



Specific Support Action
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Workshop on

**Ecomaterials and Processes:
Characterization and Metrology**



April 19 – 21, 2007, St. Kirik, Plovdiv, Bulgaria

Organised by the

**Centre of Competence on
Multifunctional Materials and New Processes with
Environmental Impact (MISSION)
at the Institute of General and Inorganic Chemistry,
Bulgarian Academy of Sciences**

<http://metecomat.igic.bas.bg>

Supporting organizations

Institute of General and Inorganic Chemistry at the Bulgarian Academy of Sciences

Acad. G. Bonchev Str., bldg. 11, 1113 Sofia, Bulgaria, <http://www.igic.bas.bg/>

The Institute of General and Inorganic Chemistry is one of the principal and oldest chemical institutes of the Bulgarian Academy of Sciences. The activities of the institute include basic and applied research, consultancy, industrial practice and teaching in three main research areas:

- ✓ inorganic materials science;
- ✓ chemical analysis;
- ✓ adsorption and catalysis.

The Centre of Competence on Multifunctional Materials and New Processes with Environmental Impact (MISSION)

Acad. G. Bonchev Str., bldg. 11, 1113 Sofia, Bulgaria, <http://mission.igic.bas.bg/>

The Centre of Competence MISSION, funded by the European Commission, was established on May 1, 2005 at the Institute of General and Inorganic Chemistry of the Bulgarian Academy of Sciences. The aim of this project is to establish an innovative leading Centre for the development and management of advanced materials for clean energy production and multifunctional materials for environmental protection. Attention will also be paid to the natural chemical resources as regards mainly their utilization and management. An important part of the efforts will be the development of a new strategy for evaluation and certification of environment friendly multifunctional materials.

Workshop on

**Ecomaterials and Processes:
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St. Kirik, Plovdiv, Bulgaria

Dear Colleagues,

On behalf of the Organizing Committee, it is my pleasure and honor to welcome all participants in the MetEcoMat workshop.

The MetEcoMat workshop is devoted to all aspects of characterization and metrology of ecomaterials and processes. The thematic area of the workshop comprises advanced laser materials for ecology, functional materials for environmental protection, and materials for energy application. The metrology topics are focused on method validation and quality assurance of environmental analysis. Thermodynamic modeling of ecomaterials and processes in order to predict novel properties are presented. Green technologies for production of ecomaterials will be discussed with the intention to solve the global environmental issues. The workshop program is divided into presentations on a number of key topics followed by specific case studies and discussions. We hope that the program and diversity of the topics will be a basis for an exciting meeting and thought-provoking discussions.

We would like to thank the European Commission for the support of the MetEcoMat workshop.

We look forward to welcoming you to the resort “St. Kirik” - a former XIV century monastery, located in the Rhodopes Mountain, near Plovdiv, Bulgaria.

Yours sincerely,

Dr. Radostina Stoyanova
Scientific Secretary of
the MetEcoMat Workshop

Workshop Topics

- A.** Characterization of Ecomaterials;
- B.** Quality Assurance of Environmental Analysis;
- C.** Method Validation and Environmental Reference Materials;
- D.** Thermodynamic Modeling of Ecomaterials and Processes;
- E.** Green Technologies for Ecomaterials;
- F.** Advanced Laser Materials for Ecology.

Organizing Committee:

Konstantin Hadjiivanov

Radostina Stoyanova

Ivan Havezov

Radostin Nickolov

Stefka Tepavicharova

Velin Nikolov

Project Coordinator

Scientific Secretary

Invited Speakers

Topic A. **Prof. Hartmut Fuess** - Institute of Materials Science, Darmstadt University of Technology Darmstadt, Germany

"In-situ characterization by synchrotron (diffraction and absorption) of functional materials (battery, fuel cell, piezoceramics)"

Prof. Sefik Suzer - Department of Chemistry, Bilkent University, Ankara, Turkey

"X-Ray Photoelectron Impedance Spectroscopy: A different Way of Doing Surface Science"

Topic B. **Prof. Gillian Greenway** - University of Hull, Hull Environmental Research Institute, Environmental monitoring and modelling group, UK

"Micro and Nano scale chemical measurements devices"

Dr. Wolfram Bremser - BAM Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany

"Managing quality in environmental analysis: From MRA and KC to lab control samples"

Topic C. **Prof. Freddy Adams** - University of Antwerp, Antwerp, Belgium

"Synchrotron radiation as a validation tool on the micro/nanoscale level"

Prof. Dimitar Tsalev - Faculty of Chemistry, University of Sofia, Bulgaria

"Method validation in environmental analysis – mission possible"

Topic D. **Prof. Wolfgang Voigt** - TU Bergakademie Freiberg, Institute of Inorganic Chemistry, Freiberg, Germany

"Thermodynamic modelling for mineral-based ecomaterials"

Topic E. **Prof. Jurgis Staniskis** - Institute of Environmental Engineering, Kaunas University of Technology, Kaunas, Lithuania

"Cleaner Production and Product Ecodesign: Strategies and Implementation"

Topic F. **Prof. Jürgen Eichler** - Technische Universität Berlin, Optisches Institut, Germany

"Advanced laser materials for application in ecology"

Plenary Lecture **Dr. Christophe Quétel** - Institute for Reference Materials and Measurements, JRC, Geel, Belgium

"Metrology and isotopic measurements, some perspective"

Scientific Programme (Preliminary)

18.04.2007 (Wednesday)

- 10:00 - 23:00 **Registration**
20:00 - 22:00 **Welcome Party**

19.04.2007 (Thursday)

- 08:00 - 12:00 **Registration**
9:00 - 9:15 **Opening Ceremony**

Chairman - Prof. Jürgen Eichler

- 9:15 - 9:55 **Prof. Hartmut Fuess** (Institute of Materials Science, Darmstadt University of Technology Darmstadt, Germany)
In-situ characterization by synchrotron (diffraction and absorption) of functional materials (battery, fuel cell, piezoceramics)
- 9:55 – 10:35 **Prof. Sefik Suzer** (Department of Chemistry, Bilkent University, Ankara, Turkey)
X-Ray Photoelectron Impedance Spectroscopy: A different Way of Doing Surface Science
- 10:35 - 10:45 **Panel Discussion**
- 10:45 - 11:15 **Coffee break**

Chairman - Prof. Wolfgang Voigt

- 11:15 - 11:55 **Dr. Gillian Greenway** (University of Hull, Hull Environmental Research Institute, UK)
Micro and Nano scale chemical measurements devices
- 11:55 - 12:15 **Prof. Karol Florian** (Department of Chemistry, Technical University of Kosice, Slovakia)
A long-term Characterization of Gravitation Dust Sediments
- 12:15 – 12:25 **Panel Discussion**
- 12:30 - 14:00 **Lunch**

Chairman - Dr. Christophe Quétel

14:00 - 14:40	Prof. Freddy Adams (University of Antwerp, Antwerp, Belgium) <i>Synchrotron radiation as a validation tool on the micro/nanoscale level</i>
14:40 - 15:20	Prof. Dimitar Tsalev (Faculty of Chemistry, University of Sofia, Bulgaria) <i>Method validation in environmental analysis – mission possible</i>
15:20 – 15:30	Panel Discussion
15:30 - 16:00	Coffee break
16:00 - 17:30	Oral Presentation of the Poster
17:30 – 19:00	Poster Session
19:30 - 21:00	Dinner
21:00	Concert – orthodox

20.04.2007 (Friday)

Chairman - Dr. Gillian Greenway

9:00 - 9:40	Dr. Wolfram Bremser (BAM Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany) <i>Managing quality in environmental analysis: From MRA and KC to lab control samples</i>
9:40 - 10:00	Prof. Nonka Daskalova (Institute of General and Inorganic Chemistry, Bulgaria) <i>The role of Inductively Coupled Plasma Atomic Emission Spectrometry in the analysis of environmental materials</i>
10:00 - 10:20	Dr. Miroslava Vaclavikova (Institute of Geotechnics, Slovak Academy of Sciences, Slovakia) <i>Toxic Oxy-anions in Aqueous Systems – Speciation Study</i>
10:20 – 10:30	Panel Discussion
10:30 – 11:00	Coffee break

Chairman - Prof. Freddy Adams

11:00 - 11:40	Dr. Christophe Quétel (Institute for Reference Materials and Measurements, JRC, Geel, Belgium) <i>Metrology and isotopic measurements, some perspective</i>
11:40 – 12:00	Prof. Ivan Havezov (Institute of General and Inorganic Chemistry, Bulgaria) <i>Validation of Chemical Methods in Quantitative Analysis</i>

12:00 – 12:15	Panel Discussion
12:30 - 14:00	Lunch
14:30 - 22:30	Excursion and Dinner (Bachkovo Monastery "Virgin Mary")

21.05.2006 (Saturday)

Chairman - Hartmut Fuess

9:00 - 9:40	Prof. Wolfgang Voigt (TU Bergakademie Freiberg, Institute of Inorganic Chemistry, Freiberg, Germany) <i>Thermodynamic modelling for mineral-based ecomaterials</i>
9:40 - 10:20	Prof. Jürgen Eichler (Technische Universität Berlin, Optisches Institut, Germany) <i>Advanced laser materials for application in ecology</i>
10:20 – 10:30	Panel Discussion
10:30 - 11:00	Coffee break

Chairman - Prof. Sefik Suzer

11:00 - 11:40	Prof. Jurgis Staniskis (Institute of Environmental Engineering, Kaunas University of Technology, Kaunas, Lithuania) - <i>Cleaner Production and Product Ecodesign: Strategies and Implementation</i>
11:40 – 12:00	Prof. Annik Fet (Norwegian University of Science and Technology NTNU, Norway) - <i>Product category rules (PCR) and environmental product declarations (EPD) as tools to promote sustainable products</i>
12:00 – 12:20	Dr. Jürgen Hassler (ESK Ceramics, Germany) - Trace Element Determination Using State of the Art ETV-ICP-OES Equipment – A Multi-Matrix-Investigation
12:20 – 12:30	Panel Discussion
12:30 - 14:00	Lunch
14:00 – 14:15	Closing (Best Poster Award)
14:30 -	Excursion (The Old Town of Plovdiv)

22.05.2006 (Sunday)

Departure from St. Kirik

Plenary Lecture

Metrology and Isotopic Measurements, Some Perspective

Christophe R. Quétel

EC-JRC-IRMM

Isotopic measurements are essential, and ability to measure variations in isotope ratios and isotopic compositions gives insight into many processes of either natural or anthropogenic origin.

Two concepts are essential to achieve reliability and comparability and thus to improve the quality of measurements in chemistry, including isotope ratio measurements. There is the traceability of the results to a common and long-standing system of reference, like the *Système International d'Unités* (SI), and there is the estimation of realistic combined uncertainties associated to the measurement results.

Figures are comparable not because they are of the same order of magnitude, as it is often said, but because they can be traced back to the units or to the ratios of units of the same system of reference. Among the reasons why it is rarely discussed though there is the perception that it is a 'non issue', misinterpretation and confusion with relationships to specific organisations (arising from the use of specific analytical methods and/or reference materials developed there) rather than to values, and the difficulty eventually in establishing a traceability scheme that faithfully respect the reality and the complexity of the measurement process. Moreover, working out the traceability of a measurement result is not sufficient. A result must be reliable and reliability derives from the demonstration that this result most likely encompasses the range of possible 'true' values, or at least that the difference between both is equal or below what was expected before undertaking the measurement. This can be achieved through validation of the measurement process. According to the ISO-17025 guidelines, "validation is the confirmation by examination and the provision of objective evidence that the particular requirements for a specific intended use are fulfilled". There are multiple and complementary ways of validating a method, including the sound use of certified reference materials, re-measuring and/or providing additional independent measurement results etc. Within that frame, describing the entirety of the measurement process (i.e. from sample preparation to the instrumental and the data evaluation steps) under the form of (not necessarily complex) mathematical expressions, and establishing the functional relationship between a measurand and the input quantities, serves two major purposes. First it gives the transparency that is necessary for understanding, and if necessary explaining, the way the reported result was obtained. It is explicit and it brings objectivity to the description of the reality as perceived (also required for the establishment of the traceability). Second it is an essential mean for the estimation of a realistic combined uncertainty figure and, this way, uncertainty budgeting is considered to provide adequate validation of the measurement process.

Historically, the Isotope Measurements unit at the EC-JRC-IRMM has been involved in measurements of radioactive isotopes. The projects we conduct have now diversified and cover a much broader range of applications, isotope systems (including non radioactive), concentration levels (down to ng g⁻¹ or below) and sample matrices. We certify isotope ratios for the production of candidate isotopic CRMs, but also for studies involving isotopic signatures as proxies of particular mechanisms (environmental pollution sources, food origin etc.). We also certify element amount contents in a range of sample matrices using isotope dilution as a primary method of measurement. My presentation will provide examples of isotopic measurement applications carried out in the inductively coupled plasma mass spectrometry group of IRMM. It will illustrate the way current concepts of chemical metrology are implemented to support our measurement results.

Topic A.

Characterization of Ecomaterials

In-situ Characterization by Synchrotron Radiation (Diffraction and Absorption) of Functional Materials (Batteries, Fuel cells, Piezoceramics)

Hartmut Fuess

Institute for Materials Science, University of Technology, Darmstadt, Germany.

Electromagnetic radiation is produced at many synchrotron facilities in the energy range between γ -rays and visible light. The main properties of synchrotron radiation (SR) are: High brilliance, good coherence, tunability, polarization. Most synchrotron sources are optimized to produce X-rays (energy range 1-20 KeV), but a trend to higher energies is observed. Monochromatic radiation for specific experiments is obtained by optical devices like mirrors and monochromators.

A powder diffractometer is operated by our group at HASYLAB [1] equipped with an image plate detector and a sample environment for in-situ observation of structural changes under various external conditions. In addition X-ray absorption experiments (EXAFS or XANES) are carried out in order to investigate changes in the electronic structure.

Examples are given for the structure of lead zirconate titanate ceramics in the morphotropic phase under an external field [2] and of Li(Co,Ni)O₂-battery materials measured as a function of charge and discharge [3]. The observation of X-ray absorption in polymer fuel cells provides information of the condition of oxidation in the membrane electrode assembly (MEA) [4]. Neutron powder diffraction is available as a complementary method. Access to both methods (SR, Neu) will be discussed.

References:

1. M. Knapp, C. Baetz, H. Ehrenberg, H. Fuess, *J. Synchr. Rad.* 11 (2004) 328.
2. K. Schoenau et al., *Phys. Rev.*, accepted.
3. T. Gross et al., *Sol. State Ionics* 176 (2005) 1193.
4. C. Roth et al., *J. Amer. Chem. Soc.*, 127 (2005), 14607.

X-Ray Photoelectron Impedance Spectroscopy: A Different Way of Doing Surface Science

Sefik Suzer

Chemistry Department, Bilkent University, 06800 Ankara, Turkey.

A novel technique is introduced for probing charging/discharging dynamics of dielectric materials in which X-ray photoemission data is recorded while the sample rod is subjected to ± 10.0 V square-wave pulses with varying frequencies in the range of 10^{-3} to 10^3 Hz. We name this technique as “X-Ray Photoelectron Impedance Spectroscopy”. Accordingly, for a clean silicon sample the Si2p(Si⁰) peak appears at correspondingly -10.0 eV and +10.0 eV binding energy positions (20.0 eV difference) with no frequency dependence. However, the corresponding peak of the oxide (Si⁴⁺) appears with less than 20.0 eV difference and exhibits a strong frequency dependence due to charging of the oxide layer, which is faithfully reproduced by a theoretical model. Various applications of this technique for characterization of surface structures will be presented and discussed.

A Long-term Characterization of Gravitation Dust Sediments

Karol Flórián, Ladislav Lux, Dagmar Remeteiová, and Mikuláš Matherny

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The contribution will be devoted to the long-term observation and evaluation of the gravitation dust sediments in the industrial-urban area of Košice. The atmospherically dustiness has three origins: the emission dustiness, the emissions and the deposited part. The last mentioned forms gravitation dust sediments with the diameter higher than 10 μm . These parts of the dust contaminate the soils, the urban areas as well as the atmospheric rains. Therefore, their chemical character is determining for the standpoint of general environmental hazards. The last mentioned part of the dustiness was patterned in the residential agglomeration of the city Košice during the ten years period (1997-2006). The monthly sampling was given by the Bergerhoff-method [1]. The sampling was made on two independent sampling places: in the centre and on the periphery of the city. Besides the evaluation of the amounts of the total dust sediment, the amount of the total monthly sample enabled also the determination of some chosen heavy metal elements using the solid-sampling atomic spectroscopic methods. The evaluation of the obtained results was performed in three directions. Firstly, the total dust amounts were compared within a year and between years; suitable statistical test was used in searching for trends. Secondly, all sets of data, i.e. monthly data for each element in each year were statistically evaluated; part of these evaluations was also searching for extreme values. Thirdly, the correlations between dust amounts and element concentrations were checked in order to find out some relations, as e.g. relation between the total dust amount and the Fe-concentration. Some results were published in [2] and in Slovak-Bulgarian cooperation in [3]. Last, but not least the fractionation analysis was used for evaluation of ecotoxicity and bioavailability of the physical-chemical element forms. The basic results were published in [4].

