetics
6. electronics
7. mechanical engineering
8. electronic technics and technologies
9. computer systems and technologies
10. chemistry
11. physics

Requested documents:

1. CV
2. Motivation letter
3. Written application addressed to the Chief Executive Director of Neochim PLC
4. Copy of the students book

Applicants for scholarship should also send us: a document to certify that the applicant is a student and a recommendation note from a lecturer

REALIZED PROJECTS

- 2004 – Neochim PLC invested 6 million Euro in modernizing the reforming furnace of its ammonia plant.
- 2007 – Neochim PLC started using/introduced the first production line for blended fertilizers. Combining them with best-selling brand ammonium nitrate provides optimal yields and balanced soil and crops nutrition.
- 2008 – Neochim PLC started producing electricity for its own needs by building a turbine plant. The implementation of this project contributed to a significantly more competitive position of the company against the ever-increasing energy prices globally.
- 2008 – 2009 The company invested 18 million BGN for increasing the ammonium nitrate production capacity of its typical AN – 72 plant, from 1360 MT/Day(name plate) to 2350 MT/Day utilizing the existing prilling tower and keeping the AN and ammonia emissions at BAT levels. Furthermore, the company invests heavily in building an automated system for production management,which will contribute to greater efficiency in the technological process of the used energy resources and to improve the working conditionsof the employees. The first stage of the project is in the workshop for ammonia production. In 2008 Neochim PLC signed contracts with leading companies to design, supply and introduce the automated systems.

COMPANY PROFILE

Laboratory Technics Engineering is a reserved trade mark of Medical Technics Engineering Ltd. (MTE) – a private Bulgarian company with 20-years experience in the field of the **trade with medical and laboratory products** for the need of the laboratories from all areas of science and industry, as well as the health establishments country-wide.

MANUFACTURERS REPRESENTED/APPARATUSES OFFERED:

Leica Microsytems, Germany&Switzerland – Light and stereomicroscopes, digital cameras and specialized software; complete equipment of pathological laboratories, reagents, consumables and antibodies for histology, cytology and immunohistochemistry
Walter Uhl, Germany – measuring microscopes, microhardness testers
Bruker Optics, Germany- FT-IR, NIR, Raman, Terahertz spectrometers, monochromators
Biochrom, UK – UV/Vis spectrometers, ELISA systems, aminoacids analyzers
Analytik Jena, Germany – PCR equipment and consumables
Andreas Hettich, Germany - Centrifuges, ultra-freezers

Binder, Germany - Thermostats (incubators), CO2 incubators, dry sterilizers, drying chambers, vacuum dryers
Denver Instrument, Germany - Electronic and technical analytic balances, pH meters, hygrometers
Liebherr, Germany – freezers and refrigerators
Systec, Germany – Laboratory autoclaves and media preparators
Carl Roth, Germany– cabinets for storage of chemicals, lamps and cold light sources, magnifiers, refractometers, measuring devices (thermometers, timers, conductivity meters, moisture meters, hydrometers, luxmeters, oxymeters, colony counters, barometers, air-conditioning stations, calibration balances and devices, photometers), disintegrators, homogenizators, water baths (cooling, oil, water, sand), mills, rotators, shakers, stirrers, mixers, muffle furnace, ultrasound baths, vacuum and peristaltic pumps, evaporators, dryers and many others
GFL, Germany – freezers, water baths, water baths-shakers, destillers and bi-destillers, incubator-shakers, hybridization incubators, mini incubators, shakers
Capp, Danemark – pipettes, pipettors, stands
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Faster, Italy – vertical and horizontal laminar boxes, microbiological laminar boxed of class II, cupboards for cytostatics, fume cupboards.

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ЛАБИМЕКС ООД е оторизиран дистрибутор на водещи европейски и световни компании, специализирани в производството на лабораторни химикали и реагенти, стандарти, лабораторни консумативи, стъклария и пластмаса, общолабораторна и специализирана апаратура.

Единствено чрез Лабимекс ООД вече и българските потребители ще могат да работят с висококачествените реактиви, производство на THERMO FISHER SCIENTIFIC:

- ACROS ORGANICS – Органични химикали и реагенти за научно-изследователска и общолабораторна работа
- FISHER CHEMICALS – Широк спектър аналитични реагенти – разтворители (безводни, HPLC, GC, GC-MS, спектрофотометрични), соли, ултрачисти химикали за елементен анализ, фармакопейни реактиви по Ph.Eur., USP, BP.
- FISHER BIOREAGENTS – реактиви за протеинов анализ, молекулярна и клетъчна биология
- MAYBRIDGE – иновативни химикали за медицинска и синтетична химия

От три години българските клиенти използват висококачествените продукти на белгийската компания CHEM-LAB NV. Продуктовата им гама включва:

- TITREX - Титриметрични разтвори
- PHARMEX - Фармакопейни реагенти съгласно Ph.Eur.
- IONEX – Стандарти и референтни материали за AAS, ICP, IC, HPLC, GC, GC-MS и др.
- AUTOMATEX - Реагенти за автоанализатори и индустриални on-line анализатори
- HYDREX - pH буфери и еталони за проводимост и мътност
- TAYLOR MADE SOLUTIONS - разтвори по поръчка, според специфичните нужди на клиента

LABIMEX Ltd. is an authorized distributor of leading European and World manufacturers specialised in manufacturing of laboratory chemicals and reagents, standards, laboratory consumables, glassware and plastic ware, laboratory equipment for routine and specific application.

