Symposium A Advanced Materials: *From Fundamentals to Applications*

INVITED LECTURES





- 1. Potassium hydroxide
- 4. Sodium hydroxide
- 7. Calcium hydroxide
- 10. Calcium nitrate
- 13. Barium carbonate
- 16. Barium chloride
- 19. Aluminium chloride
- 22. Potassium silicate
- 25. Silicon fluoride

- 2. Potassium hydride
- 5. Sodium hydride
- 8. Calcium carbonate
- 11. Calcium chloride
- 14. Barium sulphate
- 17. Aluminium sulphate
- 20. Alum
- 23. Potassium calcium silicate
- 26. Ammonium potassium
 - compound

- 3. Potassium carbonate
- 6. Sodium carbonate
- 9. Calcium sulphate
- 12. Barium hydroxide
- 15. Barium nitrate
- 18. Aluminium nitrate
- 21. Potassium silicate
- 24. Potassium barium silicate
- 27. Ethylene chloride

Chemical symbols used by Dalton, 19th century

Binuclear Complexes as Tectons in Designing Supramolecular Solid-State Architectures

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We are currently developing a research project on the use of homo- and heterobinuclear complexes as building-blocks in designing both oligonuclear species and high-dimensionality coordination polymers with interesting magnetic properties. The building-blocks are stable binuclear complexes, where the metal ions are held together by compartmental ligands, or alkoxo-bridged copper(II) complexes. The binuclear nodes are connected through appropriate *exo*-bidentate ligands, or through metal-containing anions (e. g. $[Cr(NH_3)_2(NCS)_4]^{-}$, $[M(CN)_6]^{3-}$, $M = Fe^{III}$, Cr^{III}). A rich variety of 3d-3d and 3d-4f heterometallic complexes, with interesting architectures and topologies of the spin carriers, has been obtained¹.

A particular case is the one concerning the 3d-4f binuclear nodes. The building principle is based on the employment of symmetrical (dicarboxylato anions, bis(4-pyridyl) derivatives) or of unsymmetrical spacers (e. g. the isonicotinate anion), which act selectively with the different (3d, 4f) metal ions.

Following this strategy we were able to obtain coordination polymers containing three different spin carriers (2p-3d-4f; 3d-3d'-4f). The magnetic properties of the newly synthesized compounds have been investigated and will be discussed.

Acknowledgements

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Interphase in Fiber Reinforced Composites: Characterization and Design

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The properties of fiber reinforced composite materials largely depend on the nature and properties of interphase region. Interfacial phenomena control stress transfer to, and distribution between, the fibers and also govern mechanisms of damage accumulation and propagation. Recently the interphase is treated as a three-dimensional entity, extending further than the atomic dimensions of the boundary.

The existence of an interphase, whose properties are different from those of the bulk matrix, is related to several factors, such as: specific adsorption and wetting behavior of fibers, chemical and physical interactions between the matrix and the fiber, specific polymer morphology and an existence of transcrystalline interface (in semicrystalline thermoplastic composites), etc. The nature and properties of the interface are unique to each fiber/matrix system, however, certain common features apply, and will be discussed in this paper. Interfacial analysis encompasses both chemical and mechanical characterization of the interfacial region. Different approaches to the characterization are developed, involving wetting studies, surface spectroscopies, microthermal analysis, differntial csanning calorimetry, atomic force microscopy, micromechanical tests, etc., in an attempt to describe and optimize the boundary region. However, the question of interfacial optimization is a complex one without simple answers, owing to the complexity of the chemical and physical nature of the interface and the variety of roles it is called on to perform.

The possibilities of controlling interfacial strength by means of target-oriented variation of strength, structure and thickness of the interphase, created between differently treated (sized, plasma treated, untreated) glass and carbon fibers and thermoplastic and thermoset matrices, are discussed in this paper. In order to correlate the mechanical response with the characteristics of the interface, micro- and macromechanical methods were applied to investigate glass and carbon fiber composites with thermoplastic and thermoset matrices.

New Insight into the Role of Extra-Framework Cations in Zeolite Materials Chemistry

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An approach to preparation for a novel material is sometimes found in the developments of new structural elements, new arrangements or combinations of them, and new preparation technique as a total system. Microporous systems are becoming increasingly important as the host material for new arrangement of the guest materials. Properties of porous materials are intimately related to their framework topological features and chemical compositions. Currently, the most important porous materials are zeolites. Zeolites are micropurous aluminosilicate materials made up of (SiO₄)⁴⁻ and (AIO₄)³⁻ tetrahedral arranged in defined manner to give the material with an open framework structure of cavities and pores. Each aluminum atom in the framework carries a net negative charge which is balanced by a charge-balancing cation. Within zeolites, the cation exchange density is controlled by the framework Si/Al ratio. Presence of all these charged constituents produces a highly polar environment within the cavities of zeolites. Alumosilicate framework exerts a strong, localized electrostatic field that can alter the properties of chargebalancing cations. Therefore, the behavior of the cations inside the zeolite is often different then that of cations adsorbed, precipitated or exchanged into other porous solids. By considering cations as being located within specific sites in each or the many zeolite topologies, one can envision the oxide ions in the framework providing ligand centers which also impose some steric constraint around the cation. Thus, each zeolite offers its own unique crystal field, perhaps exerting multiple crystal field effects on different cation sites. In that manner, zeolites can serve as a host providing a high level of dispersion of cations, while offering multiple sites to environments. Being in these sites, cations are often coordinatively unsaturated. Differences in coordination around the cations in exchange sites could give to cation-zeolite system unusual and unexpected properties and shape selectivity associated with pores size.

This paper reviews the results of investigation of the influence of extra-framework cations, their nature and amounts, on different zeolite's features: magnetic and adsorption properties and the possibilities of phase transformations. Different zeolite topologies (SOD, LTA, FAU and ZSM5) with alkaline, alkaline earth, transition metal or large organic cations, were considered.

As a result of alkaline cations incorporation into low pore sized zeolite SOD, the change of magnetic properties of this structure was noticed. High temperature transformation of zeolites modified by alkaline and alkaline-earth cations were performed. The obtained new phases were investigated using XRD, NMR, IR, Raman and thermal analysis methods. The influence of the presence of extra-framework cations and included salts on the mechanism of high temperature transformation into new ceramic materials was evidenced. The adsorption and catalytic possibilities of alkaline, alkaline earth, and transition metal cation-exchanged zeolites were investigated using microcalorimetric and spectroscopic (MAS and IR) methods. The cations were recognized as active sites for adsorption and forming of carbonyl-like, nitrosyl-like and amino complexes. Quantitative and energetic aspects of these reactions were studied by means of adsorption microcalorimetry and TPD/MAS. Additionally, the specific interactions of incorporated large organic cations with external zeolite surface active sites were studied. The adsorption of insecticides and pesticides on some modified zeolite structures was found. On the others, catalytic decomposition of these organic compounds happened, indicating the possibility of usage of modified zeolites in wastewater treatment.

Tailoring the Properties of Highly Uniform Metallic Particles

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The importance of finely divided metals, ranging in size from a few nanometers to several micrometers, is now recognized in numerous technological fields. Some of these applications like electronics, catalysis, metallurgy, and pigments are already well established, employing large quantities of metal powders. Many others (medical, biological, ferromagnetic fluids, super high density magnetic storage, photonics, transparent conductive coatings, etc.) are in various stages of development and are likely to require metallic particles with very well defined and controlled properties. The presentation will review the most widely used preparation techniques to generate highly uniform simple and composite metallic particles (Au, Ag, Pd, Ag/Pd, Pt, Cu, Ni, Co, etc.) and will discuss in detail the mechanisms of their formation in homogeneous solutions. The ability to tailor the size, morphology, composition, internal structure, and surface properties of the dispersed metallic phase to specific needs by either adjusting the parameters of the precipitation process or by employing suitable coating techniques will be amply illustrated.

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The thermodynamics of the vitreous state and the kinetics of glass-formation and stabilization are considered and re-examined in the framework of a new generic theoretic approach.

It is based on the thermodynamics of irreversible processes and so developed that the thermodynamic properties of glasses can be derived in a simple, geometric representation. Frozen-in values of the configurational disorder in glasses and their correspondingly increased free energy, chemical reactivity, vapour pressure and solubility are calculated in dependence of methods of glass synthesis and especially: on the rate of change of external state parameters (temperature, pressure, magnetization etc.). The chemical constants of vitreous solid materials (carbon glass, silica, metallic glasses etc.), when participating in heterogeneous chemical reaction kinetics are determined.

Classical examples and newly obtained experimental results are reported on the employment of vitreous materials in bulk or as micro- or nano-sized precursors in the synthesis of quartz crystals from aqueous solutions, and for diamond growth from vitreous carbon via heterogeneous chemical reactions.

Possible new and unexpected applications of glasses as solids with increased reactivity in crystal synthesis, in chemical catalysis, in medical applications and in agriculture are discussed and new visions and ways of employment of glasses as a particular form of disordered solid matter are outlined.