References:

1. VDI/DIN Handbuch:Reinhaltung der Luft, Band 4. VDI 2119, Blatt 2. Beut Verlag, Berlin,1996.
2. K.Uhrinová, K.Flórián and M.Matherny: Slovak Geol.Mag .9, 181-187 (2003).
3. P.Simeonova, V.Simeonov, L.Lux, I.Dakova, T. Spanos: Ecol. Chem. And En. 12, 727-737 (2005)
4. D.Remeteiová, E. Sminčáková and K.Flórián: Microchim.Acta 156, 109-113 (2007).

XPS Characterization of TiO₂ Layers for Gas Sensor Application

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Gas sensors play an important role in detecting, monitoring and controlling the presence of hazardous and poisonous gases in the atmosphere at very low concentrations. The present work is aimed at developing acoustic sensors for registration of NH₃ in the atmosphere. For that purpose, resonator structures are created by deposition of sorption TiO₂ layers on quartz plates.

The TiO₂ thin films were prepared by Liquid Phase Deposition (LPD) method, including reaction between metal fluoro-complex and boric acid in an aqueous solution. The films were then annealed at 500 K for an hour. The morphology and the chemical composition of the films were studied by scanning electron microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS).

The SEM study revealed that the TiO₂ films are amorphous. The as-deposited films exhibited broad Ti2p photoelectron peaks, corresponding to a mixture of Ti³⁺ and Ti⁴⁺ oxidation states, indicating a sub-stoichiometric composition. Depth profiling of the as-deposited samples performed by Ar⁺ ion sputtering, established stoichiometry of TiO_{1.86}. After annealing at 500 K, the binding energy and the shape of the Ti2p peaks became characteristic of Ti⁴⁺ oxidation state.

Gas sensing properties were tested by measuring the mass loading when the films were exposed to 100-500 ppm NH₃. XPS study of the surface of the films exposed to NH₃ revealed the presence of nitrogen-containing species in the form of adsorbed ammonia and nitrates.

X-ray Photoelectron Characterization of Amorphous Materials in the MoO₃-CuO-PbO System

Margarita Milanova¹, Reni Iordanova¹, Yanko Dimitriev², and Krassimir L. Kostov¹

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MoO₃ is known as non-conventional network former but a series of two- and multicomponent glasses on its bases have been synthesized. Their structural characterizations is informative to control the chemical resistance and crystallization ability of the compositions and hence to the possibilities of its practical applications. One particular problem is immobilization of molybdenum in high level nuclear waste glasses. According to Hand et. all. [1] the higher oxidation state of molybdenum and its fourfold oxygen coordination are the main reasons for deterioration of the vitrification process. That is way it is interesting to investigate the chemical state of Mo in different glass compositions containing molybdenum.

The aim of this study is to determine the oxidation state of Mo, in the presence of PbO and another transitional metal oxide (CuO) using X-ray photoelectron spectroscopy. XPS results obtained indicate that molybdenum ions are mainly in a higher oxidation state (Mo⁶⁺) in all melt quenching samples. Addition of CuO to MoO₃ causes MoO₆→MoO₄ transformation which increase with CuO content [2]. In the ternary MoO₃-CuO-PbO glasses the molybdenum oxidation state does not change (Mo⁶⁺) but the tendency to decrease the coordination state is stronger. In the binary MoO₃-CuO glasses the presence of both Cu⁺ and Cu²⁺ ion is registered. Small amount of PbO (10 mol. %) inhibits the reduction process of cooper ions.

The results obtained show that glass samples in the model MoO₃-CuO-PbO system contain Mo is in a high oxidation state (Mo⁶⁺). CuO and PbO do not stimulate the reduction of molybdenum and causes MoO₆→MoO₄ transformation.

References:

1. R. Hand, R. Short, S. Morgan, N. Hyatt, G. Möbus, W. Lee, Glass Technology, 46 (2) (2005) 121.
2. R. I. Iordanova, M. K. Milanova, K. I. Kostov, Phys.Chem. Glasses: Eur. J. Glass Sci. Technol. B. 47 (6) (2006) 631.

DFT and HREELS Studies of Adsorbed 1,3-cyclohexadiene on Si(001)-(2x1)

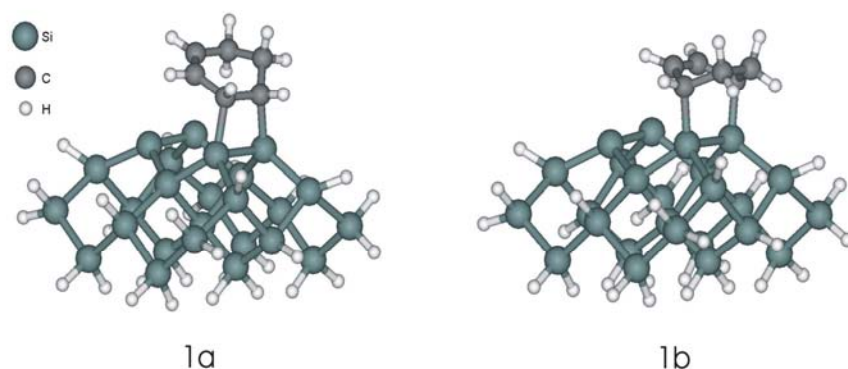
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The studies of the interactions of hydrocarbons with silicon surfaces are important not only for many technological processes but also from a scientific point of view in order to understand the possible adsorbate structures and the role and behavior of the Si dimers in the formation of a hydrocarbon-Si surface bond. Density functional computations of structural and vibrational features are used as a complementary study to the experimental spectra measured by the method of High-Resolution Electron Energy Loss Spectroscopy. Comparison between measured and computed frequencies shows on-top adsorbed cyclohexadiene bonded to one Si dimer to be the most probable adsorption configuration on Si(100)-(2x1). Within this configuration, two models are considered:



(i) [2+2] cycloaddition product in which the hydrocarbon ring is almost perpendicular to the surface (Fig.1a);

(ii) adsorbate resulting from a [4+2] cycloaddition reaction with ring almost parallel to the surface (Fig.1b).

The product from a [4+2] cycloaddition reaction (fig. 1b) is found to be the energetically most favorable one.

Acknowledgement:

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Infrared Spectroscopic Characterization of Admixtures in Minerals

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A method of crystal matrix infrared spectroscopy is proposed for determination of admixtures included in minerals. The method provides important information for the type of the incorporated entities. When polyatomic ions are doped in host lattices at low concentration the correlation field splitting, the dispersion of phonon curves (due to the interactions between identical oscillators) and LO/TO splitting effects (due to the long-range forces of electrostatic origin) are neglected. Thus, the vibrational spectra of the guest ions are essentially determined by the site symmetry, which is assumed to be the same as that of the respective host ions (substitutionally mixed crystals). The matrix-isolated XO_m^{n-} guest ions in different host matrices undergo structural distortions involving changes in the both X–O bond lengths and O–X–O bond angles as compared to those in the neat compounds. Consequently, the method used allows distinguishing the isomorphous or isodimorphous admixtures in minerals from those included mechanically.

Infrared spectra of minerals $MeXO_4$ (X, X' = S, Se, Cr; Me = Ca, Sr, Ba, Pb) as well as those of matrix-isolated $X'O_4^{2-}$ ions are reported and discussed in the regions of the stretching and bending modes of the tetrahedral ions. The influence of different crystal chemical parameters (the sizes of the ionic radii, the unit-cell volumes, i.e. the repulsion potential of the host lattices, the site symmetry of the host ions, the Me–O bond lengths) on both the number and the positions of the infrared bands corresponding to the normal vibrations of the matrix-isolated sulfate, selenate and chromate guest ions is analyzed.

CO as an IR Probe Molecule for Characterization of Supported Gold Catalysts

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IR spectroscopy of probe molecules is a unique technique with a big potential for studying gold catalysts. In this work, we summarize our data on the application of CO as a probe molecule for determination of gold speciation.

Isolated Au⁺ sites and CO form carbonyls registered in the 2180-2150 cm⁻¹ region. Because of the synergism between the σ - and the π -bond, these species are relatively stable. The exact wavenumber depends on the support (e.g. 2175 cm⁻¹ for Au/Al₂O₃ and Au/TiO₂, and 2183 cm⁻¹ for NaY).

Metal gold is monitored by CO with bands around 2100 cm⁻¹ characterizing Au⁰-CO species. The Au-CO bond is weak and the Au⁰-CO species are easily destroyed by evacuation. Only defect metal sites are able to interact with CO.

Oxidation of surface gold atoms leads to formation of the so-called Au ^{δ +} sites (Au⁺ cation on metal particles) which form carbonyls detected in the 2160 – 2120 cm⁻¹ region. These sites are able to share the positive charge with the gold bulk. As a result, both, the CO stretching frequency and the stability of the carbonyls are intermediate between those typical of Au⁰-CO and Au⁺-CO species.

With CO the Au³⁺ ions form only weak electrostatic bonds. Normally these cations are blocked by water and do not form carbonyl species. Attempts to eliminate water result in auto reduction of Au³⁺. Avoiding sample contact with air allowed us to produce Au³⁺-CO species absorbing in the 2206 – 2170 cm⁻¹ region.

Conclusions. To assign bands of different gold carbonyls one should take into account the stretching frequency and the stability. The CO stretching frequency of gold carbonyls generally decreases with the gold oxidation state. The stability of gold carbonyls decreases in the sequence: Au⁺-CO > Au ^{δ +}-CO > Au⁰-CO > Au³⁺-CO.

Acknowledgments:

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Use of CO as an IR Probe Molecule for Determination of Nickel Speciation in Supported Nickel Catalysts

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The oxidation and coordination states of nickel ions are decisive for the catalytic performance of nickel-based catalysts. Therefore, the determination of nickel speciation in such catalysts is of great importance. In this work we shall discuss the possibilities of use of CO as a probe molecule for characterization of nickel ions. Special attention will be paid to determination of the number of free coordinative vacancies of the nickel adsorption sites.

It is known that cations in zeolites are more coordinatively unsaturated as compared to the same cations supported on oxides. Indeed, low temperature CO adsorption on Ni/SiO₂ samples revealed formation of Ni²⁺-CO species (2195 cm⁻¹) which were not converted into dicarbonyls even at low temperature. Similar species were produced with Ni²⁺ ions in zeolites: Ni-ZSM-5, NiY, Ni-BEA (bands in the 2220 – 2200 cm⁻¹ region). A considerable part of the Ni²⁺-CO species in the Ni-BEA sample were converted into Ni²⁺(CO)₂ dicarbonyls. The fraction of Ni²⁺ ions in Ni-ZSM-5 able to coordinate two CO molecules was smaller, and no dicarbonyls were produced with the NiY sample. The results demonstrate that the number of effective coordinative vacancies of Ni²⁺ ions depends on the type of the zeolite, i.e. the position they occupy. The Ni²⁺ ions in NiY penetrate plane of the O-ring to which they are coordinated and thus, for steric reasons, no dicarbonyls can be formed.

Reduction of Ni-ZSM-5 and Ni-BEA by CO resulted in appearance of a fraction of Ni⁺ cations. These cations were able to coordinate stepwise one, two and three CO molecules. The monocarbonyls were detected around 2110 cm⁻¹ and the polycarbonyl structures were proven by coadsorption of ¹²CO and ¹³CO. Therefore, the use of CO as an IR probe reveals three coordinative vacancies of Ni⁺ ions in zeolites. The results are explained by the larger ionic radius of Ni⁺, as compared to Ni²⁺, which hinders penetration of Ni⁺ in the O-rings.

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Metal Complexation Modeling of Dithiocarbamate Fungicides: Stability and Vibrational Properties

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There is much interest in the potential environmental impact of alkyldithiocarbamates (DTCs) usage in agriculture as protective fungicides and its effect on human health. High coordination ability of DTCs to transition metals in soil and the formation of complexes influences the biological activity and physical properties of the soil. The biological activity is based on the complex formation of the active DTC group with metal atoms of metal-containing enzymes, producing enzyme inhibition. From the other side, the complexation of DTCs with metals in soil slows down their decomposition and elimination from the natural environment. Due to the selective coordination properties of DTCs they are used as complexing agent for determination of the total content of M(II) in soil by means of the extraction spectrophotometric method. Theoretical studies could provide essential information on the factors responsible for chemical behavior (structural, conformational and reactivity) of the DTCs and their metal complexes. Systematic theoretical studies of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) complexes with dimethyl – and diethyldithiocarbamate ligands are done to characterized the metal-ligand bonding strength in dependence on the metal- and the dialkyl substituent type. The complexes are modeled in a real $M : DTC = 1 : 2$ ratio in agreement with X-ray diffraction data. The character of the M-L bonding is estimated through calculations of electrostatic, covalent and repulsive energy contributions. A detailed analysis of the electron density has been performed using natural population analysis. The thermodynamic stability in gas phase and solution is theoretically evaluated and discussed. The IR and Raman spectra are interpreted on the base of DFT frequency calculations. The computations were carried out with density functional theory and B3LYP functional using Gaussian03 program package.

EPR Characterization of Mn⁴⁺ local environment in lithium-nickel-manganese oxides obtained under high-pressure

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Lithium-nickel-manganese oxides have been considered as alternative to up-to-day used LiCoO₂ cathode materials for lithium ion batteries since they deliver a higher reversible capacity at room and elevated temperatures. High-pressure synthesis has been used for the preparation of new structural modifications of lithium transition metal oxides.

The aim of this work was to obtain the high pressure modifications of lithium-nickel-manganese oxides: Li_{1+x}(Ni_{1/2}Mn_{1/2})_{1-x}O₂ with x=0 and 0.2. The local cationic distribution was analysed by EPR spectroscopy. The changes in the local metal environment during Li extraction/insertion were monitored by EPR and IR spectroscopy.

A solid state reaction between NiMnO₃ and Li₂O at 3 GPa yields a LiNi_{0.5}Mn_{0.5}O₂ phase characterized by a disordered rock-salt type structure. However, a short-range cationic ordering is still preserved. The paramagnetic ions stabilized in this oxide are mainly Ni²⁺ and Mn⁴⁺, together with some amount of Mn³⁺ (about 10%). The disordered structure does not permit reversible Li extraction and insertion. Oxidation of Ni²⁺ to Ni³⁺ in the lithium-nickel-manganese oxides was realized when Li₂O₂ was used instead of Li₂O as an initial reagent in the high-pressure synthesis. The higher oxidation state of Ni favours the stabilization of the layered modification, as a result of which Li(Li_{0.2}Ni_{0.4}Mn_{0.4})O₂ oxides are formed. The paramagnetic ions stabilized in the layered oxide are mainly Ni³⁺ and Mn⁴⁺ ions. Contrary to the disordered oxides, the layered modification displays reversible lithium extraction/insertion. The electrochemical reaction is due to oxidation of the nickel ions and phase separation into Li_yNi_{0.4-y}Mn_{0.4}O_{1.88} (0<y<0.2) and Li_{1-x}Ni_{1+x}O₂ (x ≈ 1/3). A reversible Li insertion and extraction proceeds on further cycling, which is associated with the Ni^{2+/3+}/Ni⁴⁺ ionic couple within the layered Li_yNi_{0.4-x}Mn_{0.4}O_{1.88} phase.

Microstructural characterization of mixed $\text{LaNi}_y\text{Co}_{1-y}\text{O}_3$ ($0 \leq y \leq 0.25$) perovskite-type oxides prepared from citrate precursors

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Mixed $\text{LaNi}_y\text{Co}_{1-y}\text{O}_3$ oxides with a perovskite-type structure were recently considered as promising cathode materials for solid oxide fuel cells. The electrochemical performance of these mixed oxides has been shown to depend on their microstructure. Irrespective of the intensive structural studies on LaCoO_3 , little work has been done on the relationship between the microstructure and the synthesis procedure of Ni substituted LaCoO_3 .

In this contribution we provide data on the microstructural characterization of mixed $\text{LaNi}_y\text{Co}_{1-y}\text{O}_3$ oxides ($0 \leq y \leq 0.25$) obtained by thermal decomposition of freeze-dried citrate precursors. Microstructural characterization was made by electron paramagnetic resonance spectroscopy (EPR). For assignment of the EPR signals, $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and La_2NiO_4 oxides were used as EPR references.