Exclusively through Labimex Ltd Bulgarian end-users will be able to work with high quality reagents produced by THERMO FISHER SCIENTIFIC:

- ACROS ORGANICS – Core organic chemicals and reagents for research and development and for routine laboratory work
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chemicals for elemental analysis, reagents according to Ph.Eur., USP, BP
- FISHER BIOREAGENTS – Reagents for protein chemistry, molecular and cell biology
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Bulgarian customers have been using high quality products of Belgian company CHEM-LAB NV for last three years. Most popular products of CHEM-LAB NV are:

- TITREX – Titrimetric solutions
- PHARMEX – Reagents according to European Pharmacopoeia
- IONEX – Standard solutions for AAS, ICP, IC, HPLC, GC, GC-MS, ICP-MS etc.
- AUTOMATEX – Reagents for automatic analyzers and industrial on-line analyzers
- HYDREX – Buffer solutions, reference materials for conductivity and turbidity
- TAYLOR MADE SOLUTIONS – Products manufactured according to specific customer specifications.

ACM2

ACM2 Ltd., Sofia 1404, 23 Tvardishki prohod, Str.,
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office@acm2.com, www.acm2.com

ACM2 Ltd. was founded and operates on the Bulgarian market since 1997. Over the years ACM2 established itself as one of the main suppliers of analytical and medical equipment. Reasons for this are as good business relations with our world leader partners as the professionalism, and perfect team work of all employees. Challenges on the Bulgarian market and increasing demands of the environment required constant evolutionary development of relations between the company and its partners - customers and suppliers. ACM2 Ltd. operates under the requirements of standard EN ISO 9001:2008. In 2010 ACM2 received the award for "Management" from the main supplier company - Thermo Scientific, which is evidence of good management team and the right direction of development.

The main product groups offered by ACM2 are:

- **Chromatography equipment:** Gas Chromatography systems (GC) and High-Performance Liquid-Chromatography systems (HPLC) in different configurations. GC and HPLC columns, chromatography consumables and accessories;
- **Mass Spectrometry:** Mass spectrometry for chromatography systems (GC/MS and LC/MS), High-resolution magnetic sector MS, Isotope Ratio MS and Multicollector Thermal Ionization MS;
- **Spectral analysis equipment:** UV/VIS and flurorescence spectrometers; FT-IR and Raman spectrometers;
- **Elemental analysis equipment:** Atomic Absorption Spectrometers, ICP and ICP/MS for elemental analysis in different matrixes. Total Organic Carbon analyzers (TOC). Elemental analyzers;
- **X-Ray analysis;**
- **Surface analysis equipment;**
- **Laboratory Information Management Systems, LIMS;**
- **Laboratory Water Purification Systems;**
- **Hematology analyzers, reagents and control materials for hematology analysis;**
- **On-line process water analysis.** All kind of the waste water analysis – industrial and public. They are effective in fuel, pharmacy, food, packing, semi-conductor producing. They can be used in airport water control.
- **Full range of equipments for testing of pharmacy products: tablets, liquids and gel forms.**

ACM2 has an authorized service center in Bulgaria and high level qualified service engineers.

Gas Chromatography


Trace GC Ultra


TSQ Quantum GC

ISQ GC/MS


ITQ Series

- GC
- GC Columns
- GC/MS Single Quad
- GC/MS Triple Quad
- GC/MS Ion Trap

Liquid Chromatography


SpectraSystem


Accela HPLC

- HPLC
- HPLC Columns
- UHPLC
- LC/MS Single Quad
- TurboFlow Technology
- Multiplexing

Mass Spectrometry

- Hi Res & Accurate Mass MS
- LC/MS Triple Quad
- LC/MS Ion Trap
- Gas Isotope Ratio MS
- Hi Res GC-MS
- Hi Res ICP-MS
- GD-MS
- MC-ICP-MS
- TIMS
- Noble Gas MS


DFS


LTQ Orbitrap XL


LTQ XL


Exactive


TSQ Vantage

Support Plans Qualification Maintenance
Training Upgrades Consumables

Elemental Analysis


iCAP 6500


iCE 3500


XRD

- Combustion
- ICP
- ICP-MS
- OES
- XRD
- XRF

Molecular Spectroscopy & Microanalysis


Evolution 600


DXR Micro


Antaris II


Nicolet iS10

- FT-IR
- UV-Vis
- FT-NIR
- Raman
- X-ray Microanalysis
- Microbeam XRF
- Imaging & Microscopy

Surface Analysis


Theta Probe


K-Alpha

- AUGER
- XPS ESCA

Lab Water Systems


PURELAB OptionQ


Reservoir


Medica 7/15

- Type I water
- Type II water
- Type III water
- Clinical & healthcare wate
- Water Storage

Pharmacy products testing

- Dissolution testers
- Disintegration testers
- Friability testers
- Tablet presses
- Blister checker
- Hardness testers
- Fluid Bed Systems
- All Purpose Equipment
- Granulate testers
- Roller compactors


DT 720


TAR


ZT 220

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ХРОМА ООД извършва продажба, доставка и сервизно обслужване на аналитична апаратура и общо лабораторно оборудване.

Лабораторното оборудване е на:

Perkin Elmer - Analytical Instruments (USA)

- Спектрометри - AAS, ICP/OS, ICP/MS, FTIR, UV/VIS, UV/VIS/NIR, поляриметри, флуориметри
- Хроматографи - HPLC, GC, GC/MS
- Апарати за термичен и елементен анализ
- Консумативи и резервни части

ХРОМА ООД осигурява сервиз на доставената апаратура, обучение и консултации на специалистите, работещи с нея. Периодично организира тематични семинари за популяризиране на нови продукти и области на приложение.

Оборудвали сме над 200 лаборатории в страната, в това число, аналитично-химични, диагностични, клинично-химични, и научно-изследователски звена.

Notes

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