Nanoporous Materials

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Zeolites and related porous materials are crystalline solids able to interact with guest molecules, ions and atoms not only at their surfaces but also within the bulk. Their crystal structures, comprising 3-dimensional fully cross-linked open frameworks, possess very regular (micro)porous structures having sieve-like properties on a molecular level. Zeolites are widely used in a variety of technologies as catalysts and catalyst supports in petroleum industry for various types of shapeselective conversion and separation reactions, as adsorbers and ion exchangers. They form the basis for new technologies, like energy and gas storage, waste disposal, sensors, air pollution control and numerous novel reactions, due to their unique structural and/or surface physicochemical properties. Zeolitic materials are inorganic polymers based on a 3-dimensional arrangement of TO₄ tetrahedra (SiO₄, AlO₄, PO₄, etc.) linked through their oxygen atoms thus forming large lattices. Their stable structures with ordered channels and cavities of different sizes can be used for precise separation and discrimination of molecules. The introduction of divalent transition metals into zeolite frameworks gives rise to the formation of active Brønsted and/or Lewis acid or redox centres. A control over specific pore structure and chemical composition can be achieved by using new strategies and techniques for the syntheses and contemporary characterisation methods.

The focus of our research is the synthesis and structural characterisation of new aluminosilicates, aluminophosphates and similar zeolitic materials with pore diameters of up to 2 nm, modified with low concentrations of transition metals (Mn, Fe, Co, and Zn) for oxidation reactions and alcohols-to-hydrocarbons conversions. We have concentrated on rational hydrothermal syntheses using carefully chosen organic structure-directing agents to induce both structure tailoring and particular pore geometry.

Framework structures, extra-framework cations and molecules, active metal acid centres and catalytic activities of the products are evaluated by using X-ray diffraction, thermal analyses, spectroscopic analyses (NMR, EXAFS/XANES, X-ray absorption and *in situ* IR) and test catalytic reactions. Emphasis is placed on X-ray diffraction, which has always been the basic and most useful tool for the characterisation of zeolitic materials. However, there are several features of zeolitic crystals that make unambiguous structure determinations difficult, such as the low partial site occupancies of framework metals, which cannot be definitively assigned. Combining X-ray diffraction with solid-state NMR, EXAFS/XANES and others, we get powerful tools for the comprehensive analyses of long- and short-range order of a local structure of active sites within zeolitic solids.

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We examine polymer-surfactant solutions (mainly the PEO/SDS system) as media for inorganic crystallization reactions. We use the formation of metal sulfides as a typical inorganic reaction example. A complex physicochemical behavior is observed, which can be summarized as follows:

- Crystallization of metal sulfides in polymer-surfactant solutions is strongly affected by metalsurfactant interactions.
- Metal-SDS interactions follow the series $Pb^{2+} > Cu^{2+} > Ni^{2+}$, $Co^{2+} > Cd^{2+}$.
- Lamellar M(DS)₂ crystals often compete with metal sulfides, leading to very interesting hybrid (probably metastable) structures.
- PbS creates layered structures and nanotubes. The walls of these nanotubes consist of PbS nanoparticles and alternating surfactant layers.
- For T<T_{Krafft} the "copper sulfide" system appears to favor Cu(DS)₂ while for T>T_{krafft} we observe the formation of various CuS_x phases. A copper redox equilibrium plays an important role by depleting Cu(II).
- There exist ion-polymer interactions, which may be responsible for some of the phenomena observed during the initial stages of the crystallization process.

The examples presented in this seminar illustrate the point that polymer/surfactant solutions provide a rich, interesting, and until now unexplored terrain for inorganic chemistry and materials synthesis.

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Rod-Coil Block Copolymers with Amylose via Enzymatic Polymerization

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Hybride materials have been synthesized which combine the properties of biogenic compounds (amylose) with synthetic macromolecules (silica particles or polystyrene, respectively). For this purpose the enzymatic glycogen synthesis with potato phosphorylase (E.C.2.4.1.1) could be utilized. This enzymatic process was used in vitro in a grafting from manner.

Although the resulting structures are not soluble in the primary medium of polymerization (aqueous buffer), it was shown that the enzymatic grafting from polymerization with potato phosphorylase does occur from insoluble amylose primers. Due to this advantage, both amylose-modified silica particles and polystyrene block copolymers were synthesized.

The amylose modified silica particles showed good chiral discrimination in the chromatographic separation of enantiomers. The separation efficiency can be further enhanced by the analogous polymer modification of the amylose hydroxy groups.

The synthesized amylose-block-polystyrene copolymers display the expected amphiphilic behavior as shown by dynamic light scattering. In THF solution species of different sizes become observable. These different species have been visualized by scanning force microscopy and by electron microscopy. Additional evidence comes from fluorescence correlation spectroscopy and field flow fractionation. It was also shown that the obtained micelles are not static but are in a dynamic equilibrium.

At elevated temperatures and pressures it was possible to dissolve the block copolymers in water and to obtain inverted micelles. The solutions are stable in water and THF solubility is extremely hindered due to the rigid amylose corona. The obtained inverse micelles are much more uniform than the micelles in THF which was shown by dynamic light scattering and scanning force microscopy.By variation of the block copolymer composition (utilizing dynamic light scattering and scanning force microscopy) scaling laws for the dependence of the micellar size on the degree of polymerization of amylose and polystyrene were obtained.

Chemical Solution Deposition of Pb(Zr,Ti)O₃ Thin Films

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Ferroelectric thin films have been widely studied for a range of applications such as memories, capacitors, sensors or microelectromechanical devices. In chemical solution deposition (CSD) of thin films the main processing steps include the synthesis of a heterometallic precursor, typically in a nonaqueous medium, the deposition of the film, and the processes occurring upon thermal treatment: drying, consolidation and crystallization of the target ferroelectric phase.

Understanding the structural transitions in the process of film formation from the sol would allow a better tailoring of the properties of the final product. The sols for $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT) thin films were prepared by 2-methoxyethanol-route from lead acetate, titanium n-propoxide and zirconium n-propoxide, the latter either unmodified or modified with acetic acid, and deposited on sapphire (0001) or platinized silicon substrates. The addition of the modifier evokes the crystallization of the perovskite phase in the films at a lower temperature as determined by XRD. In this work the persistence of Zr-O-Zr bonding formed in the sol is traced through the process of film synthesis by EXAFS spectroscopy. A decreased number of Zr-O-Zr links in the acetic acid modified PZT sol, compared to unmodified sol, is retained also in the amorphous film, implying a more homogeneous constituent metal distribution. The improved chemical homogeneity is reflected in the improved functional response of the acetic-acid modified PZT films.

The characteristics of ferroelectric capacitors are strongly dependent on the electrode material.

Lead zirconate titanate (PZT)-based capacitors exhibit better fatigue characteristics when in contact with conducting oxide electrodes than with platinum. $(La,Sr)CoO_3$ (LSCO) is an attractive material for oxide electrodes due to its pseudo - cubic perovskite structure with lattice parameters close to PZT and low electrical resistivity at room temperature. While there are frequent reports on physical deposition methods to prepare LSCO bottom electrodes, only a few studies on Chemical Solution Deposition of LSCO have been made.

The La_{0,5}Sr_{0,5}CoO₃ thin films were prepared from water solutions of lanthanum nitrate, strontium nitrate and cobalt nitrate with the addition of polyvinyl alcohol (PVA) to avoid wetting problems. The LSCO precursor solutions were deposited on Pt/TiO₂/SiO₂/Si substrates by spin-coating, dried and annealed in an RTA furnace between 650°C and 900°C to obtain crystalline layers. The sols for (Pb(Zr_{0.53}Ti_{0.47})O₃ (PZT 53/47) thin films were prepared by the 2-methoxyethanol based route and deposited on LSCO/Pt/TiO₂/SiO₂/Si or Pt/TiO₂/SiO₂/Si substrates, dried and annealed between 500 and 600°C.

PZT 53/47 films on LSCO/Pt electrodes crystallize in the perovskite phase at as low as 500°C. Cross section SEM shows a columnar grain structure of PZT films on fine-grained LSCO. The ferroelectric response of the heterostructures depends on the annealing temperature of the LSCO layer. The remanent polarization and coercive field of the PZT annealed at 550°C deposited on LSCO annealed at 800°C are in the range of 20 - 25 μ C cm⁻² and 80 - 120 kV/cm respectively, comparable to the values obtained for PZT films on platinized silicon substrates.