A well-crystallized single phase of a rhombohedrally distorted $\text{LaNi}_y\text{Co}_{1-y}\text{O}_3$ perovskite was prepared from the citrate precursors at temperatures even at 600 °C. For a fixed Ni-to-Co ratio, the a parameter, which expresses the distance between two neighbouring metal ions in the perovskite structure, remained nearly the same for the samples prepared between 600 and 900 °C, while the c parameter displays a tendency to decrease with increasing preparation temperature. In the same order, the mean oxidation state of metal ions decreases with increasing the preparation temperature. This dependence is more pronounced for Ni-rich oxides. For pure LaCoO_3 prepared from citrate precursors, EPR reveals ferromagnetic Co^{3+} and Co^{4+} couples, which are located mostly on the interface between pasted LaCoO_3 primary particles. Depending on the synthesis procedure used, an EPR response from exchange coupled nickel ions is detected for LaCoO_3 substituted with 10 and 25 % of Ni. In addition, a low-intensity EPR signal is observed for LaCoO_3 substituted with 10% of Ni. The appearance of the latter signals can be related with the formation of nickel-rich regions into the perovskite structure. The results obtained indicate that EPR spectroscopy can be used to monitor short-scale chemical inhomogeneities in the structure of mixed nickel-cobalt perovskite-type oxides.

Electrodeposition and Characterization of Mixed ZrO_2 - CeO_2 - $YO_{1.5}$ Thin Films

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The ceria and zirconia thin films are used for three-way catalysts (TWC). CeO_2 has a multiple effects on the catalyst state and performance. The role of CeO_2 as an efficient “oxygen buffer” is directly related to its capability to undergo effective reduction and reoxidation under rich and lean conditions, respectively¹. The addition of yttria increases the thermal stability of the system and concentration of oxygen vacancies, which are responsible for the high ionic conductivity in CeO_2 . Thus the properties of ZrO_2 - CeO_2 - $YO_{1.5}$ solid solutions make them suitable for application as TWC, electrodes, or for modification of electrolyte surfaces in the medium-temperature SOFCs².

The substantial meaning of this system necessitates finding of inexpensive technique for it producing. We have successfully electrodeposited ZrO_2 - CeO_2 - $YO_{1.5}$ thin films on stainless steel and platinum from nonaqueous electrolytes consisting of a mixed solution of $CeCl_3$, YCl_3 and $ZrCl_3$ salts. We have optimized the conditions of the deposition. The obtained films are dense and have a good adhesion. We have investigated the electrodeposited films by XPS and SEM. By XPS we have established the chemical composition and the valence state of the components. We have determined from Ce3d spectrum that cerium in as-deposited samples is in +3 valence state. SEM investigation showed cracks on the surface. This was attributed to an increased internal stress in the layers.

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Electrocatalytic Activity of Electrodeposited Cobalt-Based Multilayers for Direct Borohydride Oxidation

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Nanostructured Co-based multilayers are obtainable by electrodeposition on different supports [1]. Some of them exhibit relatively high catalytic activity for some important reactions [2, 3].

In the present study, the electrocatalytic activity of newly synthesized CoNiMnB electrodeposits for direct borohydride oxidation has been examined. Electrodes, prepared by electrodeposition from complex sulfamate electrolytes on Ni-foam at different potentials were anodically polarized and corresponding polarization curves were plotted. Simultaneously, the rate of generated due to borohydride hydrolysis hydrogen was monitored at each current loading. The values of overpotentials at given current densities were estimated and compared with those previously obtained with CoMnB electrodes.

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Characterization of „Run-off“ Effects of Metal Materials Exposed at Atmosphere Using Artificial Neural Network

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Environmental pollution caused by „run-off“ effects of metals from construction exposed at atmosphere depend on various factors such as local temperature, relative humidity, concentration of main pollutants (SO_4^{2-} , Cl^- , O_3) and exposition time [1]. Classical analytical and mathematical functions are of limited use to describe this type of non-linear system depending on various metereochemical parameters and interaction between them and material factors. Thanks to existing climate programme in Europe (ECE/EMEP) through which metereochemical data are daily measured, huge amount of data were handled and extraction of vital information is needed. One elegant way is use an Artificial Intelligence in the form of Neural Networks serving for prediction of atmospheric corrosion of metals.

We have used database of metereochemical parameters as input variables and corrosion rates in the form of mass losses of weathering steel samples from long-term exposition under atmospheric condition as output parameters. For better prediction were chosen several atmospheric locations with different corrosivity.

So finally, application of this technique would allow corrosion or any environmental engineer at local environment to select material with smaller “run-off” effects and finally not only protect before environmental pollution but also prolong life-time of metal construction. Using this methodology it was observed, that the error encountered maximum 17% in prediction made from weight loss analyses.

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Characterization of Calcium Phosphate Phases Obtained During the Preparation of Sintered Biphase Ca-P Ceramics

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Biomaterials suitable for reconstruction of periodontal osseous defects are a subject of constant investigations and the search for the ideal material is still a desired goal and technological challenges.

This study was aimed in preparation of calcium phosphate (Ca-P) biphase bioceramics by sintering calcium phosphate precipitate. The specificity of the Ca-P ceramics behavior during sintering determines the need of experimental studies on the conditions of preparation of Ca-P bioceramics with desired composition, structure and properties. In our study sintering at different time intervals under the controlled conditions: calcium-to phosphorus (Ca/P) ratio, phase contents, texture of the sintered material and parallel control of the chemical and phase composition was performed.

Complex chemical, powder X-ray diffraction (XRD), scanning and transmission electron microscopic (SEM and TEM) methods characterization was used for a control of calcium phosphate (Ca-P) biphase ceramics.

Two bioceramics composition have been obtained - hydroxyapatite and α -tricalcium phosphate (HAP and α -TCP) and hydroxyapatite and β -tricalcium phosphate (HAP and β -TCP).

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Characterization of Ti- containing Zeolites Using as Catalysts for Oxidation Reaction with H₂O₂ in Mild Conditions

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The titanium containing zeolites are often used as catalysts in several catalytic reaction of different organic compounds oxidation. Most of these substrates are environmental unfriendly waste products from different chemical and biological production. Ti-Beta and TS-1 catalysts can easy oxidize aliphatic and aromatic hydrocarbons to corresponding alcohols and phenols and further to aldehydes or ketones.

The TS-1 and Ti-Beta catalyst were synthesized with slight modifications according to a synthesis procedure called "wetness impregnation method"[1].

Different methods are used in order to characterize the zeolites samples. BET measurements of surface show, that typical surface areas for Ti-Beta zeolite, are about 700 m²/g and for TS-1 samples about 400 m²/g. The water content of the zeolites Ti Beta is with about 14 wt % higher than that of the TS-1 (about 4 %). AAS was used, for the quantitative determination of the Al and Ti contents in the Ti-Beta and TS-1 samples. With the help of powder XRD the crystal structure of some samples were investigated. The oxygen coordination of the titanium species in the zeolite matrix was analyzed spectroscopically. The diffuse reflectance UV-VIS spectra of the TS-1 and Ti-Beta samples, exhibit a strong band around 210 nm, which can be attributed to tetraordinated Ti(IV) on zeolite framework positions. Most interesting in IR-spectroscopy of titanium-containing zeolites, is the vibrational band at 960 cm⁻¹. This band is observed only in the IR-spectra of zeolites containing Ti, V, Ta, Nb, and other metal on framework sites. This corresponds to a perturbation of the stretching Si-O vibrational mode by the neighboring heavy metal ion.

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Ammonia Detection Using SnO₂ Acoustic Sensor

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Detection and measurement of ammonia concentrations is of considerable commercial and medical interest. Our interest lies in room temperature sensing of ammonia using high surface area metal oxide-based sensors. A quartz piezoelectric crystal detector with SnO₂ evaporated onto the electrode as a sensor substrate has been developed for the detection of small mass changes caused by the selective adsorption of ammonia vapor from an air.

SnO₂ thin films are grown on quartz substrates by physical vapor deposition. Au and Ag were used as electrodes. The morphology and the chemical composition of the films were studied by scanning electron microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS).

SEM analysis showed that the deposited SnO₂ thin films possess a porosity suitable to fabricate gas sensors. The stoichiometry and chemical state in a depth of the layers were studied by Ar⁺ ion sputtering. XPS studies revealed significant difference in the thickness and the stoichiometry of the deposited SnO₂ films depending on the use of Au and Ag electrodes. The calculated O/Sn intensity ratio is 1.0 and 1.43 for the films on Au and Ag electrodes, respectively. In both cases the deposited film is non-stoichiometric and its molecular formula may be SnO_{2-x} (0 < x < 1). The binding energies of Sn 3d peaks at 486.3 eV and 494.8 eV, and the binding energy of O 1s peak at 530.2 eV were observed, which are in good agreement with the reported data for SnO₂.

Gas sensing properties were tested by measuring the mass loading when the SnO₂ films were exposed to 100 – 500 ppm NH₃. The studies in this work confirmed the potential use of the SnO₂-based detector as an air pollution sensor.

Modified Activated Carbon With Thioetheric Sites for Gold Sorption

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Activated carbon is one of the sorbent materials that have been most often used for solid-phase extraction of metal ions from aqueous solutions.

The modification of activated carbon with sulfur-containing ligands is of particular interest as a way of obtaining sorbents selective for metal ions with affinity towards sulfur, like the toxic heavy metals and the precious metals, considered nowadays as widespread environmental pollutants.

An activated carbon sorbent containing thioetheric sites (ACTS) was prepared by modification of the activated carbon with 2,2'-thiodiethanol.

The specific surface area, pore volume, concentration of oxygen-containing groups and sulfur content of the sorbent were determined. The sorption behavior towards ions of some precious metals - Au(III), Pt(IV), Pd(II) and heavy metals - Ni(II), Zn(II), Fe(III), Cu(II), Pb(II), Cd(II) and Co(II) was studied. Selectivity towards gold in the pH range 1-9 with a capacity of 80 mg g⁻¹ was found. The sorption of Au(III) at pH 1 is not affected by milligram amounts of Ni(II), Zn(II), Fe(III), Cu(II), Pb(II), Cd(II) and Co(II). The sorbed gold species is Au(0) which was confirmed by X-ray photoelectronic spectrometry (XPS) study of ACTS samples loaded with milligram amounts of gold.

Carbonized Alumina-Zirconia as Catalyst Support for Electrode Applications in Electrochemical Cells.

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The materials used as catalyst support in anodes and cathodes of electrochemical cells must present a high electrical conductivity. Catalytic electrodes are usually made of an active phase deposit lying on a conducting support, like carbon. However, these carbon-supported electrodes have several disadvantages such as a high capacitance when used in aqueous solutions, and also its analysis with FTIR or Raman techniques is difficult because the samples absorb almost the totality of the irradiated energy.

This project presents the development of new composite catalyst supports of catalysts with possible applications on electrodes for electrochemical cells.

Different Alumina-Zirconia materials were prepared following the sol-gel method [1], with different proportions of each oxide (ZrO_2 : 0.0, 0.25, 0.50, 0.75, 1.00). These materials were carbonized by cyclohexene pyrolysis [2] in a fixed bed reactor at 400°C, with three different values of the time-on-stream parameter. In this way, carbon is deposited in order to provide the material with electron-conductivity.

Different techniques were applied to characterize the synthesized materials: the BET surface area and pore size distribution were measured by nitrogen physisorption. X-ray diffraction (XRD) was used to evaluate the crystal structure of Al_2O_3 - ZrO_2 phases. The surface acidity was measured by Temperature-Programed Desorption (TPD). Thermogravimetric analysis (TGA) was applied in order to quantify the carbon amount attached to the inorganic support.

Electrodes were elaborated with these supports, by making a paste of each composite with Nafion® resin. Their behavior as electrode materials was tested by means of cyclic voltammetry in a three-electrode cell, in acid aqueous electrolytes.

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Vitrification Ability in the System $\text{MoO}_3\text{-CuO-SeO}_2$

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Molybdate glasses possess a variety of specific properties and now some of them are potential candidates for technological applications as amorphous semiconductors, infrared transmission components, in non linear optical devices, sensors, reflecting windows, soluble microfertilizers, for nuclear waste storage, etc. One of the particular difficulties with the vitrification of the waste storage is the presence of molybdenum in tetrahedral coordination against oxygen. These units (MoO_4^{2-}) provoke the separation of scheelite molybdate structures and increase the solubility of the material [1]. That is why it is interesting to control the oxidation state and the coordination of molybdenum in the glasses. In our previous investigations it was proved that depending on the composition molybdenum could participate in the amorphous network as MoO_4 , MoO_6 , Mo_2O_7 and Mo_2O_8 units [2]. The main difficulties in the preparation of molybdate glasses are connected with the high crystallization tendency of the compositions, because MoO_3 is not able to form a glass itself at a slow cooling rate. It is well known that the better glass-forming tendency in $\text{SeO}_2\text{-MoO}_3$ glasses is related to the creation of disorder in the SeO_3 chains by MoO_6 polyhedra at a suitable compositional ratio. The three component system $\text{MoO}_3\text{-CuO-SeO}_2$ has been selected as a model. The glasses obtained were prepared in silica ampoules evacuated at a pressure of $P = 0.1$ Pa and heated at 750°C . The samples were cooled with a rate of $100^\circ\text{C}/\text{min}$ and were characterized by X-ray diffraction and IR spectroscopy. After heat treatment, the main crystal phases were CuSeO_3 and MoO_3 . The stable glasses were situated near the SeO_2 corner. IR spectroscopy proved that the increase in CuO content led to transformation of the amorphous network from polymer SeO_3 units ($\text{Se}=\text{O}$) to isolated SeO_3 groups. The same reason caused transformation of MoO_6 to MoO_4 groups. The results obtained can contribute to accumulating more knowledge in order to design an amorphous network with a definite degree of polymerization and an appropriate ratio of the different coordination polyhedra. This is related directly to the chemical resistance and crystallization ability of the compositions.

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Synthesis and Characterization of α -Fe₂O₃ - an Ecomaterial for Lithium Ion Batteries

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Studies of active materials for Li-ion batteries have focused recently on transition metal oxides M_xO_y (M = Mn, Co, Ni, Cu). But they are expensive and relatively toxic. These drawbacks have created interest in the development of cheaper and environmentally benign electrode hosts. In this regard iron oxides are attractive active materials for lithium ion batteries due to their abundance, low cost, toxicity and high volumetric specific characteristics.

The paper deals with the effect of the synthesis method on the microstructural characteristics, morphology and electrochemical behaviour of α -Fe₂O₃ samples, prepared from various precursors at the same temperatures.

The phase composition, morphology and crystallinity of the materials obtained were investigated by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). The electrochemical behaviour of the samples synthesized was studied within voltage range 0,01-2,5 V and various current densities.

The electrochemical behaviour of the active materials obtained was found to depend mostly on the ratio between mean particles size (MPS) and mean coherent domain size (MCDS). The ratio depends on the synthesis method and calcination temperature.

By optimization of the synthesis processes it was prepared α -Fe₂O₃ with optimum microstructure and particles size, a promising active material for lithium ion batteries.

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Topic B.

Quality Assurance of Environmental Analysis

Micro and Nano Scale Chemical Measurements Devices

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This presentation will discuss novel methods of making chemical measurements and the materials need to achieve these methods. Different methods of achieving rapid speciation will be discussed including the use of monolithic porous columns¹ and lab on a chip devices with ICPMS².

This will then be followed by a discussion on the advantages of miniaturising the chemical measurement process by using lab on a chip devices to make portable measurement systems. An example for the analysis will be given for the analysis of hydrogen peroxide in rainwater and snow using chemiluminescence detection will be discussed.³ More recent work in which we are incorporating cells into the chip devices to develop rapid toxicity screening test to help SMEs comply with the new EU REACH regulations relating to chemical safety will then presented.

Further recent work has included the development of nanoprobes that operate within cells⁴ and some recent work on developing magnetic nanoscavenging sensing devices to overcome sampling problems for lab on a chip devices will be discussed.

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Managing Quality in Environmental Analysis: From MRA and KC to Lab Control Samples

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Quality assurance (QA) has become an increasingly important topic, as environmental monitoring bodies realised that accuracy of measurements can depend very much on how the measurement is taken. QA of analytical measurement is, however, not specific for environmental analysis but follows widely accepted principles. Organisational and managerial aspects are comprehensively covered in the ISO 9000 series of standards [1, 2], while ISO/IEC 17025 [3] also covers technical QA aspects. The talk gives a short overview on general and sectorial international standards and guidelines relevant for managing quality in the analytical laboratory, and in particular focus on the EURACHEM/CITAC Guide [3]. This guide describes appropriate method selection, method validation, equipment control, the use of reference materials for proof of trueness and establishment of traceability, and participation in proficiency tests on a regular basis as the key technical elements of QA in the analytical laboratory.