Morphometric Properties and Topological Features of Porous Solids

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The most common kind of porous materials are the ones possessing a disorder or random porous network, like silicas, aluminas, aluminophosphates, aluminosilicates etc. For such materials the N₂ adsorption-desorption isotherms at 77K are the most usual and valuable technique from which the specific surface area (S_p, m²/g), the specific pore volume V_p (cm³/g), the hydraulic mean pore diameter d_p=4V_p/S_p (nm) as well as the pore size distribution (psd) can, and are, estimated on routine base in various labs all around the globe. Unfortunately, the *morfí*, that is the form, the shape and the pattern of porosity in such porous systems seems intractable – in contrast to the ordered porous solids, i.e. zeolites and MCM for which the *morfí* is well understood and easily drawn in textbooks or scientific papers [1,2]. Nevertheless for the random porous solids, the following morphometric properties can be also calculated from N₂ adsorption – desorption data:

- The Fractal Dimensionality D of adsorption [3]. This property provides a measure of the surface topology.
- The Pore Connectivity C. The estimation of this property can take place by the method suggested by Seaton [4] but also via Monte Carlo simulations [5]. The parameter of connectivity has a paramount influence on the diffusion rate into the pores [6].
- The Lacunarity L of psd. This morphometric property can be estimated from the psd using a suitable methodology [7]. We emphasize the fact tat the properties C, D and L are interrelated.
- The tortuosity *r* of pore network. This property was recently estimated via a semi-empirical methodology [8] and is related in a rather complex way with the pore connectivity.
- The Information Entropy S₁ of the psd. This property is related to the information entropy suggested by Shannon and is related to the connectivity of the porous network [9].
- The pore Anisotropy b. This property is defined by the relation b_i=L_i/r_i where L_i, r_i the length and the radius of each group of pores i. The distribution of b_i can be found from the values of S_i (m²/g) and V_i (cm³/g) at various P/P_o of adsorption [10].

Those morphometric properties – D, C, L, τ , S_I and b – are of intensive physicochemical character and convey a health of information about the topology of porous materials. This information is extremely useful in designing adsorption, separation and catalytic operations.

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Advanced Carbon Materials for a Healthier Environment: From Fundamentals to Applications

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Introduction

It is now understood, by scientists and politicians alike, that the resolution of most practical issues requires both a <u>multi</u>disciplinary and an <u>inter</u>disciplinary approach; in a certain sense, globalization has become a mandate not only for economists and politicians, but for scientists as well. Perhaps surprisingly, much disciplinary 'inertia' remains to be overcome in many branches of science. The development of advanced carbon materials in the search for solutions to pressing environmental problems is a superb example of this challenging journey from multidisciplinarity to interdisciplinarity. Here I shall illustrate how the noninteracting 'disciplinary' circles have grown, either painstakingly or by accident, to develop the interdisciplinary interfaces (see Figure 1) that led to the key scientific advances which in turn revealed new technological options.





Figure 2 Schematic representation of key chemical features on the surface of carbon materials.

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Carbon Surface Properties

A major boost to the commercial applicability of high-surface-area carbon materials has been a consequence of a breakthrough in the understanding of their chemical surface properties and in the appreciation of their importance in both gas- and liquid-phase adsorption processes. Indeed, the term 'advanced' is applicable to those materials in which, in addition to the shape and size of particles or fibers and their pore size distribution, the quantity and the nature of the functionalities shown in Figure 2 can be tailored for specific applications. Thus, for example, the behavior of carbons as catalyst supports has been largely clarified on the basis of their amphoteric properties, with dissociated carboxyl groups giving rise to a negative surface charge and the donor/acceptor interactions of the delocalized π -electrons being responsible for the positive surface charge.

Removal of Air and Water Pollutants

Once the special amphoteric character of carbon surfaces was revealed, their tailoring for removal of specific water pollutants became a much clearer target; the goal is to maximize both dispersive and electrostatic attraction. Such optimization is also of interest in gas-phase adsorption processes, including the key environmental challenges of CO_2 sequestration and H_2 or CH_4 storage.

Selective Manipulation of Biomolecules Using Metal Oxide Nanoparticles

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A new class of functional hybrid materials is composed of specifically designed nanoparticles capable of combining the robustness and photoresponsiveness of inorganic materials with the recognition properties of biological molecules was developed. This synthesis exploits our discovery that the surface of metal oxide nanocrystalline particles differs from that of the respective bulk materials, and is characterized by a highly reactive under-coordinated surface. This can be viewed as a curse or as an opportunity. The coordination sphere of the surface metal atoms is incomplete and thus traps light-induced charges reducing their potential for useful chemistry. On the other hand, the incomplete surface exhibits high affinity for oxygen-containing ligands and gives the opportunity for their chemical modification. Oxygen rich enediol ligands form strongly coupled conjugated structures by repairing the coordination of the surface. As a consequence, the intrinsic properties of a semiconductor change and new hybrid molecular orbitals are generated by mixing the orbitals of chelating ligands and the continuum states of metal oxides. This makes the optical properties of metal oxide nanoparticles tunable throughout the entire visible region. Understanding electron tunneling in this system provides the foundation to investigate how biological redox reactions are coupled to the chemical events and molecule conformations central to catalysis, signal transduction, and energy conversion.



Figure 1. AFM image of TiO₂ nanoparticles linked to 20-base pair long DNA oligonucleotides in conjunction to photoinduced EPR spectrum obtained at 4.2 K.

The enediol ligands were found to be a conduit to bridge the electronic properties of semiconductors to attached electroactive biological moieties such as DNA. Therefore, these unique conjugate hybrid systems (TiO₂/enediol) provide means to attach selective functionalities that will lead to development of highly specialized nanometer scale sensors of nanomachines. Particularly, we have found a method to control and initiate chemical reactions in double-stranded DNA. Additionally, hole scavenging in these nanocomposites was altered in the presence of single stranded and mismatches in DNA.

Multiple Polymerization of Ethylene with Alpha Olefins a New Challenge in Polymer Science and Technology

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For more than half a century polyethylene dominates the polymer industry and research is bustling with activity. Copolymerization of ethylene with alpha olefins on transitional metal catalysts was responsible for the birth of LLDPE, the youngest member of the family. The continuous development of heterogeneous and homogeneous catalyst and more recently the latest transition metal catalyst produced an unprecedented effervescence in the field. On the other hand the type of comonomer used with its influence on polymer properties added a new dimension in the application of each discovery in this field. In a logical trend homopolymerization was followed by copolymerization and more recently by terpolymerization. Following this trend it was recently presented the copolymerization and terpolymerization of ethylene with odd carbon olefins [1]. However the latest challenge for both science and technology in the polyolefin field is the multiple polymerization of ethylene with more than two other olefins [2].

I this paper we review advances in this latest area of investigation and present new opportunities and the new challenges for polymer science and technology. These are illustrated by typical feature of microstructure, morphology and rheology of ethylene copolymers, terpolymers and multiple polymers. Some particularities in the degradation of multipolymers are related to their composition. Finally application opportunities in different fields are highlighted. Crystallinity is related to type, length and number of branches. Short term deformation follows crystallinity trends while fracture properties are related to the type, length and number of branches.

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ORAL PRESENTATIONS





Distilling apparatus from John French's *The art of distillation*, London 1651.

← Previous page: **Distillation equipment** from Greek alchemical manuscripts

Multiphase Synthesis of Phosphorus Compounds

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Starting from 1947, when Wittig and coworkers introduce the concept of phase transfer catalysis in the scientific literature, many important researches and results were communicated. Most multiphase system studies were done on liquid-liquid and liquid-solid, but also gas-liquid or liquid-liquid-solid systems were used. Because of the simple procedure, mild conditions, inexpensive and environmentally friendly reagents and the easy in scaling-up, the multiphase synthesis has become one of the most important and used methods in organic synthesis.

Few years ago, we have started the studies of multiphase synthesis of the organophosphorus compounds.

As multiphase synthesis we focus on three main directions:

- 1. synthesis of organophosphorus compounds;
- 2. synthesis of phosphorus containing polymers;
- 3. synthesis of grafted phosphorus and/or nitrogen containing polymers.

This paper concerns with the first two directions.

The first direction concerns with the synthesis of some organophosphorus compounds like mixed alkylphosphites and phosphates, mixed phosphonates, dialkyl α -hydroxyphosphonates. Two systems were generally used in such multiphase synthesis: liquid-liquid and liquid-solid. Sometimes the multiphase synthesis of such compounds seems to be not the best one, but futher researches must confirm or infirm this results. The reactions of thiophosphoryl chloride with phenols were also investigated, using both liquid-liquid and liquid-solid system, respectively. The conditions for the obtaining best yields were also studied.

The second direction concerns with the synthesis of phosphorus containing polymers, polyphosphonates and polyphosphates, respectively. As multiphase systems both interfacial liquid-liquid and gas-liquid system were used. Spectacular results were found using gas-liquid system.

Synthesis of Nanocrystalline Lead-Titanate Based Powders

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Lead-titanate powders have been synthesized by sol-gel and hydrothermal methods, in two-step process. First by controlled hydrolysis of titanium-butoxide with distilled water, and than by further reaction of the formed $Ti(OH)_4$ particles with Pb⁺² ions, in highly alkaline solution. Sol-gel synthesis has been performed at ambient pressure and temperatures up to 80°C, whereas hydrothermal synthesis has been conducted in an autoclave at temperatures up to 170°C. The assynthesized sol-gel powders are amorphous, and crystallize in the tetragonal perovskite phase after calcinations at 500°C. The calcined powders consist of very fine crystallites with the average size of about 20 nm. On the other hand, the as-synthesized powders obtained under the hydrothermal conditions are crystalline. Powders synthesized at lower temperatures, have dominant pyrochlore phase, which could be transformed to the perovskite lead-titanate only after calcinations at temperatures above 500°C. The as-synthesized powders prepared at higher temperatures consist of crystalline particles with perovskite structure. Hydrothermal lead-titanate powders are hardly agglomerated.

Single Chain Magnets

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The design of new magnetic systems in the nanometer size regime is motivated by the continuum interest in fundamental, as well in the applied aspects of nanomagnets. One of the fields developing rapidly in this area is the chemistry and physics of molecular systems with a slow relaxation of the magnetization. We reported the occurrence of a slow relaxation of the magnetization and Arrhenius behaviour of the relaxation time in an unique one-dimensional system. The system illustrate a theoretical model designed by Glauber for anisotropic Ising system and opened the perspective of a potential use of single chain magnets (SCM) for information storage. To obtain a SCM, three essential conditions need to be considered: (a) a ferro- or ferromagnetic coupling, (b) strong uniaxial anisotropy and (c) strong intra-chain and very weak inter-chain interactions are required in addition to the Ising anisotropy.

The present work outlines the use of Mn(III) complexes as rational way to introduce the microscopic anisotropy due to interplay between Jahn-Teller type manifestation, spin-orbit and exchange coupling.

The combine dc and ac measurements (including Cole-Cole diagram) performed on the polycrystalline sample emphasize the one-dimensional magnetic character, showing a slow relaxation of the magnetization. The best set of parameters obtained is τ_0 = 4.00·10⁻¹⁰s and Δ/k_B =30.5 K, where τ_0 is the preexponential factor in the thermal variation of the relaxation time described by an Arrhenius law and Δ the energy barrier to reverse the magnetization.



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Effects of Multiple Charged Nitrogen Ion Irradiation on Glassy Carbon

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Interests in carbon nitride have been encouraged since Cohen and Liu predicted a β -C₃N₄ phase harder than diamond¹. However, most of the attempts to synthesize this phase have resulted in the growth of amorphous carbon nitride (C_xN_y) with a nitrogen content far below 43 at.%, often with hydrogen atoms incorporated into the structure. There has been considerable research exploring both the film structure and properties. Essentially, the thermal properties of C_xN_y films depend on their basic structure characteristics such as bonding configuration, bonding energy and degree of cross-linking between graphitic domains. Low-energy nitrogen ion implantation of graphite² and diamond surface³, diamond-like carbon films and amorphous carbon thin films⁴ yield predominantly amorphous CxNy product,.

Our approach was to use glass-like carbon (GC) and precursor polymer carbonized at different temperatures as a target exposed to the N-ion beam irradiation in order to reveal the carbonization stage where irradiation has maximum influence to the structural and surface properties of the target material.

Four samples were chosen for the experiment: phenol-formaldehyde polymer precursor treated at 150 °C, two partially carbonized samples heated up to 500 and 700 °C as well as GC sample carbonized at 1000 °C. Samples produced at the different temperatures were exposed to N⁺, N³⁺ and N⁵⁺ ion beam irradiation, extracted from the mVINIS Ion Source of Tesla accelerator, at a dosage of 1×10^{17} cm⁻². The irradiated samples were examined using scanning electron microscopy, EDX analysis and X-ray diffraction. FTIR spectra reveille changes in the chemical composition of the surface functional groups after N-ion irradiation.

After the ion irradiation and examination, samples were carbonized in flowing nitrogen atmosphere to 1000 °C with heating rate 10 °C/h in order to produce GC. Carbonized samples were characterized by X-ray structural analysis and scanning electron microscopy. The contraction of the surface and consequent cracking was the indication that N atoms could be incorporated into the sample during irradiation. The significant increase of nitrogen content was observed only in the case of the sample pretreated at 700 °C.

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All classical explanations of polymerization propose that polymer chain propagates by addition of one by one monomer molecule (M) to a growing chain (P_n^*) (1). Kargin and Kabanov [1] noticed that there are some cases when monomer molecules are organized and exist as clusters (mM). Each cluster behaves as a single physical and chemical entity. Hence, the whole cluster is enchained at once in a single propagation step (2):

$$\mathsf{P}_{\mathsf{n}}^* + \mathsf{M} \to \mathsf{P}_{\mathsf{n}+1}^* \tag{1}$$

$$P_n^* + mM \rightarrow P_{n+m}^*$$

The fundamental difference is that the propagation is random on the molecular level in disorganized, while it is determined on the molecular level but random on the supra-molecular level in the organized systems. Hence, in the second case the both polymerization kinetics and polymer structure depend on the organization and arrangement of monomer molecules in the clusters.

Recently, a charge percolation mechanism (CPM) of olefin polymerization by supported metal complexes has been presented [2]. According to CPM, a polymer chains is formed by polymerization of regularly arranged monomer molecules. Knowing the kind of the arrangement, it is possible to predict the structure of polymer (Table 1.)

Polypropylene structure		Example 13 in [3]		Example 14 in [3]	
		Predicted	Experimental	Predicted	Experimental
		by CPM	[4]	by CPM	[4]
Isotactic bonds	mm	0.67	0.63	0.46	0.57
Atactic bonds	mr	0.16	0.20	0.25	0.23
Sydiotactic bonds	rr	0.17	0.17	0.29	0.20
Molecular mass	Mn	44121	54646	66474	95445
MWD	Mw/Mn	12.3	9.9	14.5	10.1

Table 1. Prediction of polypropylene structure by charge percolation mechanism

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Polymeric Networks *via* Metal Coordination Directed Self-Assembly Processes: Crystal Structures and Magnetic Behaviour

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Since the early works of Lehn [1] and Padersen [2], construction of coordination polymers *via* metal coordination directed self-assembly processes has attracted much attention to scientists of different areas, ranging from chemistry to material science and even biology, because of the promising applications such as bio-mimic models [3] or functional materials for catalysis, absorption, nonlinear optics, and molecular magnetic materials [4] *etc.*

Since the properties of any material are largely due to its structure, control over the structure allows us to manipulate these properties. One of the points to be seriously considered for the preparation of these systems is the selection of the appropriate ligands, an aspect that is specially relevant when specific properties have to be obtained. Dicarboxylate spacers *e.g.* terephthalate, fumarate, malonate, oxalate, or pseudohalogens like azide ligand, or neutral spacers as pyrazine, piperazine, 4,4'-bipy, 1,2-bis(pyridine)-ethane, etc., are some of the tectons used in the examples reported. The use of these ligands in association with the metal ions represents a continuous challenge in the chemistry engineering for the construction of such polymeric compounds. A large number of framework solids make use of H-bond, beside the ligand-to-metal coordinative linkage, to connect individual component. In some instances, one or more independent frameworks forming «interpenetrated nets» occupy the voids associated with one framework.In this contribution some examples will be described and discussed among the numerous compounds recently prepared [5] and structurally characterized. Particular emphasis will be focus on interpenetrated networks in the crystal structures. These studies were conducted in collaboration with Prof. N.R. Chaudhuri of the Indian Association for the Cultivation of Science, Kolkata (India).



Figure 1. An adamantane cage detected in the 3D coordination polymer [Ni(fumarate)(1,3-bis(4-pyridyl)propane)]_n

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Bismuth oxide (α -, β -, γ - and δ -Bi₂O₃ polymorphs) and the family of bismuth-containing compounds with layered perovskite structures are important materials for electronics and are frequently applied in the field of electrooptics, acustics, piezotechnics and dielectrics.

Several Bi-containing compounds were prepared by mechanochemical synthesis in a planetary ball mill and used as model systems for detailed studies of mechanochemical phenomena. Influence of the milling parameters (angular velocity, number of balls), as well as the milling medium (steel or zirconia) on the structural changes (lattice parametters, crystallite size reduction, amorphous phase fraction) occurring during mechanochemical treatment were investigated.

A series of γ -Bi₂O₃ phases doped with Fe, Pb, Si, or Zn was prepared starting from a powder mixture with a nominal composition $6Bi_2O_3 \cdot MO_x$ (or $12Bi_2O_3 \cdot Fe_2O_3$) where MO_x is PbO, SiO₂ or ZnO. The investigation of reaction kinetics and mechanism showed that $\alpha \rightarrow \gamma$ transition is fast, and involves reduction of α -Bi₂O₃ crystallite size and mechanochemical reaction. Under experimental conditions used in this study, these two processes occur simultaneously. As expected, mechanochemical reaction is faster when injected mechanical power (*i.e.* number of balls) is higher. The experiments performed allow constructing, at least tentatively, the milling map of investigated systems. The threshold value of injected mechanical power is in the range $4.2 - 4.5 \text{ W g}^{-1}$. Bellow this value the initially formed high crystalline γ -Bi₂O₃ phase is subjected to the amorphization with prolonged milling. Above the threshold the crystallinity of products is slightly lower, but amorphization is negligible.

Concurrent mechanochemical treatment of powder mixture of Bi_2O_3 and TiO_2 in 2:3 molar ratio and pulverized $Bi_4Ti_3O_{12}$ compound prepared by reactive sintering shows that after some milling time, a steady state characterized by very disordered, amorphous-like structure was reached. Thus, systems evolve towards non-equilibrium stationary state regardless of different initial thermodynamic states. It was demonstrated that steady state (nanocrystalline/amorphous phase ratio) depends on milling conditions: higher milling intensity induces "nanocrystallization" of amorphous phase, *i.e.* precipitation of crystallites with the average size bellow 20 nm.