Guidance to appropriate method selection will be exemplified by an official list of accepted methods in soil analysis which was compiled by the Federal Institute for Materials Research and Testing (BAM). Method validation will be discussed elsewhere and throughout the conference. Control samples are an effective tool for maintaining the quality attained and documented during method validation. Given their importance, preparation and proper use of control samples will be covered by a new guide under preparation in the ISO/REMCO committee. Considerable progress was achieved in the other aspects mentioned above. More and more proficiency testing schemes and reliable reference materials become available. Beside this, metrological approaches were extended to environmental analysis. The talk will cover the current status of

- the MRA, key comparisons and CMC related to environmental analysis within the framework of CCQM
- proficiency testing in environmental analysis, with special emphasis on the schemes operated by the Federal Institute for Materials Research and Testing (BAM)
- reference materials for environmental analysis, with a specific view to the ERM initiative.

Some guidance will also be given on publicly available sources of information on both proficiency testing schemes and reference materials, including their providers.

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The Role of Inductively Coupled Plasma Atomic Emission Spectrometry in The Analysis of Environmental Materials

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The concentration levels of heavy and toxic elements circulating in the environment have increased due to various industrial activities. Accumulations of pollutants in different type of environmental materials results in a high risk for plants, animals and human health.

The trend in development of Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) goes to the improvements in the optics, detection and sample introduction systems and line selection for trace analysis with a view to spectral interferences [1,2]. ICP-AES was applied to accurate determination of trace elements by using of the following methodology: (a) quantification of spectral interferences in the presence of Al, Ca, Mg, Fe and Ti as a complex environmental matrix around prominent lines of As, Hg, Se, Sn, Tl; Pb, Cr, Cu, Mn and Cd; (b) line selection for trace analysis; (c) calculation of the total background signal under the selected analysis line and comparison with the other background correction procedures. Certified reference materials or independent methods for analysis were used to evaluate the accuracy of the ICP-AES analytical results. The methodology was experimentally demonstrated in the determination of impurities in samples of air, waters, soils and sediments by using a 40.68 MHz ICP and spectrometer with 5 pm spectral bandwidth.

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Trace Element Determination Using State of the Art ETV-ICP-OES Equipment – A Multi-Matrix-Investigation

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ETV-ICP-OES combinations are well known as powerful and cost effective systems in the industrial routine analysis especially when they are equipped with automatic sample changers. The field of application is far diversified and is extended from general inorganic raw materials beyond ceramic, geological and environmental samples up to biological materials like human, animal or plant tissues, as well as liquids of all kinds including blood, serum and petroleum products.

In the present study a state of the art ETV device is coupled with an Echelle ICP spectrometer equipped with a CID-camera for spectral detection. Transition area and gas streams (carrier gas, bypass gas and reaction gas) are optimised to achieve best transport efficiencies. The ETV-unit is supplied with an inside temperature measuring cell for real temperature controlled furnace runs. The possibilities of the ETV-ICP-OES method for trace element determination in solid samples using calibration standards of non identical matrices are investigated. It is demonstrated that aerosol formation, transport efficiency and selection of analytical lines has more influence on analytical results as compared with sample material, except for extreme differences between sample and calibration standard matrix.

Trace elements are determined in certified reference materials with different matrix as plant materials (leaves, grains and hay), foodstuff, animal tissues, industrial products (SiC and Si₃N₄), environmental samples (city ash and sludges) and geological materials (soils and sediments). There is a good agreement between certified and experimental values.

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A New Generation of Cyanide Ion-selective Membranes for Flow Injection Application. Part III. An Electrochemical Protocol for On-line Cyanide Speciation

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The maximum admissible discharge limits for toxic cyanides are getting tighter and tighter every year due to their extreme toxicity. The Ecological Protection Authorities has imposed a distinction between the “free” and “total” cyanide levels to characterize cyanide pollution.

A new generation of flow-injection potentiometric detectors (FIPD) for cyanide has been developed in this laboratory [1,2] based on thin electroplated silver chalcogenide membranes of non-trivial composition and surface morphology $\text{Ag}_{2+\delta}\text{Se}$, $\text{Ag}_{2+\delta}\text{Se}_{1-x}\text{Te}_x$, Ag_2Se and $\text{Ag}_2\text{Se}_{1-x}\text{Se}_x$ exhibiting double Nernstian response as low as 130 ppb.

The present investigation is focused on developing a new on-line protocol for total cyanide determination. The extremely high selectivity of the new cyanide FIPD was made use of to develop an electrochemical flow procedure for decomplexation of the bound cyanide. A flow electrochemical cell is constructed in which silver amalgam nano-templated working electrode (cathode) is used. 100 % efficiency for the metal reduction of the following complexes $[\text{Ag}(\text{CN})_2]^-$, $[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Zn}(\text{CN})_4]^{2-}$, $[\text{Cd}(\text{CN})_4]^{2-}$ and $[\text{Hg}(\text{CN})_4]^{2-}$ has been achieved using this cell both in off-line and on-line modes. The newly developed protocol is simple, cost effective and competitive to the commonly used for this purpose flow-injection procedures.

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Various Applications of Quartz Crystal Microbalance in Environmental Analysis

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The developed in the last decade methods on the basis of converse piezoelectric effect for in-situ mass determinations in nano-gram or pico-gram scales are from very high importance for the environmental analysis. They allow very fast and dynamic measurements in minute mass changes at surfaces, thin films or interfaces as well in liquid media. Combination of QCM – sensors with the well known system for flow-injection analysis (FIA) make possible direct determinations of very toxic for the environment compounds like CN^- in concentrations under these allowed from European Protection Agency for fresh water. Required conditions and methodology for applying QCM-sensor for CN^- - detection in closed FIA-system are discussed. A new closed flow cell for quartz crystal application in flow injection mode is proposed.

The QCM – methods are not only techniques for mass determinations. They are as well a powerful tool for different electrochemical interface determinations. Using the approach of the electrochemical quartz crystal microbalance (EQCM) combined coulometry- QCM protocols have been developed in this laboratory for real-time compositional analysis of the electrodeposited films. They allow stoichiometry or phase compositions of deposited films to be monitored in real time as a function of membrane thickness. Thin films of binary and ternary semiconductor chalcogenide compounds such as Ag_ySe , Cu_{2-x}Se , CuAgSe , electrodeposited on conducting substrates, most often Pt, have been successfully used as active membranes for ion-selective detectors for Cu(II), Ag(I), CN^- and Hg(II), working under steady state and in flow-injection mode signal recording. The newly developed methods for real-time compositional analysis are best illustrated on the examples of Ag_ySe and CuAgSe membranes and their advantages and limitations are broadly discussed.

The Environmental Influence of Liquids and Gaseous Effluents Resulted from Heavy Water Detritiation Plant Running

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This paper is a theoretical and experimental study attach of influence to environmental of liquids and gaseouses effluents results from functioned of heavy water detritiation plants and to realized of a program to environmental monitoring [1].

We try in this study to present few research directions:

- Sources identification, the transfer modeling of radionucleides on environmental, identification of exposure ways, of critical groups for the DEL -derivate emissions limit - calculation.
- Monitoring in effluents radionucleides medium receiving, liquids and gaseouses, wich results from accredited nuclear activity of detritiation, in normal operating conditions and in emergency radioactivity situations [2].

Key words: *effluent, monitoring, DEL account.*

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Identification of Heavy Metals and Toxic Trace Elements Collected by Filter Technique in the Industrial Regions of Czech Republic

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The contribution of environmental dust to atmospheric processes and health outcomes is of great importance. The ambient particulate matter was enriched with heavy metals or toxic trace elements. The samples of atmospheric particles were collected by filter technique. The nitrocellulose filters were used (from 48 to 96 hours' exposure). The samples were collected from Czech meteorological stations Milesovka (837 m above sea level) and Kopisty (240 m above sea level). This is one of the most polluted industrial region, so called "black triangle" of the Czech Republic [1, 2]. The inductively coupled plasma atomic emission spectrometry (ICP-AES) was used for quantitative determination of traces of As, Ba, Cu, Mn, Pb and Zn after sample extraction with aqua regia, according to ISO 11466:1995. The content of pollutants was compared with the corresponding threshold concentration levels.

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Analysis of Surface Water by Inductively Coupled Plasma - Atomic Emission Spectrometry in Preserve Parangalitz, Blagoevgrad region (Bulgaria)

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The concentration levels of heavy and toxic elements circulating in the environment have increased due to various industrial activities. The aim of this environmental study is to establish the distribution of Ba, Cr, Cu, Zn, Cd, Mn and Pb as pollutants of surface water samples in preserve Parangalitz, Blagoevgrad region. These elements are studied according to the both Bulgarian and International Environmental legislation related to water quality monitoring. River and rain - water samples are collected. Three monitoring points in Blagoevgradska Bistritza River are chosen.

The water samples are collected and preserved according to ISO 5667-“Water quality-Sampling” The measurements are performed with the Jobin Yvon (France) inductively coupled plasma atomic emission spectrometer model JY 38. The most prominent lines in pure solvent are used as analysis lines. Line selection for analysis of water samples is discussed in accordance with ISO 11885- “Water quality. Determination of 33 elements by ICP-AES”.

LA-ICP-MS – An Important Reference Method for Analysis of the Mineral-forming Solutions Trapped as Fluid Inclusions in Minerals

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The fluid inclusions in minerals are representative objects for investigation the composition of the ancient mineral-forming fluid.

LA-ICP-MS- method was used for individual – qualitative and quantitative – analyses of more than 50 single fluid inclusions in quartz from “Krushev dol” deposit (Madan, Bulgaria). The masspectral signals for 10 elements (Li, Na, Mg, K, Ca, Mn, Cu, Zn, Cs and Pb), as well as Si, were measured. The mol ratios (X / Na) were calculated after preliminary measuring of the total salinity (wt % NaCl eqv.) by microcryometry. The salinity obtained was in the range 3.70 ÷ 9.34 wt % NaCl eqv. Some of the most informative mol ratios (mol/mol) were in the ranges: K/Na 0.053 ÷ 0.22; Ca/Na 0.016 ÷ 0.065; Mg/Na, 0.0021 ÷ 0.0086; Mn/Na 0.0013 ÷ 0.010 respectively. These results are in a good agreement with those obtained by the bulk method of the water leachets for samples of the same quartz specimen [1].

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Potentiometric Sensor for Sulphur Dioxide Detection

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Sulphur dioxide is one of the main gases for the environmental pollution, the presence of its microconcentrations in the air is very dangerous for health (the average day value TLV =0.05 mg/m³). Potentiometric methods with gas-sensing sensors have many advantages: universality, selectivity and a minor error in the determinations. Electrode function of these sensors followed Nernst expression, thus metrological attestation is convenient. Known potentiometric sensors of sulphur dioxide detection either provide no high sensitivity, or have no long lifetime as gas-permeable membrane can be clogged.

We have worked out a new potentiometric nitrogen-gap sensor for sulphur dioxide detection. A glass-disc solid state pH-electrode with a thin film of potassium chloride solution on its sensitive surface was used as the indicator electrode in its construction. Besides the sample a saturated sodium sulphate solution and 0.1 M sulphur acid were put in the sensor glass vessel. The function of the sensor is based on the reaction of sulphite ion with nitric acid. Formed nitrogen dioxide diffused through gas-gap (nitrogen) and was adsorbed by the film of electrode solution, changing the indicator electrode potential. Sulphur dioxide concentration was calculated using calibration curve $E=f(-\lg[\text{Na}_2\text{SO}_3])$, its slope was 58 mV according to Nernst equation. For the sulphur dioxide determination in the air measure out in doses gas mixture was passed through 0.01M alkali solution. Aliquot of obtained solution was used for the analysis.

The linear range of electrode function $E=f(-\lg[\text{Na}_2\text{SO}_3])$ with the designed sensor was $1 \cdot 10^{-6}$ - $5 \cdot 10^{-3}$ M, that is allow to detect sulphur dioxide in the air in the range 0.01-1000 mg/m³ with average precision about 3% (n=5, P=0.95). Nitrites and nitrogen oxides influence the determination.

Reliable and Convenient Method of Arsenic Speciation in Waters

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Arsenic can be present in several forms in natural waters. Speciation of inorganic and organic forms of arsenic is often as important as total quantification because of the varying degrees of toxicity and removal mechanisms of the different species. Inorganic species, namely arsenite [As(III)] and arsenate [As(V)], usually predominate in ground waters. However, organoarsenicals monomethylarsonate (MMA) and dimethylarsinate (DMA) can often also be significant in surface waters, especially when they have been impacted by human activities. Several methods are available for arsenic speciation in a good equipped analytical laboratory. It is of utmost importance to know the concentration of the most toxic forms As(III) and As(V), which are however unstable and prone to transformations on storage (O_2 oxidation, adsorption losses, bacterial attack).

The present scheme for fractionation of both inorganic and organic As species is suitable to be applied at the sampling site. The separated species are further quantified by electrothermal atomic absorption spectrometry (ETAAS) in the laboratory. Water sample (5 ml) is adjusted to 0.05 mol/l HCl and is passed through anion exchange cartridge filled with Dowex 1x10 in acetate form with a flow rate of 0.5 ml/min followed by 0.05 mol/l HCl as eluent. The following fractions are collected:

- first 7.5 ml – this fraction contains As(III) and DMA;
- from 13 ml to 15 ml – this fraction contains MMA;
- from 17 ml to 20 ml – this fraction contains As(V).

The first fraction is further (in the laboratory) passed through a column with cation exchanger Dowex AG 50Wx8 in H^+ form to separate DMA. The latter is eluted with 1 mol/l HCl. As(III) remains in the effluate. The separated fractions are finally subjected to ETAAS analysis. Limit of detection of this procedure is 0.1 $\mu\text{g/l}$ for any As species. Recoveries were similar for two spiked hard groundwater samples indicating that dissolved minerals are not likely to be problematic. These results suggest that this methodology can be used for analysis of the four primary arsenic species of concern in drinking water supplies.

Uncertainty of Flame Atomic Absorption Determination of Trace Elements in Waters

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Atomic absorption spectrometry (AAS) has been widely used for determination of trace elements in various areas, such as environmental, biological, clinical and material analyses. The system of the flame atomic absorption spectrometer is relatively simple. However, there has been no paper on the estimation of the uncertainty for the instrument. Several works on the estimation of uncertainty in AAS have been reported. Kurfuerst studied the uncertainty in the analysis of solid materials by graphite furnace AAS comparing sample digestion AAS and solid sampling AAS. Stringari evaluated sample grinding methods for analysis of plant samples by graphite furnace AAS. Bettencourt applied their uncertainty validation method to the analysis of leaves by acid digestion–graphite furnace AAS. Synek studied the uncertainties of mercury determination by cold vapor AAS and reported that the contribution of the sample absorbance component was highest. Also an example of estimation of uncertainty in AAS was introduced in the Eurachem/CITAC Guide. However, in these works, most of the discussions are concentrated on the uncertainty of sample preparation procedures. Despite the fact that the uncertainty of instruments is thought to be important, it was treated as one factor and the uncertainty sources of the instrument have not been analyzed further. In some reports, the estimation of uncertainty for the instrument was limited to those concerning the calibration of the instrument, while the instrument itself was considered as a black box. We studied the uncertainty in flame AAS determination of trace elements. In estimating the uncertainty of the atomic absorption spectrometer, we considered the measurand of the atomic absorption spectrometer is a value of related absorbance. Therefore, in this study, we identified uncertainty sources (drift of lamp intensity, drift of sensitivity, background correction, especially at lower wavelengths, nonlinearity of the calibration curve, stray light of the monochromator, flame conditions, blank values, spikes recovery) affecting measurement of the absorbance with the flame AAS, and evaluated those sources.

**Participation of the National Center of Metrology, Bulgaria in CCQM P64
Comparison – ICP MS Determination of Cu and Zn in Nonfat Soybean
Powder**

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The Comité Consultatif pour la Quantité de Matière (CCQM) was created by the CIPM (Comité International des Poids et Mesures) in 1993 to coordinate the activities of national metrology laboratories in establishing traceability to the SI at the highest level and to stimulate understanding of the concept of uncertainty and the assignment of uncertainty statements in chemical measurements. The CCQM working groups are involved in the identification, development and execution of a series of international comparisons that will establish the technical basis for the mutual recognition of measurement capabilities among the metrology organizations and some designated partners.