Powder mixture of Bi_2O_3 and ZrO_2 in 2:3 molar ratio was mechanochemically treated in steel or ZrO_2 medium. Structural analysis reveals that contamination arising from vial and balls debris has important influence on the phases obtained by subsequent reactive sintering. When mechanochemical treatment was performed in steel medium, depending on the milling time and sintering temperature, the phases: γ -Bi₁₂(Zr_xFe_{1-x})O₂₀, Bi(Zr_xFe_{1-x})O₃ and Bi₂(Zr_xFe_{1-x})O₉ were obtained by reactive sintering, whereby the Fe originates from vial and ball debris. On the other hand, when ZrO_2 is used as milling medium, the reactive sintering and quenching produce metastable $Bi_4Zr_3O_{12}$ compound with orthorhombic crystal structure, regardless of mechanochemical pre-treatment duration (from 10 min to 50 h).







Alchemists at work from Jean-Jacques Manget's Bibliotheca chemica curiosa, Geneva 1702

A Piperazine-Containing Azamacrocyclic Fluorescent Sensor for Metals

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The design and construction of molecular scale sensors are challenging issues in modern nanotechnology. Molecular sensors are sensitive devices which are used for rapid detection of very small amounts of various compounds and metals. The detection of toxic metals such as Hg, Pb, Cd are crucial for environmental protection as well as for medical and pharmaceutical technology.^{1,2} The design of molecular sensors is based on an interdisciplinary approach, which links different fields of chemical science, from organic to materials chemistry and biochemistry.² The new fluorophoric ligand **1** was designed in our group as a potential chemosensor for metals. It is synthesized starting from the simple bisally olefin of the protected 3.5-dibydroxy-1-benzoic acid

is synthesized starting from the simple bisallyl olefin of the protected 3,5-dihydroxy-1-benzoic acid and mono-Boc-protected piperazine via sequential regioselective hydroformylation and reductive amination.³



Recognition of ions Zn^{2+} and Co^{2+} by the macrocycle **1** has been detected by fluorescence spectroscopy, and was also confirmed by NMR spectroscopy. The interaction of these metals with the macrocycle is very selective, and can be detected using different wavelengths of excitation. If the complex is excited with a wavelength of 280 nm, fluorescence enhancement is higher in the **1**+Zn²⁺ complex while at an excitation wavelength of 400 nm, fluorescence enhancement for the complex **1**+Co²⁺ was higher.⁴ These results indicate different stabilities of the electronic states formed by interaction of the metals with macrocycle. The observed selectivity for different metals will result in even more applications of these macrocycles, studies which are currently on going.



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Synthesis of Doped CeO₂ Nanopowders by Glycine /Nitrate and Self-Propagating Room Temperature Procedures

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Common strategy in SOFC cost reduction involves not only reducing the operating temperature but also reducing both the cost of materials to be applied and the technology for their production. CeO_2 is found to be very suitable and less expensive material for solid electrolyte with high ionic conductivity at relatively low temperatures. It is known that by doping, ionic conductivity of ceria increases. Most frequently Ga, Sm, and Nd are considered as dopant cations.

On the other hand, there is a demand to use nanopowders since it is known that nanoparticles will contribute to decreasing sintering temperature, as well as to increasing grain boundary conductivity compared to micrometer size materials.

In this paper, two different methods of nanopowder synthesis will be described. Namely, ceria powders doped with different concentrations of Y, Ga, Nd, Sm were synthesized by two different procedures:

-modified glycine nitrate process (MGNP) and

-self-propagating room temperature method.

For both procedures nitrates of dopant cations were used. In the first case, it is about a selfcombustion process using nitrates as oxidant and glycine (aminoacetic acid) as a fuel, i.e.

$4C_{2}H_{5}NO_{2}+2/(1-x)Ce(NO_{3})_{3}.6H_{2}O+xMe(NO_{3})_{3}.6H_{2}O/+2O_{2}\rightarrow 2Ce_{1-x}Me_{x}O_{2-y}+22H_{2}O+5N_{2}\uparrow+8CO_{2}\uparrow$

Burn up takes place at low temperatures producing very fine nanosized particles.

Second method is based on the self-propagating room temperature reaction between metallic nitrates and sodium hydroxide, i.e.

2/(1-x)Ce(NO₃)₃.6H₂O+xMe(NO₃)₃.6H₂O/+6NaOH→2Ce_{1-x}Me_xO_{2-y}+6NaNO₃+15H₂O + 3/2O₂↑

which was performed without milling the reacting chemicals. The reaction proceeded at room temperature and does not seem to need any source of energy to start propagating.

X-ray diffraction analysis, SEM, measuring specific surface area, and chemical analysis were used to characterize the obtained powders. It was found that by both methods nanosized particles of all the powders synthesized were obtained. The amount of obtained powders pro batch does not seem to be limited as in many of known methods. The properties of powders obtained by the two methods will be compared, as well.

The Key Role of Chemistry in Determining the Quality of Life in the Future

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A forecast of possible principle achievements of chemistry in future is given.

It is always reasonable to use tips of the past - as milestones for future events. Recent history of progress in chemistry offers a number of examples of this kind. So, practically all man-made materials are produced out of trivial raw materials (abundant and low-prized as, e.g. coal, oil or sand are), but they acquire properties of valuable products due to sophisticated chemical transformation. The road that led to this progress was paved with intensive research and development. Mankind stubbornly continues the same way, so that it will not be a surprise if new 'wonderful' materials will be engineered in future. It is quite possible that their synthesis, properties, processing and application will fundamentally differ from anything imaginable at present time.

There are already a lot of announcements of future promotions. By crafting the properties of one class of materials onto another one, completely new frontiers were open.

Recent substantial improvements and diversification of e.g. polymer and ceramic materials are an example. Next to conductive polymers, organic metals were synthesized that possess electrical conductivity typical for metallic materials. Plastic ceramic materials (non-brittle and machinable but still refractory, strong and light) are here.

Nano-sized materials whose properties are dominantly determined by their surface rather than the bulk are already familiar.

Solid-state technology has adopted (as its long-term strategic focus), the dream of creating programmable matter - matter that changes its physical, optical or electrical behavior under the influence of electrons or photons only. Similar achievements could be trivial events in mankind's future.

No matter how some expectations seem less realistic than in its medieval ancestor, our future will not be an era of new alchemy.

Analyzing the past, we have to be aware of the mistakes previously made. Simply, the mistakes should be recognized, understand what was wrong with them (on a long-term scale!) and then one should do our best not to repeat similar sins. Examples of yesterday's high praised achievements - today's misfortunes (or disasters) are numerous. Such is the case, e.g., with innovation of halocarbon-based refrigeration, leaded gasoline or NH₃ synthesis (benefits shaded after many water habitats were seriously deoxygenated due to accumulation of nitrates washed out of the fertilized soils).

To be honest, there are far more examples of innovations that did improve the quality of life without jeopardizing any of its many aspects.

Being aware that Earth's population will continue to rise, it is wise to ask ourselves: "How will the future needs be satisfied with the depleted/exhausted reserves of raw materials, fossil fuels, energy, etc?" The most frequently offered answers contain the word *sustainability*, e.g. *we will recycle, reduce, rationalize, etc.* But it seems reasonable to continue with the question: "What if all our efforts fail? Shall we experience a Global disaster, or even extermination?"

My pledge is that chemistry (and science in general) will help to overcome future shortages in materials and even develop new materials/classes of materials with superior properties and in sufficient quantities.

Incapsulation of Radioactive ^{99m}Tc in Fullerene Cages by the Metal Ion Implantation Technique

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Introduction

The biological behavior of fullerene derivatives shows their considerable potential for medical applications. We have produced, characterized and purified (in milligram quantities) endofullerenes containing gamma-ray emitting ^{99m}Tc by the metal ion implantation technique (introducing negatively charged C₆₀ and C₇₀ into a low-temperature T_c plasma column by a strong axial magnetic field). Identification of ^{99m}Tc@C₆₀ and ^{99m}Tc@C₇₀ has been accomplished by application of ultra-low level radiation detection methods and mass spectrometry (TIMS and MALDI-TOF). Appropriately derivatized ^{99m}Tc – radioendofullerenes could be used as a radiopharmaceutical for medicine imaging. Such encapsulation of radionuclide in the carbon cage could facilitate their inert transport through biological systems and await further studies. Below is a typical mass spectrum (TIMS) of endohedral metallofullerene.





Iron Influence of Iron Precursor over Structure of Iron Oxide Nanoparticles Prepared by Sol-Gel Method in Silica Matrix

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Sol-gel Fe₂O₃-SiO₂ nanocomposites have been obtained, using tetraethoxysilane as precursor and ferric salts (chloride and nitrate). Thermal treatments in air, respectively in vacuum of the xerogels lead to several nanocomposite samples with different crystalline phases of iron oxide. The samples were characterized by thermal analysis coupled with mass spectrometry, transmission electron microscopy, X-ray diffraction and Mössbauer spectroscopy. The presence of rare phase ϵ -Fe₂O₃ was observed in the nanocomposites treated in air. Some of the resulting materials display superposed superparamagnetic and ferrimagnetic character at room temperature, which is indicating a distribution of particles size in nanometer range. The obtained results suggest that the nucleation and growth of iron oxide crystalline particles were significantly related to the precursor's nature and the annealing atmosphere.

Thermodynamics of *n*-Alkane Adsorption onto Nanostructured Silicon Nitride Powder

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Silicon nitride (Si₃N₄) is an important ceramic material used for various applications, due to its superior mechanical and electrical properties at elevated temperatures. A number of books and review papers devoted to the preparation and properties of this material have been published recently. However, there are no literature data on Si₃N₄ as an organic molecules sorbent in gas chromatography.

In the present work, the inverse gas chromatography (IGC) method was used to study the thermodynamic functions of *n*-alkanes adsorption on silicon nitride.

The powder chosen was commercial Si₃N₄ (MI, USA) with the following characteristics: ultrafine amorphous powder with specific surface area 92 m²g⁻¹; Si (wt.%) 54; N(wt.%) 38; and 0 (wt.%) 8. The adsorption measurements were carried out with a Spectra Physics Model 7100, USA, chromatograph with a flame ionization detector (FID). Alkanes (*n*-pentane, *n*-hexane, *n*-heptane and *n*-octane) were selected as adsorbates because of their inert nature vis-à-vis silicon nitride surfaces, and therefore, the adsorption mechanism due only to dispersive types of forces. The retention times for each adsorbate with Si₃N₄ were measured at 70, 80, 90, 100 and 110 ^oC.The adsorbate net retention volumes, *V_N*, were used for the calculation of the surface partition coefficient, *K_s*, defined as the net retention volume per unit of the adsorbent surface area.

Knowing the partition coefficients, the standard free energy change of adsorption, ΔG_a^o , standard-

state enthalpies of adsorption, $-\Delta H_d^o$, and the corresponding standard-state entropy changes of

adsorption, ΔS_a^o , were determined.

Experimental data have confirmed that the logarithm of the partition coefficients of the *n*-alkane homologue series linearly increases with the increasing chain length, molecular weight, boiling points and molar refractions, as expected. This trend is valid for all temperatures. It has also been found that the ΔH_d^o and ΔG_a^d values of *n*-alkanes increase linearly with the number of carbon atoms. The more negative ΔH_d^o , and ΔG_a^d values, the greater the interaction between the adsorbate and adsorbent. The differences observed between the experimental and predicted (calculated according to De Boer) entropy changes, i.e., additional entropy loss found experimentally, may result from the restricted rotational and vibrational freedom of the adsorbates on the investigated silicon nitride surface.

Role of Li, Na and Ca Cations on the Hexacelsian to Celsian Transformation in the Barium Aluminosilicate (BAS) System

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High oxidation resistance, low and linear dielectric constant and low coefficient of thermal expansion, make barium aluminosilicates (BAS), particularly in the monoclinic form attractive as matrix material for ceramic composites for high temperature applications. One of the difficulties of BAS ceramics for these applications is that the hexacelsian phase, which shows high thermal expansion coefficient appears in the beginning of heat treatment of any raw materials (1).

Hexacelsian once formed sluggishly transforms into monoclinic form so that some additives for acceleration of the transformation has been necessary to prepare monoclinic celsian ceramics. The vast numbers of studies concerning the synthesis of celsian indicate the great complexity of the hexcalelsian to monoclinic celsian transformation. Phase transformation investigations become additionally complicated if the certain mineralize are present in reaction mixture (2). The mechanism of polymorphic transformation promoted by mineralizes is not clear.

Thermally induced phase transformations of Ba exchanged zeolite LTA are particularly suitable for synthesis of the celsians and mineralizes relation studies in the BaO-Al2O3-2Sio2 system (3, 4).

Fully exchanged Ba-LTA zeolite has the same composition as celsian phases (BaAl2Si2O8). The desired starting composition of the system may be easily reproduced and properly adjusting in the cation exchange procedure. The thermal collapse of zeolite structure give rise to amorphous phase with composition that is perfectly homogeneous at the atomic scale.

The main objective of the present investigation was to pursue the role of M = Li, Na, Ca cations on enhanced kinetics of hexa to monoclinic celsian transformation of M-Ba exchanged and fully Baexchanged LTA zeolite. The samples were thermally treated at temperatures ranging from 700-1250 °C for times up to 70 h and subsequently were characterized by XRPD, 29 Si MAS NMR, Raman and IR spectroscopy. The Na, Li, Ca content in Ba-exchanged zeolite and ion exchange procedure were found to affect the temperatures and times at which the transformations of hexacelsian to monoclinic celsian occur.

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Germanate glasses have attracted much interest in recent years, especially because of their technological applications, for example, in optical fibres and nonlinear optical devices.

Alkali germanate glasses are characterised by the presence of maximum of physical properties such as density, glass transition temperature etc.^(1,2) as a function of alkali oxide content. This behaviour is widely known as the "germanate anomaly" effect in comparison with monotonic property - composition relations exhibited by alkali silicate glasses.

Addition of alkali oxide to GeO₂ glass converts some of the germanium from four to six coordination without breaking Ge-O-Ge- bridging bonds.

The number of such six co-ordinated germanium increased until alkali oxide content is about 15 to 20 mol. $\%^{(3)}$, while higher alkali oxide content causes formation of non-bridging oxygen containing germanate tetrahedra.

In the present study, the effect of replacing 20 mol. % of GeO_2 by TiO_2 on some properties of potassium tetragermanate glass in which content of potassium oxide is corresponding to maximum in glass transition temperature, was investigated. The effect of TiO_2 , that can behave as network former or network modifier, on the glass transition temperature and devitrification behaviour of potassium tetragermanate glass, was studied by differential thermal analysis (DTA) and X-ray diffraction (XRD).

The replacing of 20 mol. % of GeO₂ by TiO₂ in potassium tetragermanate glass leads to a glass having higher glass transition temperature and lower tendency for crystallization . Presence of two exothermic peaks on DTA curve for potassium tetragermanate glass suggests a two step crystallization mechanism. XRD pattern of potassium tetragermanate glass heated up to the temperature of crystallization peak was attributed to presence of two phases GeO₂ i K₂Ge₇O₁₅. Phase which crystallized during heating of potassium-titanium-germanate glass up to crystallization peak temperature was K₂TiGe₃O₉, identified by XRD.

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Potential Valorization of Red Mud in Ceramic Technologies

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Disposal of red mud from the Bayer technology in special basins could not prevent the environmental pollution. Due to it's chemical and mineralogical content, red mud presents valuable industrial raw material (more then 65% wt. Fe₂O₃, T_iO₂, SiO₂, alumina, caustic base, etc). This paper presents experimental investigation with the aim of red mud valorization in brick production technologies. Base mixage for the brick production is prepared on the base of red mud, clay and feldspat. Base mixage content of red mud is 10 % wt., 20 % wt., 30 % wt., 50 % wt. Brick specimens are formed in two manners:

- Powder pressing on elevated temperatures of 573 K in the cylindrical shape (Φ = 2.9 cm and H = 0.8 cm)
- Manual shaping of the plastic mass in the parallelopipedic shape (7.7 cm, 3.9 cm, 1.6 cm).

Based mixage was characterized previously (chemical, mineralogical, granulometric content as well as microscopy examination). Specimens were sintered on 1373 K and 1473 K. Sintering was followed by examination of porosity, shrinkage and compressive strength [1]. X-ray analysis was performed to obtain mineralogical content. Investigation of the red mud content was a relevant parameter induce that the best value for the good shrinkage, porosity and strength is obtained with 40 % wt. content, sintered on the 1473 K.

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Densification of Si₃N₄ with Li-Exchanged Zeolite Additive

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This paper deals with the densification and phase transformation during pressureless sintering of Si₃N₄ with Li-exchanged zeolite as the sintering additive. The dilatometric shrinkage data show that the first liquid forms as low as 1080°C, resulting in a significant reduction of sintering temperature. Upon sintering at 1500°C the bulk density increases to more than 90% of the theoretical density. However, no phase transformation from α -Si₃N₄ to β -Si₃N₄ takes place. At 1550°C the secondary phase has been completely converted into a glassy phase and total conversion of α -Si₃N₄ into β -Si₃N₄ takes place. The grain growth is anisotropic, leading to a microstructure, which has potential for enhanced fracture toughness. At higher temperatures (>1650°C) Al and O dissolve in the β -Si₃N₄ grains, leading to partially transient liquid phase (Fig.1). The grain boundary phase is significantly reduced due to evaporation and the final material might have promising mechanical properties as well as promising high temperature properties in spite of the low sintering temperature.

XRD, SEM and TEM techniques have been used to characterize samples. The results show that the Li-exchanged zeolite can provide very effective low-temperature sintering additives for silicon nitride.



Fig. 1. TEM image of Si_3N_4 material sintered at 1650 ° C.

Crystillisation Behaviour of Silicate Glass Doped with Flourine Anions

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Glass crystallization opens a wide range of possibilities for modeling new glass-ceramic materials of specific properties. The dominant process that determines the microstructure of glass-ceramics is nucleation. The high grade glass-ceramics demands fine-grained microstructure, developing in glass at a high nuclei density. This can be achieved by homogenous nucleation, occurring in many glasses on the large undercooling. Previous studies have shown that an efficient way for obtaining high quality glass-ceramics is the addition of selected nucleating agents. As a results of using nucleating agent, the change of the glass crystallization mechanism from surface to volume crystallization take place.