Besides toxic and harmful elements, essential elements in food are given attention because the lack of them can result in serious innutrition and potential diseases. Ca, Fe, Cu and Zn are essential micronutrients for human beings, especially for children – adequate mineral intake supports appropriate growth and development and helps to prevent diseases in future. The 64th CCQM Pilot Study was focused on the determination of Ca, Fe, Cu and Zn in soybean as it is one kind of typical foodstuff and a raw material of many food products. Soybean is human's important source for the intake of protein and some essential elements.

In this work, the participation of the National Center of Metrology, Bulgarian Institute of Metrology in the 64th CCQM Pilot Study – determination of trace elements in nonfat soybean powder – will be presented. A detailed description of the microwave digestion method and the ICP MS conditions used will be provided. The results of Cu and Zn determination will be discussed. The uncertainty budget for the measurement of Cu and Zn in soybean powder by ICP MS with external calibration established following the CETAC-Eurachem Guide will be presented and discussed in details.

Investigation on Soil Contamination Caused by Scrap Deposition

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The problem of scrap deposition and its influence on environment contamination is still one of the extremely important economic, social and political milestones in our country. A typical example is the scrap depository in Mladost quarter of the city of Sofia.

The present study describes an investigation on soil contamination caused by this depository. Soil samples were collected from several places around it. Extraction of trace elements from the soils using *aqua regia* was carried out following procedure described in [1]. Elemental analyses of the extracts were performed by means of inductively coupled plasma atomic emission spectrometry [2]. The results obtained were compared with the threshold concentrations according to regulations of Bulgarian Ministry of Environment and Water. It was found, that the soils were polluted with a number of elements as As, Cd, Ni, Pb, Cu and Zn.

In order to estimate the rate of soil contamination in the region, the concentration coefficients as well as the coefficients of poly-component contamination were calculated. Due to the pollution with heavy metals the investigated soils are unsuitable for agriculture. The presence of the studied scrap depository caused also chemical destruction of soils in its neighbourhood, which substantially enhanced their acidity [3].

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Characterization of Marine Sediments Toxicity based on Structural Information

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The marine sediment toxicity was previously studied for eight ordnance compounds: 2,4,6-trinitrotoluene (2,4,6-TNT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 1,3-dinitrobenzene (1,3-DNB), 1,3,5-trinitrobenzene (1,3,5-TNB), Royal Demolition Explosive (RDE), tetryl, and picric acid [1]. Based on the obtained experimental data, the lethal concentration to 50% of the test organisms (LC₅₀) and the effective concentration to 50% of the test organisms have been modeled by using the molecular descriptors family on structure activity relationships (MDF-SAR) approach [2].

For five organisms and nine endpoints, the MDF-SAR models with two variables were obtained. The statistical characteristics of the obtained MDF-SAR models are:

No.	Organism	EndPoint	r ²	s	F	r _{cv-100} ²	n
1	sea urchin (<i>Arbacia punctulata</i>)	fertilization	0.9999	3.83·10 ⁻⁵	9.16·10 ⁸ †	0.9999	5
2		embryological development	0.9999	8.64·10 ⁻³	5.86·10 ⁴ †	0.9998	7
3		germination	0.9991	3.75·10 ⁻²	2.95·10 ³ †	0.9976	8
4	green macro-alga (<i>Ulva fasciata</i>)	zoospore germination	0.9998	1.74·10 ⁻²	1.13·10 ⁴ †	0.9984	8
5		germling length	0.9992	3.33·10 ⁻²	3.13·10 ³ †	0.9984	8
6		Germling cell number	0.9999	5.88·10 ⁻³	1.08·10 ⁵ †	0.9999	7
7	polychaete (<i>Dinophilus gyrociliatus</i>)	survival and reproductive success	0.9996	2.70·10 ⁻²	6.31·10 ³ †	0.9991	8
8	redfish (<i>Sciaenops ocellatus</i>)	larvae survival	0.9999	6.13·10 ⁻³	4.59·10 ⁴ †	0.9999	7
9	opossum shrimp (<i>Mysidopsis bahia</i>)	juveniles survival	0.9999	5.24·10 ⁻³	2.13·10 ⁴ †	0.9997	7

r² = squared correlation coefficient; s = standard error of estimated; F = Fisher parameter; r_{cv-100}² = cross-validation leave-one-out score; n = sample size; † p < 0.001

The analysis of the obtained models with two descriptors revealed that the MDF-SAR approach is able to provide valid and reliable model for marine sediments toxicity characterization.

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Determination of the Limit of Detection in Gas Chromatographic Analysis of Pesticides in Non-fatty Foods

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A procedure for determination of Limit of Detection (LOD) is applied using standard deviation of the background in chromatograms of blank samples. Limit of Detection of different pesticides in the range of the peaks of standard spectra of the pesticides is determined. The method is applied using both: height calibration curve and area calibration curve as well. Practical limits of detection of pesticide residues in non-fatty foods are calculated on the basis of determined GC LODs. Finally samples with pesticide concentrations around the limits of detection are prepared and chromatograms for comparison are acquired.

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Topic C.

**Method Validation and Environmental Reference
Materials**

Synchrotron Radiation as a Validation Tool for Micro-Nano Analysis

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Accurate elemental analysis at the microscopic/sub-microscopic level is of growing importance in many areas of scientific research for the characterization at the sub-micron and nano-scale in materials technology. It is becoming increasingly important to invest in the development of the research infrastructure for accurate and traceable chemical microanalysis that is able to assist in the characterization of the base products of a growing number of important technologies in modern society.

During the last decades a number of efficient and sensitive microscopic analytical methods (e.g. secondary ion microscopy and imaging (SIMS), X-ray photoelectron spectroscopy (XPS), Auger microscopy, micro proton induced X-ray emission (μ -PIXE) and derived techniques such as Rutherford Backscattering spectroscopy (RBS) and microscopic X-ray fluorescence analysis (μ -XRF)) have been developed. They offer means for solving many of the analytical questions raised by science, technology and industry at the microscopic level. Laser ablation inductively coupled plasma mass spectrometry (ICP MS) is also quickly developing as a tool for this. Current 'beam' methods of analysis are relative i.e. the signal measured requires comparison to a reference material or comparison with quantitatively reliable methods of analysis. At present, few reference materials for microscopic analysis have been produced.

The concepts of traceability for chemical measurements are concerned with the direct or indirect linkage of analytical results to the international metric system of units (SI) thereby showing a way in achieving comparability in chemical analysis. Metrologically sound measurements require at least one absolute (primary) method of analysis to link the results of chemical measurements to the SI system of units. Traceability concepts need to be critically evaluated for "beam methods" of analysis.

Of all the beam methods of analysis μ -XRF has the highest potential for being developed as a certification or calibration tool and as a reference method for other micro-analytical techniques. The major reason for this privileged status is that the interaction of X-rays with matter is well understood as follows from modeling experiments by Monte Carlo simulation. A realistic goal is to reach an average accuracy of quantification in the range of 3-5 % for micron sized objects or portions thereof at the concentration level at or below 1 ppm, and this for a wide range of elements. These characteristics can only be achieved with focused synchrotron radiation (SR) based sources of X-rays of the so-called third generation such as those available at the European Synchrotron Radiation Facility in Grenoble.

We will concentrate in this talk on the results obtained in a shared cost RTD action of the EU "Synchrotron Microanalysis: accurate and traceable elemental analysis on the microscopic level" The goal of the project was to develop the existing infrastructure and experience for accurate and traceable micro-analysis in two distinct European SR facilities and to make this infrastructure available for research and industry in Europe.

Method Validation in Environmental Analysis - Mission Possible

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Nowadays there is a great concern about quality [1, 2] and particularly the quality of analytical measurements in accredited testing and calibration laboratories [3]. Compliance with the requirements of ISO/IEC 17025:2005 guide [3] requires validation of methods: “Validation is the confirmation by examination and the provision of objective evidence that the particular requirements for a specific intended use are fulfilled” [1, 3]. An important final component of validation is the proof and statement that the method is fit for the intended use (“fitness for purpose”) [4].

This lecture will treat in a tutorial manner [5] the basics of validation of (an analytical) method, with an emphasis on specific problems encountered in the vast application field of environmental analysis. Material is supplemented with and illustrated by numerous examples from the literature and the author’s own research and experience.

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Validation of Chemical Methods in Quantitative Analysis

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All methods used in analytical chemistry are subject to error. Therefore it is vital that each method should be evaluated and tested to ensure that it produces results which make it suitable for the intended purpose. Method validation and verification is the implementation of this evaluation process. However, the extent and rigor with which a particular method is evaluated is dependent on the intended use and past experience with the method. Method validation is the process in which every stage of a new analytical method is subjected to rigorous series of tests to ensure that the method will be able to deliver all the outcomes required of it. The confidence that the method can deliver these outcomes is expressed in terms of statistical probability over the whole analyte concentration range established during the validation process. Verification of a method is a simplified form of the validation process. It involves the testing of a series of method parameters to ensure that a previously validated analytical procedure performs as reported when it is introduced into a new environment where, at the very least, equipment may not be identical to that employed in the initial validation. Established methods must, as a minimum requirement, be verified when introduced into a laboratory for the first time. Verification, strictly speaking, is also necessary if the method is modified or applied to a new situation, for example a different sample matrix. A new method must be subject to a much more searching series of validation procedures, each one of which adds further confidence in the analytical results obtained. While method validation is mandatory for assurance of analytical quality, the cost to a laboratory is significant. It is therefore important for the financial well-being of a laboratory that validation should adopt no more than those procedures necessary to ensure the analytical quality demanded by a client. An important question now is: does a validated method automatically give a validated result? And to that question the answer must be: no. There can never be a mechanism or recipe for producing automatically valid results because one can never eliminate the skills, the role and the responsibility of the analyst.

Method Validation in Environmental Analysis: Validation of ISO 18412 Photometric Determination of Cr (VI) in Weakly Contaminated Water

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According to EURACHEM validation is the process of establishing the performance characteristics and limitations of a method and the identification of the influences which may change these characteristics and to what extent or the process of verifying that a method is fit for purpose, i.e. for solving a particular analytical problem. [1]

Methods that should be validated are: a new method developed for a particular problem; an established method revised with improvements or extended to a new problem; when an established method is changing with time (from quality control charts); an established method used in different conditions (laboratory, analysts, instrumentation); to demonstrate the equivalence between two methods, e.g. a new method and a standard. [1]

The method ISO 18412-2005 describes the determination of Cr(VI) in weakly contaminated surface and ground waters. In the scope of the method laboratories are invited to validate it for use in estuarine and marine waters [2]. We tested and validated the method for use in the case of seawater. Using EURACHEM guides ([2], [3]) we determined the limits of detection and quantitation and examined the linearity of the calibration curve (from 1.0 to 5.0 $\mu\text{g}/\ell$). Precision (repeatability and reproducibility), trueness and the expanded percent uncertainty were calculated in three concentration levels (0.5-1.0-3.0 $\mu\text{g}/\ell$). The limits of detection and quantitation were determined 0.2 and 0.5 $\mu\text{g}/\ell$ correspondingly. The expanded percent uncertainty was calculated 21,9%, 14,8% and 4,1% correspondingly for the three concentration levels. Quality control procedures with the use of Shewart charts were used to monitor the performance of the method over time.

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Determination of Trace Elements in Aquatic Plants by Solid Sampling Zeeman Atomic Absorption Spectrometry (SS-ZAAS)

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Aquatic plants particularly seaweeds are used as traditional food in Asia, as food additives, fodder and fertilisers, as ingredients for cosmetics and pharmaceutical products. They contain proteins, vitamins and essential elements, but also toxic metals. An increasing need of thorough analytical control on essential and toxic elements at trace levels in seaweeds is expected and this will require rapid, low-cost, accurate and precise analytical methods.

Direct solid sampling Zeeman atomic absorption spectrometry (SS-ZAAS) is one of the fastest spectrometric methods for low-cost trace element determination. SS-ZAAS methods were developed and successfully applied to the determination of mercury, cadmium, manganese and lead in aquatic plants. With no chemical sample preparation the risk of contamination and analyte loss is reduced to minimum. The short analysis cycle after calibration delivers one result every 3 minutes and avoiding any dilution step the method achieves lower detection limits, than conventional wet-digestion AAS-techniques.

Mercury was determined by a ZAAS SM 20 (Grün) equipped with a specially designed nickel tube furnace. Cadmium, manganese and lead measurements were performed in routine by a third generation ZAAS (Analytik Jena) combined with an automatic solid sampler. The use of 3-field- and dynamic magnet field modes extended the linear range of the calibration up to one order of magnitude depending on the element. Thus higher amounts of analyte were detectable without laborious dilution of solid samples.

All measurements were based on calibrations using certified reference materials (CRMs) of organic origin. The use of matrix matching CRMs allowed simple calibration and modifier-free determination resulting in high accuracy of the method. Results obtained were in good agreement with the certified values. Precision was comparable to conventional analytical methods after sample decomposition.

Application of Certified Reference Material for Estimation of Accuracy in the Analysis of Soils and Sediments by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

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The most difficult samples from point of view of spectral interferences are soils and various types of sediments. Efficient and accurate background correction for these interferences normally requires a means of measurement of the background intensity adjacent to the analyte wavelengths.

An ICP-AES method was proposed for the determination of As, Cr, Pb, Cu, Mn and Zn in soils and sediments. The quantification of spectral interferences in the presence of matrix constituents was used and the background correction to the analyte wavelengths was made. The accuracy of analytical results was estimated by CRM's: IAEA/Soil 7 and like sediment IAEA/ SL. Two digestion procedures were used: extraction of trace elements soluble in aqua regia in accordance with ISO 11466/1995 and total decomposition of the matrix in the presence of hydrofluoric acid. In both cases the silicate matrix was separated. Influence of the matrix constituents Al, Mg, Ca, Fe and Ti on the limits of detection, the slope of calibration curves (non-spectral matrix effects), the background correction procedure and the accuracy of analytical results were investigated. The experiments were performed with a radial viewing 40.68 MHz ICP.

Ecological Method for Surface Processing of Metals and Alloys

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New method, named Electro-discharge polishing (EDP) has been developed and applied for surface processing of metals and alloys. EDP technology is efficient technique for surface modification of constructive materials by high energetic electromagnetic fields [1]. The physical-chemical processes observed when metallic parts immersed in water solutions acting as an anode biased up to 400 V are investigated and present.

The technology developed is based on the electrochemical and electro-physical processes that take place at the electrode surface dipped into a tub with solution under applied voltage. As a result a plasma phase of the solution arises near the electrode, in contrast with the usual electro-chemical polishing, which ensures higher quality of the surface cleaning. During the electro-discharge polishing a smooth and bright surface of the metal tools without any contaminations is obtained. The EDP process allows reducing the surface roughness four times for a very short time, 5 minutes. It is shown that high quality electro-discharge polishing of stainless steel of surface roughness $R_a \leq 0.02 \mu\text{m}$ is achieved by fast operating voltage rise ($dU/dt > 8$ to 10 V/s) accompanied by minimal solution temperature of 90°C .

The developed EDP technology has wide range of applications, i.e. it could be applied to different metals and alloys and does not require preliminary preparation of the surface. The method allows simultaneously treatment of all surfaces of the tools with unspecified configuration. It should be underlined that the electro-discharge process is ecological. In contrast to the electrochemical polishing, the use of acids, alkalis and poisonous solutions is avoided in a new method.

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Topic D.

**Thermodynamic Modeling of Ecomaterials and
Processes**

Thermodynamic Modeling for Mineral-based Eco-Materials

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The concept of eco-materials is directed toward the development of materials and technologies of their production, which have no negative impact to the environment or help to improve the environmental situation. An assessment of materials or processes in this respect requires quantitative information about possible chemical reactions, dissolution and distribution of the materials components in the “geo”- and bio-“sphere. Until now thermodynamic modelling with efficient computer codes for equilibrium calculations provides the most developed tool for the prediction of possible chemical and phase reactions in a complex geologic and human-living environment. The confidence we can have in such predictions depends first of all on the quality of the thermodynamic database and the correct handling of thermodynamic mixing models.

Thermodynamic modelling for eco-materials assessment raises a number of new questions:

- How can a thermodynamic database satisfy the chemical complexity of the environment?
- How accurate do we need the standard data for calculations in complex systems?
- Is there an alternative way in thermodynamic modelling to the usual strategy from simple to complex system?
- How can the end-user of databases and codes get confidence in the thermodynamic calculations?

In the lecture the present status of geo-chemical databases and related codes will be discussed.

The concept of the new German database project THEREDA will be presented.

At examples from waste isolation projects in rock salt and potash mines the role of thermodynamic modelling for the development of gypsum- and MgO-based building materials is demonstrated. Finally kinetic issues in modelling of dissolution and crystallization processes of such minerals will be discussed.

Toxic Oxy-anions in Aqueous Systems – Speciation Study

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Many pollutants, such as arsenic, chromium, boron, selenium etc. in water streams have been identified as toxic and harmful to environment and human health. Therefore, the development of techniques for the removal of toxic substances from waters has become an important issue for scientists worldwide. In most cases metals and metalloids in waters occur in more than one form. Hence their distribution between different chemical forms, i.e. its chemical speciation is very relevant parameter in the frame of tasks such as separation processes behavior and bioavailability. Metals hydrolyze in waters and may be present in water as a simple hydrated cations or anions, as inorganic complexes, complexes with natural or synthetic organic ligands, or attached to colloidal inorganic or organic matter.

The mobility of metal ions in aqueous solutions is often controlled by sorption. A molecular understanding how to sorb the metals onto mineral surfaces is needed before we can reliably model equilibria from sorption isotherm measurements. It is known that mentioned elements (As, Cr and B) in aqueous medium are in the form of oxy-anions. Most of the minerals, known as a good sorbents of cations (zeolites, clays etc.) possess negatively charged surface, and therefore, they are not efficient enough for removal of anions/oxy-anions. Thus, it is necessary to consider the speciation of metals/metalloids before starting the experiments as well as new sorbents are needed for effective removal of oxyanions from water streams.

The contribution offers an overview on geochemistry, distribution, sources, toxicity, regulations and applications of selected techniques for removal of arsenates and chromates from aqueous solutions. The chemical speciation of water solutions containing arsenic and chromium oxyanions in various ratios is calculated with the aid of computer programs (Mineql Plus and Geochemist Workbench). The effect of solution pH, total concentration of each species studied, and the presence of other species in solution is calculated and presented in the form of thermodynamic speciation diagrams.

Acknowledgement

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Modeling the Property of Compounds from Structure: Statistical Methods for Models Validation

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A molecular descriptors family on structure-property relationships study (MDF-SPR) was conducted in order to model the boiling points of alkanes using the compounds structure information.

The alkanes from C3 to C9 were included into study. Two MDF-SPR models, one with one descriptor and other with two descriptors, were identified. The estimation and prediction of the MDF-SPR models were analyzed. The methods used for validation of the obtained MDF-SPR models are presented.

The correlated correlation analysis was using in order to compare the performances of the obtained MDF-SPR models and of the MDF-SPR models comparing with previous reported model. The Steiger's Z test [1] at a significance level of 5% was applied.

The statistical analysis of the obtained MDF-SPR models demonstrated that the model with two descriptors has greater abilities in estimation and prediction compared with the model with one descriptor. More, the MDF-SPR model with two descriptors has greater abilities in estimation comparing with previous reported model. These observations were also sustained by the results of correlated-correlation analysis.

The multi-varied MDF-SPR model can be used in order to predict the property of interest of studied alkanes without any experiments and measurements, by using the MDF SPR Predictor application [2].

Acknowledgements

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Processes Kinetics Modeling: A Numerical Study

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Introduction

The kinetics study of the reaction between Cu²⁺ and S₂O₃²⁻ in solutions is not entirely studied, being reported into the specialty literature just few papers which refer the reaction in aqueous solutions.

Aim

By using of a set of experimental data obtained from stopped flow spectrophotometrical installation build at Technical University of Cluj-Napoca, to investigate the kinetic of the reaction.

Assumption

The general form of the reaction is $A + B \rightleftharpoons X \rightarrow P$

Experimental procedure

The cooper and tiosulfate aqueous solutions were prepared in different concentrations varying from 0.001 M to 0.01 M.

The reaction was detected to be a very fast one: the existence of the X intermediary was found to be below 25 ms.

The wavelength of light detection diode was found (and is 430 nm) in order to prepare the detection of intermediary forming as the wavelength which assures the best stability of the light emission in time.

A microampere meter was set in order to be used for recording of the signal from detector and the baud rate of the recording was choused to be 0.04 ms.

A digital oscilloscope with buffer was used to plot and transfer the data to the computer.

In order to minimize the experimental interferences such as dilution of the intermediary, the size of the mixing chamber was varied; a small size one was selected and used for measurements. The mixing chamber has a volume equal to 0.35cm³ and the length of optical pathway traversed by the beam through measurement chamber is 0.4 cm.

Experiments

Three experiments with equal concentration of reactants (0.001, 0.005 and 0.01 M) are the subject of this investigation.

The recording of digital data was started always after the mixing moment but near to, because of limited memory buffer of the oscilloscope (64 Kb).

The number of relevant measurements corresponding to the reaction time it varies in 1500-8000 range.

Mathematical Methods

The Lambert-Beer law was used to correlate extinction with concentration; the unknown parameter was the molar extinction coefficient. The mathematical model of the assumed reaction mechanism was numerically written; the unknown parameters were four partial reaction orders and three reaction rates constants.

The subject of optimization was squared sum of differences between experimental extinction E and theoretical approach of extinction $a[X]$. Only a first part of the experimental data records entered into the optimization procedure (1100 for 0.001 M, 1300 for 0.005 M, and 6500 for 0.01M).

Results

The optimization procedure produced the best fit of the model to the experiment with 0.962, 0.955, and 0.980 respectively correlation coefficients.

Not all unknown parameters were possible to be obtained. Reaction rates: only to the right ones. Partial orders: all, except one of intermediary for the left direction reaction. Extinction coefficient: 212 ± 22 l/mol*cm. For all obtained parameters is no significant difference between parameters values from one experiment to another with a 95% confidence.

Conclusion

Reaction kinetics was almost complete determined. Reaction rates: 2000 ± 1000 , N/A, 2200 ± 200 , partial orders: 0.789 ± 0.05 , 0.781 ± 0.04 , N/A, 1.55 ± 0.04 .

The optimization procedure was proved to be a self consistent one, despite of the number of unknown parameters used.

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Thermodynamic Modeling of Sea-Type Systems as a Tool for Optimization of Industrial Processes

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The knowledge of sea-type complex multicomponent systems is the theoretical basis for optimization of technological processes of salt crystallization and precipitation from sea waters and brines. Because of the system complexity, scientific data are easier to obtain by thermodynamic modeling. In our studies, thermodynamic modeling, based on the Pitzer model (computer program ChemSage) was performed.

The desulfatization and evaporation processes were simulated in the system Na^+ , K^+ , Mg^{2+} , $\text{Ca}^{2+}/\text{SO}_4^{2-}$, $\text{Cl}^-//\text{H}_2\text{O}$, representing the Black Sea water. The temperature range was 20 - 40°C, which corresponded to the climate conditions at the Bulgarian Black Sea coastal area. Quantitative characterizations of all simulated processes were obtained. The role of the desulfatization agent was evaluated and different ways for increasing the NaCl yield were suggested. The results were used for increasing the effectiveness of sea-salt production in solar sea-salt plants.

The evaporation and crystallization processes were simulated in the systems Na^+ , K^+ , Ca^{2+} , $\text{Mg}^{2+}/\text{Cl}^-$, $\text{CO}_3^{2-}/\text{H}_2\text{O}$ and Na^+ , K^+ , $\text{Ca}^{2+}/\text{Cl}^-//\text{H}_2\text{O}$, describing the brines that remain after sea-salt and magnesium hydroxide productions, at temperatures of 0 - 40°C. The results were used to design the processes of magnesium and potassium salts preparation from these brines.

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Thermodynamic Modeling of Inorganic Chemical Species in River Waters of the Region of Assarel-Medet Open Pit Copper Mine

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The soluble inorganic chemical species present in polluted waters of Mechenska and Luda Yana rivers in the region of Assarel-Medet open pit copper mine were evaluated by monitoring and thermodynamic modeling. Experimental data on $t^{\circ}\text{C}$, alkalinity, p_e , conductivity, salinity, O_2 , total concentrations of NO_3^- , NO_2^- , PO_4^{3-} , NH_4^+ , Cl^- , SO_4^{2-} , K, Na, Ca, Mg, Fe, Mn, Cu, Zn, Cd and Pb were obtained and used for the thermodynamic calculations. The modeling assessment was performed using a thermodynamic ion-association model (PHREEQCI computer program, version 2.11) and our new database *sst2005.dat*.

The results show that the chemical species of the elements depend on the composition of the solution, the ionic strength, pH, and redox potential. In the waters of Mechenska river, high acidity (pH 3-4), high concentrations of SO_4^{2-} (up to 2700 mg/l), Cu (up to 79 mg/l), of Mn (up to 6.65 mg/l), of Fe (up to 6.25 mg/l) and of Zn, Cd, Pb, Cl, N (up to 54 mg/l) have been established. They indicate the presence not only of M^{n+} species but also of MSO_4^{n-2} species for the elements K, Na, Ca, Mg. The last ones are the major elements in all natural waters and are usually present as free M^{n+} ions. In these studied cases, a $\text{M}^{n+}/\text{MSO}_4^{n-2}$ ratio of 9:1 has been calculated for K and Na, while 1:1 is found for Mg and Ca. A greater variety of sulfate species (MSO_4^{n-2} , $\text{M}(\text{SO}_4)_2^{n-2}$ and $\text{M}(\text{SO}_4)_3^{n-2}$), increasing with the content of SO_4^{2-} , is observed for the trace elements Mn, Cu, Zn, Cd, Pb. Sulfate species contributions to the total species sum for each of these elements vary from 50 to 80%. Only iron shows a different behavior and $\text{Fe}(\text{OH})_2^+$ species are dominant.

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Thermodynamic Modeling at Plasma-Chemical Treatment of Systems Consisting of Mineral Raw Material

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The mineral raw material is released in the environment set many environmental problems, some of them being dangerous for human health. A new direction to utilize is thermodynamic possibilities for high temperature treatment in a plasma medium [1-2] of several types mineral raw materials aimed at decreasing or completely destroying harmful emissions/gaseous phase/ and using the useful products/condensed phase/ from this process.

The results from thermodynamic calculations with high-effective universal computer program[3-6] in temperature range /1000-3700 K/, and using plasma medium for treatment of mineral raw material allow assessing the thermal dissociation of the components in gaseous and condensed phases. Thermodynamic analysis [7] of the systems is carried out in conditions of low-temperature argon plasma. The systems/Natural phosphate-NPh; Serpentine-S, and Pyrite-P/, which are treated at these conditions, have a following composition: 70 % NPh+30 % S; 70 % NPh+30 % P; NPh; P; S. Data obtained by thermodynamic analysis made can be used to plan specific and concrete investigations on plasma-chemical treatment (PCT) of these systems.

Keywords: *plasma, thermodynamic analysis, mineral raw material*

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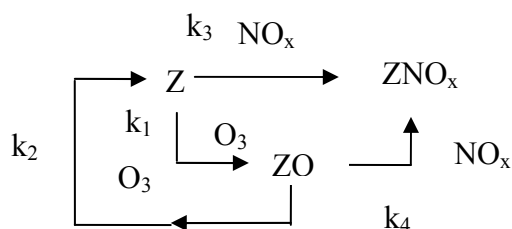
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Mathematical Modelling of the Mechanism of Ozone Decomposition on α -Fe₂O₃/ γ -Al₂O₃ Catalyst in the Presence of NO_x

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The ozone decomposition on alumina supported α -Fe₂O₃ catalyst in the presence of NO_x was investigated. The used installation for catalytic activity measurements with ozone consists of ozone discharge generator, thermostated flow reactor section and on-line fast response analyzer for ozone Ozomat GM (Anseros, Germany). It was observed a deactivation of the catalyst in the presence of NO_x and absence of a remarkable deactivation without NO_x during the timing frame of the experiment. That indicates the key role of NO_x presence, generated during the ozone synthesis from air, and the necessity of generation of ozone from pure oxygen. It was observed a competition between the two main processes – ozone decomposition and reaction of the nitrogen oxides with the catalyst surface. As a result the increase of the temperature leads to acceleration of the ozone decomposition rate followed by sharp decreasing of the catalytic activity due to poisoning of the active sites. Based on the obtained data, the following mechanism for the decomposition of the ozone was suggested:



It was suggested that the reaction of ozone with the free active sites of catalyst surface is faster than the second reaction from the mechanism (rate constant k_1 has higher value). The values of the rate constants for all four reactions increase with the temperature. As the last two reactions relate to the deactivation, the resultant influence of the temperature upon the catalytic activity is very complex. Based on the proposed mechanism a kinetic model for the reactions has been created solving numerically a system of ordinary differential equations by the method of Runge-Kutta.

Catalytic Activity of Ni-W Electrodeposits

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Previously, it was demonstrated [1] that the additivity principle, proposed by Wagner and Traud [2], can be successively used for studying the heterogeneous catalytic process of sulfide ion oxidation in alkali medium:



The upper process is one of the most effective and promising methods for removing this hazardous pollutant from waste waters.

On the other hand, Ni-W systems are known as one of the best catalysts for various desulfurization processes [3].

Applying the additivity principle, we aimed at gaining information about the reaction mechanism of sulfide ion oxidation in alkali medium over two Ni-W electrodeposits differing in quantitative ratio of both elements. The obtained results are compared with those for other catalysts and discussed.

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Topic E

Green Technologies for Ecomaterials

Cleaner Production and Product Eco-design: Strategies and Implementation

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The role of industry in the process of sustainable development is obvious. It relates to changes in production processes and products aimed at reducing the impact on the environment in the entire life cycle perspective and at improving the environmental and social performance of enterprises. To ensure sustainable economic growth, systematic application of the following tools is needed:

- cleaner production,
- environmental and integrated management systems,
- product – related measures, for instance life cycle assessment, eco – design, eco - labelling, integrated product policy, extended producer responsibility,
- assessment of environmental costs and sustainability reporting.

Over the last 15 years a great variety of different programmes in have been launched to facilitate the uptake of sustainability measures in Lithuanian industry. Many programmes have had, and continue to have, a strong technical assistance component that assists businesses with the identification, evaluation and implementation of preventive options appropriate for their operations. Paper deals with the experience and results of the implementation of sustainability measures in more than 150 Lithuanian companies and in some enterprises of East African, South East Asian and Central American countries.

Product life cycle thinking is essential in the path to sustainability because expanding the focus from production to the entire product life cycle facilitates the links between the economic and environmental dimensions within a company. Life cycle thinking is about widening views and expands the traditional focus on manufacturing processes to incorporate various aspects associated with a product over its entire life cycle. The investigation of cleaner product development based on life cycle assessment has been done in the framework of international project, where LCA was carried out for selected five products: a firewood stove, a solar sensor for passenger car, a buckle switch for passenger car, a domestic refrigerator/freezer and a corner sofa. The objectives were to find the most significant environmental aspects of the production chain and to acquire a basis for cleaner product development.

The companies were satisfied with the results of the project in terms of knowledge acquired and particular recommendations for cleaner product development (analysis of product chain, “hot spots” analysis, significant aspects’ evaluation). On the basis of the results, products can be redesigned to optimize their environmental impact in the entire products’ life cycle from raw materials extraction to manufacturing, consumption and disposal. The main results and the experience from this project are discussed in the paper.

Product Category Rules (PCR) and Environmental Product Declarations (EPD) as Tools to Promote Sustainable Products

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Manufacturing companies are exposed to an increasing demand for declaration of the environmental performance of their products. To do this in a standardised way, products category rules (PCR) can be used as guidance for the companies. PCRs help manufacturers to assess the environmental performance of the different materials in their products. This information can be used in environmental product declarations (EPDs) [1].

An EPD can be created according to the rules in ISO 14025. The data should be gathered according to life cycle assessment (LCA) procedures according to requirements in ISO 14040. The presentation will show the relations between these standards and requirements. It will further demonstrate how they can be used by companies in a systematised way and this will be demonstrated by case studies from Norway.

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Green Technologies for Utilization of Marine Chemical Resources

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Sea water is a raw resource for solar sea-salt production. The remains waste brines are a very valuable resource rich in Mg^{2+} , Na^+ , K^+ , Cl^- and SO_4^{2-} as major components, as well as a big variety of minor and trace elements. Besides, they are rich in specific types of marine microflora and microfauna.

Theoretical considerations and experimental data were used as a basis for the development of green technologies for complex utilization of marine chemical resources, for inorganic salts and for cosmetics production. The scheme includes preparation of market oriented products with different purities: (i) inorganic salts, sodium salts ($NaCl$ and $Na_2SO_4 \cdot 10H_2O$), magnesium salts ($MgCO_3 \cdot 3H_2O$, $Mg(OH)_2$, MgO , $4MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$), calcium salts ($CaSO_4 \cdot 2H_2O$ and $CaCO_3$) and potassium salt (KCl); and (ii) *cosmetics products* for talassotherapy and aromatherapy. The last ones have a rich mineral and biological composition: physiologically important minerals, microelements and traces characteristic of sea water as well as colloids, microalgae, microflora and microfauna specific for Pomorie and Burgas salt lakes of Bulgaria. All processes are optimized and a pilot-plant testing of the technologies developed has been performed. The final products are fully characterized with a view to meeting EU requirements.