In this paper the results of investigation of crystallization behaviour of glass powder with starting composition 54SiO₂·12Al₂O₃·12.5CaO·16MgO·6K₂O (mol%) were presented. As a nucleating agent 0.6 , 1.5 and 2.0 (mol %) of F - was added to the base glass. The investigation was performed under nonisothermal conditions. The glass powder with 0.6 mol% of F⁻ and grain size in the range of 0-0.10 mm crystallize by the surface crystallization mechanism. For the glass grain size of 0.1-0.5 mm the crystallization mechanism was changed from surface to volume and for grain size of >0.50 mm the volume mechanism is dominant. The glass powder with 1.5 mol% of F⁻ and grain size in the range of 0-0.15 mm crystallise by the surface crystallization mechanism. For the glass grain size of 0.15-0.60 mm the crystallization mechanism was changed from surface to volume and during the process the phase composition was changed also. Glass grain size of >0.60 mm crystallise by the volume crystallisation mechanism. The glass powder with 2.0 mol% of F⁻ and grain size in the range of 0-0.05 mm crystallise by the surface crystallization mechanism and for grain size in the range of 0.05-0.45 mm the crystallization mechanism was changed from surface to volume. Volume crystallization mechanism was occurred for the grain size of >0.45 mm. The results also shown that the leucite as a primary crystalline phase was formed and as secundary phases formed are diopside and phlogopite.

Synthesis of Ultralow Thermal Expansion $MZr_4P_6O_{24}$ (M = Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺) Ceramics

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Introduction

During the last few years, a major new structural family of low-thermal expansion ceramic materials as NZP or CTP of which $NaZr_2P_3O_{12}$ and $CaTi_4P_6O_{24}$ are the prototype compositions was developed. This type of structural material should be interesting for its thermal expansion properties, superior ionic conductivity and flexibility toward ionic substitution.

Experimental

In this paper were studied the $MZr_4P_6O_{24}$ (M = Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺) type ceramics belonging to a new family of ultra low thermal expansion were synthesized by solid state-reaction of oxides mixture and by sol-gel method. In solid –state reaction method the starting materials were reagent-grade alkaline-earth carbonates, ZrO_2 and $(NH_4)_2HPO_4$. In sol-gel technique, aqueous solution of alkaline earth chlorides, $ZrOCI_2.8H_2O$ and $(NH_4)_2HPO_4$ were used in stoichiometric amounts under stirring conditions. The stoichiometric mixtures were heat treated in 200- 1560 °C at various time periods. Their thermal expansion and sinterability were compared by dilatometry and X-ray diffraction measurement. The microstructure of sintered materials was investigated by scanning electron microscopy.

Results

 $CaZr_4P_6O_{24}$ showed a near-zero bulk thermal-expansion in the temperature range 25° to 900°C. $MgZr_4P_6O_{24}$, $SrZr_4P_6O_{24}$, $BaZr_4P_6O_{24}$ had positive bulk thermal-expansion in the same temperature range.

Polycrystalline ceramics formed from these crystals might be useful as thermal –shock –resistant materials.

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Thermal Conductivity of Pressureless Sintered Silicon Nitride Materials with LiYO₂ and LiAlSiO₄ Additive

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Si₃N₄ ceramics with different density and microstructures were prepared by pressureless sintering, using LiYO₂ and Li-exchanged zeolite (LiAlSiO₄) as sintering additives. The effect of microstructural parameters, such as grain size and volume of intergranular phase on thermal conductivity and thermal diffusivity were studied using the laser flash method, over the range from room temperature to 700 °C. Materials with thermal conductivities of 5-38 W·(m·K)⁻¹ were obtained by changing the sintering additives as well as amount of sintering additive. The thermal diffusivity of Si₃N₄ sintered with LiYO₂ is 2.5 times higher than data obtained for LiAlSiO₄ additive (Fig. 1). Also, the highest conductivity was measured for the material with the least amount of additive. Since the phase composition is the same for all sintered materials (β -Si₃N₄ + glass), the difference in thermal conductivity is attributed to the amount of glassy phase in the grain-junctions and purity of β -Si₃N₄ crystal structure.



Fig. 1. Temperature dependence of thermal diffusivity of Si₃N₄ ceramics sintered with LiYO₂ and LiAlSiO₄ additives.

Rheological Behaviour of Poly(Ester-Siloxane)s

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The influence of structure and composition on the viscoelastic properties of poly(ester-siloxane) elastomers, with hard segments based on poly(butylene terephthalate), PBT, and soft segments based on poly(dimethylsiloxane)s, PDMS, is presented in this work. Two series of poly(ester-siloxane)s were investigated: 1) series *A*, with a constant mass ratio of hard and soft segments of 57/43, but the length of both segments varying, and 2) series *B*, with the mass ratio of hard and soft segment.

The rheological measurements comprised following the storage (G') and loss (G") shear modulus, tan δ and complex dynamic viscosity (η *), with temperature and frequency. The temperature dependencies of G', G" and tan δ show two region of viscoelastic behaviour from 30 to 250 °C: a rubbery plateau region and a flow region. In the rubbery plateau region the storage and the loss modules were relatively constant, i.e. independent of changing the temperature or frequency. The rubbery plateau region is characteristic for chemically or physically cross-linked polymers and also for amorphous polymers of high molecular weight. The two-phase microstructure of poly(estersiloxane)s, which is a consequence of the chemical incompatibility of the hard, physically cross-linked PBT-segments and the soft, amorphous PDMS-segments, is responsible for the appearance of the storage modules at 50 °C were about 10⁷-10⁸ Pa. The storage modules decrease with increasing content of soft PDMS segments due to the increasing flexibility of the copolymer chains.

An important rheological parameter for phase segregated copolymers, such as poly(estersiloxane)s, is microphase separation transition temperature, T_{MST} (also referred to as the orderdisorder transition). Below T_{MST} , at room temperature, poly(ester-siloxane)s consist of a crystalline PBT-phase which is dispersed in the amorphous PDMS-phase. However, as the temperature is increased above a certain critical value, the size of the PBT-crystallites begins to decrease, while at T_{MST} the ordered microdomain structure changes to a disordered homogeneous phase (isotropic melt). The microphase separation transition temperatures for the poly(ester-siloxane)s were determined from Han's diagrams (plots log G' versus log G"). Han's diagrams show that for a fixed value of G", G' decreases gradually as the temperature is increased to T_{MST} and then remains constant, i.e. independent of temperature, at T_{MST} and above. In other words, T_{MST} is the lowest temperature at which log G' versus log G" plots cease to vary with temperature. The microphase separation transition temperatures for the poly(ester-siloxane)s depended on the block length and PBT-content, and were in range from 220 to 234 °C.

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Synthesis, Characterization and Photopolymerization of Novel Self-Initiating Dendritic Polymers

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Dendritic macromolecules (dendrimers, dendrons and hyperbranched) have attracted much attention in the last decade due to their unique properties, such as high solubility and functionality as well as low viscosity. While so far the application of dendrimers is limited to pharmaceutical industry, much cheaper hyperbranched polymers could be used in different fields ranging from toughening agents, via coatings to additives.

We present the synthesis and the properties of new DUGANOVA's hyperbranched polyesterbased urethane acrylates containing xanthate groups:



Multifunctional, low viscosity, high reactivity oligomers, obtained by simple chemistry at very high yields can be tailored to match end user's needs. UV/EB curable compositions containing this new class of urethane acrylates have excellent hardness, gloss, chemical resistance but also high flexibility, unusual for hard radiation cured films. Those oligomers can be used in adhesives, scratch resistant coatings, fiber optic coatings, automotive coatings, ink jet compositions, printing inks etc. Xanthate moieties, which are covalently bonded to the oligomer serve as photoinitiator. Crosslinking is accomplished by either using classical photoinitiators or by living polymerization with xanthate mediation, showing no or little oxygen inhibition. This, combined with hyperbranched structure and high acrylate functionality give completely crosslinked coatings with low extractable matter. The fact that xanthate groups are embedded in the crosslinked film opens numerous routes for surface modification.

Conformational Behavior of Poly(Alkyl Thiophenes)

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The conducting polymers have attracted many scientists for their novel properties as well as the high conductivity at room temperature. From the practical point of view, conducting polymers have promising prospects for application in many areas such as electronic and optical devices. Among the conductive polymers, polythiophene is remarkable for good stability in the ambient conditions. Moreover, the properties of polythiophene can be modified by synthesizing alkylsupstituted monomers to yield a polymer with a side chain of different length. Polyalkylthiophenes with long alkyl substituent reveal new properties, such as solubility in certain organic solvents, thermal chromism, fusibility and others. Most of the difficulties in understanding these polymers arise from their structural complexity. In this work an attempt was made to understand the conformational behavior of these polymers in solution and solid state. Several random copolymers based on thiophene, methylthiophene and octylthiophene have been chemically synthesized using FeCl₃ as oxidizing agent in chloroform. The performed FTIR, UV/VIS and HPLC characterization indicate side-chain ordering in the solution, giving a longer conjugation lengths compared to solid state, where the degree of conjugation was significantly lower. The differences were explained in terms of different conformational behavior of these polymers in solution and solid state, depending on the substituent length.