The products are intended for different sectors (industry, stock-farming, agriculture, SPA and Wellness centers, tourism, etc.) of the Bulgarian economy. Thus a new scheme of sustainable management of this Bulgarian industrial sector was proposed.

Acknowledgements:

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Plant Biosphere- a New Source for Rhenium Recovery from Soils and Waters

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Rhenium is one of the rarest elements in the earth's crust (its occurrence amounts to 7×10^{-8} %). The average rhenium content in its main carrier minerals is as follows: pyrite 0.3 g/t, chalcopyrite 0.6 g/t, molybdenite 114 g/t [1]. Re is recovered as a byproduct from copper-molybdenum and copper concentrates. The existing technologies for enrichment of rhenium-containing ores and its extraction from concentrates are ineffective. In these processes part of Re is lost in the environment (soils and waters) through emission of volatile Re_2O_7 and waste industrial solutions (ReO_4^-). It is known that Re is accumulated in green parts of plants in concentration exceeding many times its natural or background occurrence [2]. This property of Re can be used for developing a method for its extraction from soils and waters.

For choose the best plant biocollector for Re we determined its content in some plants growing in ore- dressing regions Asarel and Medet. The results show that the content of Re in leaves of birch, acacia, *Arctostaphylos* and pine exceeds its natural occurrence from 134 (birch and pine- tree) up to 2100 times (*Arctostaphylos*). The leaves of acacia and *Arctostaphylos* show the best capacity for Re accumulation. We found that the Re content in green and dry leaves from same plants is equal. This is a new knowledge and evidences that the dry leaves can be also used as a source of Re. We determinate the content of Re in water of river Maresh flowing out from mine Asarel and in plants growing around the river bed. We found that concentration of Re in this plants (1,400 ng/g) exceeds the water background (70 ng/ml) up to 20 times. This fact can be used for Re recovery from polluted waters. The green mass of plants could be harvested, green and dry leaves collected and than incinerated to concentrate the rhenium.

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Study of Rhenium Extraction from Plants by Incineration

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It is known that rhenium is accumulated in green parts of plants growing in regions of ore dressing and metallurgical processing in concentration exceeding many times its natural or background occurrence (1). This property of Re can be used for developing a method for its extraction from contaminated soils and waters.

The present study shows some results for rhenium extraction from plants by incineration. Experiments were carried out with plant sample with known Re content (2). The effect of temperature on ashing of leaves is studied in temperature interval from 310-520°C. The following results are obtained for Re extraction from leaves by ashing at different temperatures: a) 310°C-33.6 % Re; b) 400-410°C-66.8 % Re; c) 420-490°C-100% Re; d) 520°C- 86 % Re. The observed lower extraction of rhenium in temperature range 310-410°C could be explained with incomplete ashing of the plant material (presence of carbon). The occurrence of competitive reduction initiated by carbon is also very likely. Lower content of Re at temperatures above 520°C can be explained with losses of volatile Re_2O_7 . Experiments are carried out to select the best agent for Re extraction from the ash with different solutions, namely: 1 M and 2 M NaOH, 6.5 % NH_4OH , 96% ethanol and hot distilled H_2O . The results obtained indicate that Re is quantitatively extracted (100% recovery) from the ash with hot solutions of 1-2 M NaOH and 6.5 % solution of NH_4OH (both cold and hot). Hot distilled water and ethanol extract about 50 % of Re from the ash.

The results show that the quantitative extraction of Re from plants could be done by incineration of plant mass at temperature range- 420-490°C, followed by extraction of Re from ash by NH_4OH or NaOH solutions.

The authors appreciate the financial support of the Bulgarian Ministry of Education and Science, Project TK- X- 1602/06

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Evaluation of Hydrogen Separation Methods

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Hydrogen is forecast to become a major source of energy in the future, thus offering a potentially non-polluting, inexhaustible, efficient, and cost-attractive energy carrier.

In the last 10 years, the defining issues with respect to H₂ economics have changed dramatically. However, refineries now have become net consumers of H₂ in an effort to reduce pollution and meet environmental regulations [1].

The aim of this paper is to establish the efficiency of hydrogen separation methods in order to use the H₂ as an energy carrier or fuel offering significant reduction in the emissions of NO_x, hydrocarbons, CO, and CO₂, that is, assuming H₂ can be produced by environmentally benign means and that air is not used as the source of O₂ [2]. Molecular hydrogen is a clean burning fuel. It can be stored as a solid (in the form of hydrides), liquid, or gas. Future methods for producing H₂ could emerge based on the selective oxidation of natural gas exclusively to CO and H₂. While there are secondary issues of storage, separation, and systems integration, catalysis will play an important role in photolytic and electrolytic H₂ generation technologies [3].

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Hydriding Kinetics of the Composites 85 wt.% Mg - 15 wt.% Mg₂Ni_{1-x}Co_x Obtained by Ball Milling

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The absorption - desorption properties of the nanocomposites 85 wt.% Mg - 15 wt.% Mg₂Ni_{1-x}Co_x (x = 0.1, 0.2 and 0.3) prepared by ball milling in inert atmosphere are studied. Hydriding proceeded at T = 573, 473, 423, 373 K and P = 1 MPa, while dehydriding was studied at T = 573 K and P = 0.15 MPa. A significant improvement of the hydriding kinetics of magnesium for all composites was established. The hydrogen absorption rate being 1.36 wt.% H/min, 1.33 wt.% H/min and 1.04 wt.% H/min, for samples with x = 0.1, 0.2 and 0.3, respectively. The values of the absorption capacity (5.5 wt. % - 6.6 wt. % H₂) at T = 573 K and P = 1 MPa remained high with lowering of the hydriding temperature. It was established that the composite 85 wt. % Mg - 15wt. % Mg₂Ni_{0.8}Co_{0.2} preserved its absorption capacity even after 70 absorption -desorption cycles at T = 573 K and P = 1 MPa. The promising absorption - desorption characteristics of the nanocomposites investigated were explained by the catalytic action of the intermetallics Mg₂Ni_{1-x}Co_x, the presence of superparamagnetic Ni and Co particles on the sample surface and the effect of mechanical alloying.

Pyrolysis of Biomass for Hydrogen Production

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Biomass processing is a new technology within the area of renewable energies. Current energy supplies in the world are dominated by fossil fuels (some 80% of the total use of over 400EJ per year). Nevertheless, about 10-15% of this demand is covered by biomass resources, making biomass by far the most important renewable energy source used to date. On average, in the industrialized countries biomass contributes some 9-13% to the total energy supplies, but in developing countries the proportion is as high as a fifth to one third. In quite a number of countries biomass covers even over 50 to 90% of the total energy demand. Classic application of biomass combustion is heat production for domestic applications. A key issue for bio-energy is that its use should be modernized to fit into a sustainable development path. Especially promising are the production of electricity via advanced conversion concepts (i.e. gasification and state-of-the-art combustion and co-firing) and modern biomass derived fuels like methanol, hydrogen and ethanol from ligno-cellulosic biomass, which can reach competitive cost levels within 1-2 decades (partly depending on price developments with petroleum).

Key words: *pyrolysis, PSA process, crops.*

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Recovery and Purification of Hydrogen Using PSA Technology

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The PSA process is based on the principle that adsorbents are capable of adsorbing more impurities at a higher gas-phase partial pressure than at a lower partial pressure. The impurities are adsorbed in a fixed-bed adsorber at high pressure and then rejected as the system pressure “swings” to a lower level. Hydrogen is essentially not adsorbed. The ability to completely adsorb impurities allows the production of a hydrogen product with very high (> 99.9 vol-%) purity[1].

A complete pressure-swing PSA cycle consists of the following five basic steps:

Adsorption, Cocurrent depressurization, Countercurrent depressurization, Purge at low pressure, Repressurisation.

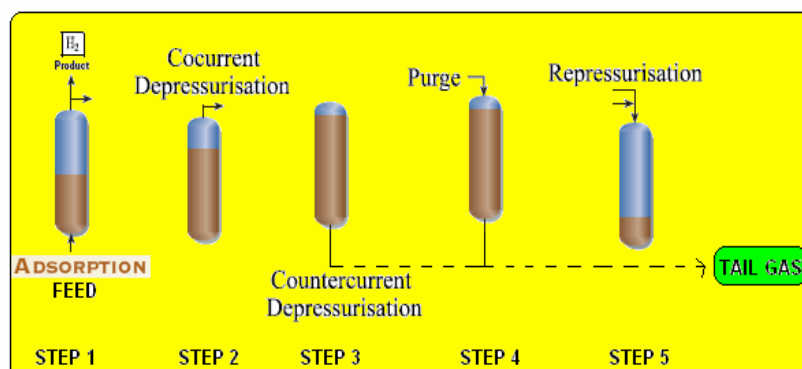


Fig. The steps of a PSA cycle

Process Parameters

The following process parameters influence the design and performance of a PSA unit[2]: Feed and offgas pressure, Feed gas composition, Required product purity.

Key words: *PSA process, recovery, purification*

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Activated Carbons Produced by Biomass Gasification Used as Eco-materials

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The activated carbons could be used as ecomaterials in the environmental purification process. They are used in the purification of polluted water and air. The source of activated carbons material can be the biomass, wich can be a several carbonaceous materials, e.g. nutshells, wood. In this paper we used the gaseification process for the production of activated carbons from biomass. For the production and processing techniques of this “eco-materials” we put accent on three aspects: nature and type of raw material available; desired physical form of the activated carbon; characteristics required for the intended application. We present a type of activated carbon wich was obtined in our Research Institute, and that has a great capacity of adsorption. The gaseification process was carried out at temperatures of 600 - 800°C in the presence of steam, wich was activated agent. There was obtained activated carbon that has a great capacity of adsorption for volatiles organics compounds. The capacity rate adsorption on activated carbon for volatiles organics compounds was determined to be between 0.04 µg/L and 0.11 µg/L.

Key words: *activated carbon, gazeification, VOC.*

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Synthesis of Oxalate-Based Active Materials Using an Ecological Technology

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The active materials are needed for development of electronics, photonics and adsorption catalysis. There is a great interest in ZnO due to its semiconducting, adsorption, catalytic and photocatalytic properties as well as the possibility to modify them using preparation methods and/or impurity additions. That determines its various applications: in solar cells, luminescent devices and chemical sensors as well as its use as catalyst and photocatalyst.

The preparation of ZnO from nitrates is accompanied by evolution of NO_x –containing gases, which necessitates the application of a special device neutralizing them. The use of catalysts with a high percentage of transition metals is also needed.

During the recent years the utilization of the sparingly soluble zinc oxalate as precursor for the preparation of ZnO, increased. One of the advantages is the possibility to use nanosized precursor. A method was developed for the preparation of doped, catalytically active ZnO by cocrystallization of Mn in ZnC₂O₄·2H₂O. The Zn-Mn precursor investigated in this work was synthesized from solutions of ZnSO₄ and K₂C₂O₄ with a Zn²⁺:C₂O₄²⁻ ratio of 1:1 and 1:2. The Mn concentration in ZnO was of the order of 0.51–15.11·10⁻² %. The samples obtained were characterized by BET, XRD, XPS, EPR, SEM and catalytic measurements.

Our method has two chief advantages: (i) No NO_x containing gases are evolved, and (ii) the catalysts obtained are highly active in the presence of low transition element (Mn) content.

Destructive Removal of Chlorinated VOCs over Mixed PMoV Heteropoly Compounds with Keggin Structure Supported on TiO₂ Carrier

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Chlorinated volatile organic compounds (VOCs) are often emitted to the atmosphere in a mixture with other non-chlorinated VOCs or carbon monoxide. For this reason, the catalytic oxidation seems to be an efficient and economic method of such emission control. In this context, the utility of heteropoly compounds as catalysts for redox and acid-catalyzed reactions has stimulated considerable interest in these compounds for destructive removal of VOCs. In the present work we attempted to evaluate the relation between the acid and redox properties and catalytic activity of TiO₂ – supported mixed PMoV heteropoly compounds with Keggin structure in the reaction of total oxidation of chlorobenzene. The effect of the temperature treatment and the number of V atoms on the surface and catalytic properties of the catalysts was studied. The acidic and reductive properties of the samples were characterized by temperature-programmed desorption (TPD) of ammonia and temperature-programmed reduction (TPR), respectively.

The results demonstrated that the introduction of vanadium atoms leads to increasing the catalytic activity; the catalysts with higher number of vanadium atoms are more active. The catalysts calcined at higher temperature showed higher conversions. It was observed that for low-temperature treated samples the introduction of V leads to increasing the total acidity of the catalysts. The increase of the temperature treatment from 523 to 723 K causes a decrease of the acidic properties. The TPR profiles of the catalysts showed that the reduction of octahedral coordinated Mo⁶⁺ of polymolybdates to a lower valence state is the easiest for the V-free sample. Increasing the temperature treatment leads to decrease of the oxidation state of molybdenum in the sample without V. It was concluded that the chlorobenzene conversions of the heteropoly catalysts depends on their acidic and redox properties.

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Synthesis and structural characterization of xanthate (KEX) in sight of their utilization in the processes of sulphides flotation

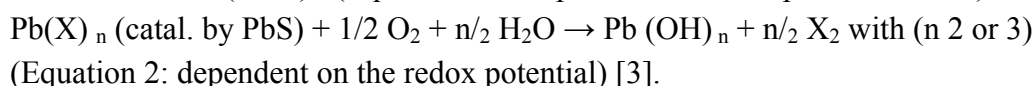
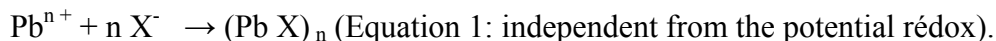
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A lot of industries (chemical, mining,) developed numerous processes based on the use of the **adsorption**, what means in big part a good mastery of the superficial ability to react of the used solids. From then on, the resolution of practice problems pass inevitably by the understanding of fundamental concepts governing the phenomena of **flotation** and the interaction in the solid- liquid or solid - gas interface [1]. In this study, we suggest proceeding to a theoretical and experimental study concerning the organic **synthesis** of an **organo metallic** product (**KEX**) by intermittent method and their use in the processes of sulphides flotation [2].

Searches showed that the surface state after grinding resulted from a combination of oxidized sorts of sulfur treat type with copper sulphate and lead oxy-hydroxide thickness of which is very superior to 200 nm. The addition of an organometallic molecule sulphurated (**Potassium ethyl xanthate KEX**) in available concentrations of 1g/l (6, 24.10⁻³ M) is going to lead the forming of an organometallic layer mixed in the **galena** surface. From weak concentrations in collector, the organometallic layer present in the mineral surface is mixed. It is formed by a complex xanthate type of lead (PbX, bandages IR in 1200 cm⁻¹), of dixanthogene (X₂ forms oxidized with the molecule of xanthate, bandages IR in 1262 cm⁻¹), of elementary sulfur and a certain proportion of initial superficial oxidized phases. The mechanism leading to the forming of PbX is the type of ionic exchanges. On the other hand, two types of different mechanisms can be at the origin of dixanthogene forming (X₂).

A first type consists of a **catalytic oxidation** in the mineral surface with reduction of the dissolved oxygen. This type of mechanism depends essentially on the potential redox of the system. A second type brings in the forming of xanthate salts of lead by a **mechanism** of Ionic exchange (eq. 1) then their catalytic degradation (eq. 2):



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An Outlook of a Romanian Green Technology for Multipurpose Carbon Materials

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The elaboration of green technologies having a strong influence on sustainable development represents a priority in this moment for Romania in the new context of being a member state of the EU. For short and medium term outlook 2008-2012 we must elaborate scenarios of: (1) GHG emission evolution; (2) preserving of water natural resources by rising the waters reuse and pre-treat prior to discharge into natural rivers; (3) natural resources preservation by wastes reuse as alternative raw materials.

The multipurpose carbon materials (MCM) manufacture represents a stringent necessity demanded by the concern for the environmental protection, having in view the alignment of our country to the environmental standards of the EU and a series of other economical applications. Over 80% of the dangerous poisonous substances emphasized on the lists of the EU “Dangerous Substance Discharges Directive” 976/464/EEC and 86/280/EEC are adsorbed on activated carbons as are MCM, the weight of liquid-phase applications representing almost 75%. The paper results are focused on MCM manufacturing from renewable raw materials and of selective purification on MCM filters of volatile organic compounds (VOC), soluble organics and heavy metals from waste waters.

The paper reveals the novelty and complex character of the green technology presented with positive impact on the environmental protection:

1. the utilization of alternative raw materials by recycling of vegetal origin wastes from industrial and agricultural processing, (coated chip/particleboard wastes, hard & soft lignocellulosic materials from natural fibres processing industry, wood waste from wood processing and furniture industrial facilities, agricultural by products that are not used in other purposes) as precious alternative renewable raw materials, instead of wood and fossil fuels, within the process of MCM manufacturing;
2. the development of a green technology, by applying a method which uses burned gases resulting from the combustion of exhausted volatile matter (tar vapours, pyrogenetic water vapours, aromatic hydrocarbons, acetone, methanol, acetic acid, fuel gas, etc.) as energy supplement and physical activation agents providing for

processes of conversion into charcoal and activation, the excess to heat up water and preheat air for the combustion chamber;

within an equipment:

- which is simplified, excluding the cooling, condensing, separation and purification operations of water;
 - which does not generate other waste amounts;
 - the gases exhausted through the chimneys into the atmosphere do not contain compounds at harmful concentrations, the respective concentrations (CO_2 below 2%, NO_x below 400 mg/m^3 , and SO_x below 8 mg/m^3) being within admissible limits provided in the Romanian legislation complying with EU legislation.
3. the creation of a new environmental friendly product - the modular MCM filters - with porosimetric and adsorption characteristics, which are similar or superior to some commercial activated carbons (obtained from wood, coconut), the specific surface area amounting to $800 \text{ m}^2/\text{g}$ for the granular type and the average radius of open pores approx. $6\text{-}9 \text{ \AA}$, allowing to be used to remove pollutants from liquid and gas streams, determine by the various environmental regulations as the Clean Water and Clean Air Acts, a major impact on the market.

The results will lead to the elaboration of a business plan concerning replication on industrial scale of a multipurpose green installation that could process for Romania (and maybe, for regional level) the whole potential of available renewable raw materials, with a major impact on sustainable development in the area.

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Surface-Treated Activated Carbons for Purification of Natural Waters from Ammonium Ions

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The extent of environmental pollution is increased by industrial development. Activated carbons are successfully applied for the purification of potable and waste water. Thanks to their highly developed porous structure and large specific surface area they exhibit a considerable adsorption capacity towards various pollutants, both organic and inorganic. Ammonia is found in nature and also produced by a number of human activities. The presence of ammonia in water is undesirable because ultimately it gets converted into nitrites and nitrates. There are different methods for removing ammonium ions from waste waters, one of them being based on adsorption. Surface-treated carbons belong to the most promising adsorbents. Our work is aimed at comparing the efficiency of model solutions of different kinds of carbons selectively oxidized with various oxidants depending on their porous texture and on the oxidation method.

Four kinds of carbons of different origins were used. The oxidants used were concentrated nitric acid, 30% H₂O₂ and moist air at different temperatures for different time intervals. The adsorption-texture parameters of the carbons were determined on the basis of their adsorption isotherms (N₂, 77.4 K). The chemical nature of the oxidized carbon surface was characterized by establishing the isoelectric point and the surface oxygen groups which were determined by the usual methods. The sorbents effectivity in the process of elimination of ammonium pollutants was determined with the use of model solutions containing ammonia (170 –1400 ppm). The ammonia concentration was determined spectrophotometrically by the Berhelot reaction. Our investigations on the removal of ammonium pollutants showed the highest efficiency with activated carbon from cherry stones. Among the oxidation methods the best results were demonstrated by the method using oxidation with concentrated nitric acid at room temperature.

The Performance of NO_x Storage-Reduction Catalyst Containing Ag

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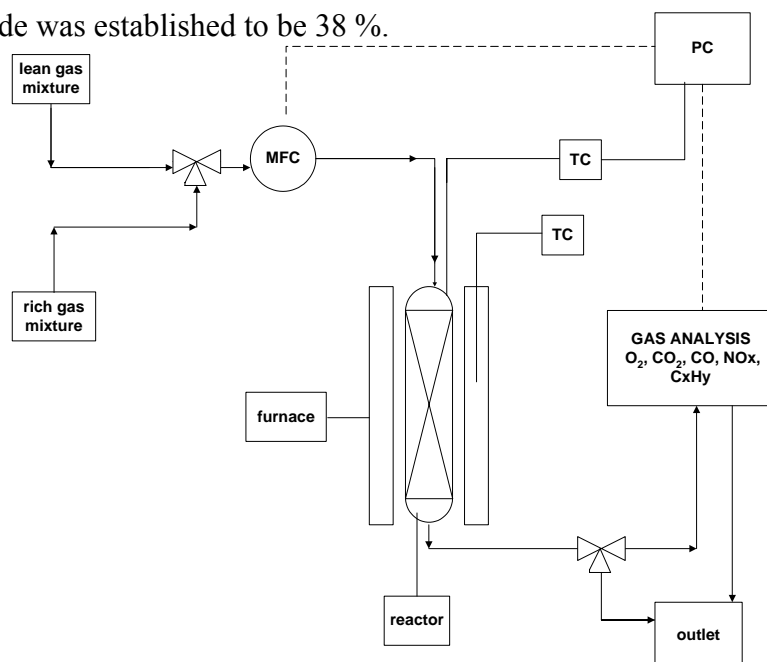
One of the most perspective methods for neutralization of nitrogen oxides in the lean-burn engines is based on the concept of the storage catalysts, containing noble metal, BaO and Al₂O₃. The NO_x in lean burn conditions store on the surface of alkali or alkali-earth oxides, supported on inert carrier, followed by reduction process on the noble metal sites. Serious problem hindering the practical application of the storage catalysts is their weak resistance to the presence of sulphur compounds in the fuel. The challenge is to find a catalyst system which gives a high conversion of NO_x to N₂ under lean conditions and is not severely deactivated by poisons in the exhaust.

The aim of the present work is to explore the possibility to use Ag/Ba/Al₂O₃ system as a storage catalyst in the reduction of nitrogen oxides in oscillating conditions regarding the inlet gas composition

Flow reactor experiments were used to study the activity of NO_x storage/release on a Ag/BaO/ Al₂O₃ catalyst. For that purpose a pulsed-flow reactor shown in Fig.1 is assembled.

The conditions of the operation cycles were chosen on the basis of data from the literature and to be near to the real practical behavior of the lean-burn engine.

In lean-burn conditions the part of the adsorbed nitrogen oxides were 86 % from the total NO_x, introduced to the catalytic reactor. At these conditions the part of the reduced nitrogen oxide was established to be 38 %.



Topic F

Advanced Laser Materials for Ecology

Advanced Laser Materials for Application in Ecology: Global H₂O and CO₂ Detection by Lidar

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It is planned to measure water vapour and carbon dioxide in the atmosphere globally by satellite based laser radar or Lidar systems to improve weather forecast and climate models. Several new Nd-doped materials have been characterized and diode pumped Nd:GSAG and Nd:YGG lasers emitting H₂O absorption wavelengths at 935 or 942 nm have been realized for water vapour detection. The required output energies have been achieved using novel highly efficient diode pump sources. CO₂ detection is possible at wavelengths at about 1600nm which can be generated by Stimulated Raman Scattering. 70 crystals have been investigated producing coherent emission with less than 2nm spacing in the visible and near infrared spectral regions so that the required wavelengths are covered.

Theoretical Study of Sm(III), Eu(III) and Tb(III) Complexes Used as Advanced Laser Materials

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Lanthanide complexes have attracted much attention because of their potential application to a wide range of processes and new technologies as advanced laser materials. Understanding the structure-property relationship and elucidation of the lanthanide(III)-ligand bonding type represent a challenging task for applications as nuclear waste separation and design of new luminescence materials. A series of Ln(III) complexes (Ln(III) = Sm(III), Eu(III) and Tb(III)) with coumarin-3-carboxylic acid (*cca*) has been investigated by hybrid density functional, B3LYP, calculations coupled with Relativistic Effective Core Potentials (RECP). The adequacy of the B3LYP approach was confirmed for the $\text{Eu}(\text{cca})^{2+}$ model by reference MP2 and CCSD(T) computations. The strength and the character of the Ln(III)-*cca* bidentate bonding was characterized by calculated Ln-O bond lengths, binding energies, ligand deformation energies, energy partitioning analysis and σ -donation contributions to the donor-acceptor interaction. A detailed analysis of the electron density has been performed using natural population and charge decomposition analyses. The effects of solvent interaction on geometries and stabilities of the Ln(III) structures were computed using a combination of both a water clusters approach and additional continuum solvation calculations. The Ln-O distances become smaller and Ln(III)-*cca* interactions increase with the decrease of the Ln(III) ion size. The calculations indicated that the increasing strength of covalent interaction is consistent with enhancing lanthanide luminescence in the order $\text{Ln}(\text{cca})_2(\text{H}_2\text{O})_2\text{Cl} < \text{Ln}(\text{cca})(\text{H}_2\text{O})_2\text{Cl}_2 < \text{Ln}(\text{cca})_3$. The anionic effect on luminescence of $\text{Tb}(\text{cca})_2(\text{H}_2\text{O})\text{Cl}$ and $\text{Tb}(\text{cca})_2(\text{H}_2\text{O})(\text{NO}_3)$ was explained with the stability of the complexes in solution. The population analysis suggested that charge transfer is realized mainly from the carboxylic oxygen atom to Ln(III). The result obtained is in line with HOMO of the Ln(III) complexes studied, which consists of in-plane orbital contribution of the carboxylic oxygens.

Physicochemical Conditions of $\text{Al}_{2-x}\text{Me}_x(\text{WO}_4)_3$ Single Crystal Growth (Me =Sc, Y, Ga and In)

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Poly- and single crystals solid solutions based on $\text{Al}_2(\text{WO}_4)_3$, are materials with various potential applications. Such materials are suitable for chemical sensors and electrochemical energy cells, due to the comparatively easy mobility of Al^{3+} ion. These materials could be used in the field of the special ceramics, due to the low thermal expansion. Besides Al^{3+} could be relatively easy replaced by Me^{3+} ions of 3d-elements (Cr,Ti), so the single crystals in these cases are suitable for matrix of solid state tunable laser elements, applied in the modern medical diagnostics and treatment; in the device production and also in the ecology monitoring.

The main purpose of the presented investigation has been to clarify the conditions of growth of single crystals by the mentioned solid solutions, as a base for further detailed study of their properties and possible applications.

In the first stage the conditions for growth of pure single crystal $\text{Al}_2(\text{WO}_4)_3$ have been studied by the “ flux “ method, from nine different solvents of the systems $\text{Na}_2\text{O}-\text{WO}_3$ and $\text{Li}_2\text{O}-\text{WO}_3$. Analyses of the results show that the most suitable solvent for growth of single crystals is the solvent with the following mole ratio: 27,5 Na_2O -72,5 WO_3 . Its main advantages are: wide concentration range of crystallization (from 57 to 35 weight %); wide temperature range (from 1060 °C to 905 °C); suitable super-saturation (0.22 g/ °C per 100g solution); low viscosity (below 20 cP); negligible weight losses due to evaporation (less than 3 mg /h); quick homogenization (less than 3 h under 30°C over the crystallization temperature).

In the second stage the conditions for growth of single crystals from solid solutions in different levels of Al^{3+} replaced by Sc, Y, Ga and In have been studied, using the already chosen solvent: 27,5 Na_2O -72,5 WO_3 (molar %).

As a result of the investigation the following parameters have been determined: temperature and concentration ranges of solid solutions crystallization, areas of existing of solid solutions, as well as distribution coefficient of the substituting ions in the system solution-crystal. The structure of the single crystals has been proved to be as $\text{Sc}_2(\text{WO}_4)_3$ -type structure and the exact chemical composition has been determined by EPMA analyses.

New Double Tungstate Crystal for Broadband Laser Applications

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The results of the present investigation show that single crystals of the tungstate of sodium and aluminum, $\text{NaAl}(\text{WO}_4)_2$, synthesized recently, can be grown successfully from nonstoichiometric high-temperature solutions of the binary oxides forming it. The solutions are characterized by extremely low (about 700°C) saturation temperatures, low viscosity and absence of evaporation and creeping of the solution at growth temperatures. The substance has no polymorphic transitions which would make the preparation of single crystals difficult. It may successfully be doped with Cr^{3+} , the distribution coefficient of chromium between the crystals and the solution being sufficiently high to permit single crystals with the desired concentration of dopant to be grown. The only serious problem during the growth of $\text{NaAl}(\text{WO}_4)_2$ crystals from their own nonstoichiometric high-temperature solutions is the great difference between the growth rates in the different directions, which may lead to appearance of defects. Special temperature gradients have to be done for avoiding these defects.

The present studies on the optical properties of the new single crystalline material $\text{Cr}^{3+}:\text{NaAl}(\text{WO}_4)_2$ show that it possesses a high value of the absorption cross-section in a region suitable for efficient pumping with laser diodes. In spite of the intermediate crystal field ($Dq/B \sim 2.51$), a broad band of luminescence centered at about 815 nm with FWHM of about 200 nm is observed at room temperature. The Cr^{3+} emission lifetime has a value of 50 μs at room temperature for activator contents up to 2.17 at.% of the Cr^{3+} content $\text{NaAl}(\text{WO}_4)_2$. No concentration dependence of the lifetime being observed. These properties and the technological convenience of the crystal growth method used (low growth temperature, high growth rate, high distribution coefficient value) make $\text{Cr}^{3+}:\text{NaAl}(\text{WO}_4)_2$ a promising material for laser applications.

Physicochemical Properties of Pure and Doped $\text{Na}_2\text{Al}_2\text{O}(\text{BO}_3)_2$ Single Crystals by High Temperature Solutions

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Oxide materials of the borate group have been the subject of increasing interest during the past years. This interest is due, above all, to the excellent nonlinear optical (NLO) and/or lasing properties of the crystals of some borates. The concentration and temperature regions of formation of crystals from different phases in the ternary system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ were determined. In the above system, the crystallization regions of Al_2O_3 , NaBO_2 , NaAlO_2 and the double oxyborate $\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$ ($\text{Na}_2\text{Al}_2(\text{BO}_3)_2\text{O}$) were determined. As $\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$ was found to melt incongruently at 970 ± 3 C, this made the high-temperature solution growth method most appropriate for obtaining its single crystals. The width of the crystallization regions of the oxyborate $\text{Na}_2\text{Al}_2\text{O}(\text{BO}_3)_2$ and the supersaturation degree of its solutions in different high-temperature solvents of the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ have been determined. On the basis of comparison, the most suitable solvent for the growth of single crystals of this oxyborate has been found to be NaBO_2 . Studies have been performed on the solubility of $\text{Na}_2\text{Al}_2\text{O}(\text{BO}_3)_2$ in this solvent and the dependences of the viscosity and density of the solutions on the temperature and concentration of the oxyborate present in them. On the basis of the data obtained, a composition of the initial high-temperature solution for the growth of $\text{Na}_2\text{Al}_2\text{O}(\text{BO}_3)_2$ single crystals is proposed. The validity of this choice has been demonstrated by the growth of a single crystal on a seed using the top seeded solution growth (TSSG) technique and slow cooling of the solution. Recommendations have been made concerning the improvement of the growth process with a view to obtaining better quality crystals. In addition $\text{Na}_2\text{Al}_2\text{O}(\text{BO}_3)_2$ single crystals were doped with 3d-elements (Cr or Ti). The absorption spectra of the crystals were measured and discussed.

Powder XRD Characterization of $\text{Al}_{2-x}\text{In}_x(\text{WO}_3)_4$ Crystals

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Mixed tungstates of trivalent metals are interesting materials with multipurpose applications. They can be used as tunable laser media, special ceramics and ionic conductors [1-6]. Single crystals of $\text{Al}_{2-x}\text{In}_x(\text{WO}_3)_4$, ($0 < x < 2$) were grown by flux method from high temperature solutions in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{In}_2\text{O}_3-\text{WO}_3$, where the solvent is 27.5 mole % Na_2O and 72.5 mole % WO_3 .

The aim of the present work is powder XRD characterization of the crystals obtained for studying the solid solution concentration limits as well as the effective distribution coefficient e.g. correlation between the composition of the crystal and the corresponding solution.

Powder XRD data were collected on Bruker D8 Advance diffractometer with $\text{CuK}\alpha$ radiation and SolX detector.

The behavior of the unit cell parameters with solution composition shows strong deviation from linearity. A positive effective distribution coefficient has been obtained. The composition of the crystals obtained by the unit cell evaluation corresponds to the composition obtained by the EDAX microprobe analyses.

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