Semi-Interpenetrating Polymer Networks Composed of Poly(N-Isopropyl Acrylamide) and Non-Ionic Polyacrylamide Hydrogels

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Recently, considerable research attention has been focused on hydrogels that are able to alter their volume and other physical properties in response to environmental stimuli, such as pH, temperature, ionic strength and electric field¹. Especially, great interest has been focused on temperature-sensitive hydrogels due to their scientific and technological importance. One of the interesting future applications of gels based on a response to temperature is their possible use for artificial muscles. Polymer gels composed of crosslinked poly(N-isopropylacrylamide) (PNIPA) undergo a sharp volume transition, i.e. gel collapse, at the temperature close to the LCST of the linear polymer. The gel dehydrates to the collapsed state due to the break down of the delicate hydrophilic/hydrophobic balance in the network structure. In PNIPA hydrogels, the volume transition is induced by the cooperative dehydration of the hydrophobic isopropyl group in the main chain coupled with the entropic force of the chains, which cause the gel to shrink.

The goal of this study was to prepare hydrogels with improved mechanical properties by using the concept of semi-interpenetrating polymer networks, semi-IPN,: crosslinked poly(N-isopropylacrylamide) having nonionic linear poly(acrylamide) inside. The effect of the structure of the polymer network, such as the crosslinking density, concentration of monomers and content of linear hydrophilic poly(acrylamide) inside the semi-IPNs on the thermoresponsive and mechanical properties, as well as on the swelling behavior was investigated.

The hydrogels were synthesized by free radical polymerization in aqueous media². Polymer networks with four different crosslinking densities were prepared by varying the molar ratio of the monomer (N-isopropylacrylamide, NIPA) to crosslinker (methylenebisacrylamide, MBA) from 25/1 to 100/1. Three series of polymer networks with four different crosslinking densities and concentra-tion of monomer NIPA 0.9 mol/dm³ were synthesized. Two series of semi-IPNs with molar ratio NIPA/MBA (50/1) and different concentrations of monomer NIPA in the feed 1.3 and 1.8 mol/dm³ in the presence of different contents of linear polymer were also prepared. The hydrogels were chara-cterized by determining the equilibrium degree of swelling at 25 °C, the compression modulus and the effective crosslinking density, as well as the ultimate hydrogel properties such as tensile strength and elongation at break.

It was found that: a) the optimal concentration of monomer NIPA for the synthesis of semi-IPNs is 1.3 mol/dm³, b) the optimal content of linear poly(acrylamide) is 2% when the mechanical properties and thermo-responsive properties are considered, i.e. the intensity of volume shrinkage and the kinetics of water uptake. The tensile strength of the semi-IPNs at equilibrium swelling was higher compared to PNIPA hydrogels. The mechanical strength of PNIPA hydrogels was improved, without diminishing the degree of swelling, by the synthesis of semi-IPNs. The elongation at break of the semi-IPNs varied between 17 and 45 % which are larger compared to single PNIPA networks (17 to 23 %). The energy at break increases from 1.7 to 3.6 times with the introduction of linear poly(acrylamide) into the PNIPA network due to a reinforcing effect. It could be concluded that the increase in storage elastic modulus due to the reinforcement with linear poly(acrylamide). From dynamic mechanical analysis it could be concluded that the mechanical properties are improved with increasing concentration of NIPA monomer. References:

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Bioprocessing of Polyester Fabric

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Wettability of fiber surfaces can be modified by changing the chemistry of the constituent polymer or by applying topical finishes. In the textile industry, polyester has certain key advantages including high strength, soft hand, stretch resistance, stain resistance, machine washability, wrinkle resistance and abrasion resistance. However, polyester is not so optimal in terms of its hydrophobicity, pilling, static, dyeability, inactive surface as a medium for adhering, i.e., softening or wettability enhancing compounds.

The twill cloche 100% polyester (homopolymer poly(ethylene terephthalate - PET) fabric (210g/m²) from *"Leteks"* – Leskovac, (Yu) with 31/23 ends/picks per cm and lipases were used in this study.

We were used two lipases (1 – porcine source, 2 - fungal source; powder and purity >90%), which are commercially products from *Biocatalysis*. Interactions of enzymes and the polyester fabric were done in aqueous buffer solutions. We selected the inorganic phosphate buffer and used it throughout this study; because, it gave the best conditions for correction several properties of polyester fabric.

Before all treatments, polyester fabric has been washed by pure distilled water at 50° C for 20min. Raw samples of polyester fabric have been processed on same way likes treatments with enzymes, but free from enzymes. The reaction, i.e. biomodification of polyester fabric, is allowed to proceed for 60min at 32° C, by a liquor : fabric ratio of 120:1 (ml/g) at pH=8.1 (phosphate buffer: Na₂HPO₄ 1M - 9.47ml + NaH₂PO₄ 1M, 0.53ml). The concentrations of enzymes were 0.3, 0.6, and 1g/l. After each process, the enzyme activity was terminated by water treatment the fabrics at 65° C for 15min. Then, the fabric was rinsed by cool water and drying. The process performed in laboratory equipment. Before any investigations, the polyester fabric was conditioned at 65% relative humidity and at 21°C temperature. Determination of water penetration - JUS F.S2.042, was used in this study. Moreover, the breaking strength and the elongation by dynamometer according to JUS ISO 5081.

Surface modification with lipase is believed to produce a profusion of new, exposed alcohol and carboxylate groups. Moreover, these groups, polar and hydrophilic, are susceptible to chemical or enzymatic derivatization with chemicals that are capable of further increasing the hydrophilic and/or charge of the surface.

Enzymes have been shown to improve the dye uptake and water penetration of polyester fibers causing a minimal loss of fiber weight and strength, lipase 2 especially.

The water penetration and absorption, i.e., the sorption properties, and the mechanical parameters of the processed fibres (strength, elongation, wear resistance) have been changed. These results confirmed a fact that the enzymes have influence on the surface of polyester fibres.

The process does not probably cause major damages of the fibre surface or major reorganisation of the surface layers of the polyester fibres, so therefore their mechanical characteristics are satisfactory.

Mechanical Properties of UV Cured Urethane Acrylates Based on Aliphatic Hyperbranched Polyesters Partially Modified with Soybean Fatty Acids

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Urethane acrylate resins based on partialy modified aliphatic hyperbranched polyesters (HBP) have been synthesized. HBP of the second and the third generation were synthesized from 2,2-bis(hydroxymethyl)propionic acid and di-trimethylol propane. The modification of some amount of OH end-groups were carried out with soybean fatty acids. The urethane acrylates with different degree of acrylation were obtained by reaction of partialy modified HBP and differential amount of NCO adduct which had been previously obtained by reaction of equimolar amount of (IPDI) and 2-HEA. The synthesized samples were caracterized by FTIR, ¹H and ¹³C-NMR and GPC. The synthesized Urethane acrylates, mixed with hexanediol diacrylate (20 wt. %) and Irgacure 184 (4 wt. %), were UV cured. A medium pressure mercury lamp (80W/cm) was used as the ultraviolet irradiating source.

The mechanical properties of UV cured samples are more dependent on the degree of acrylation than on the molar mass. The network homogeneity of UV cured samples are expressed by the width of the tan δ peak. The broad tan δ peak was observed for all samples indicating that formed networks are inhomogenous i.e. there are broad distribution of chain lengths between crosslinks.

The double bonds from unsaturated fatty acids can cure by an oxidative mechanism. It leads to the formation of new crosslinks which causes the improvement of the mechanical properties of UV cured samples.

The Influence of Radiation on the Thermal Stability of Polyimides

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Different polyimide resins were synthesized using N-[3-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)phenyl]acetamide and the following compounds with terminal amino groups: urea, 6-aminohexylamine, 2-aminoethylamine, 3-[4-(3-aminopropyl)piperazin-1-yl]propan-1-amine, 4-[(4-aminocyclohexyl)me-thyl]cyclohexanamine, 4-(4-aminobenzyl)aniline, 4-[(4-aminophenyl)sulfonyl]aniline.

The thermal behaviour of the polyimide resins was studied by thermogravimetric measurements (TG) in nitrogen. Polyimide resins have been irradiated (500 kGy) and their radiation stability evaluated on the basis of thermal behaviour of irradiated samples.

The thermal degradation of examined polyimides are complex and occur in two or more phases. The structure of the diamine component has a greater effect on the thermal stability. The thermal stability depend on the crosslinking density depending on the relative reactivity of the used diamine. The using of diamines which have smaller and/or more flexible molecules lead to formation of more stable polyimides with higher crosslinking density.

The applied dose of 500 kGy contributes to the better stability, due to additional crosslinking occuring in polyimides which were obtained from diamines which contain the longest aliphatic chain length, aromatic, cycloaliphatic or heterocyclic rings. The improvement of stability is the greatest for the sample which was synthesized from 4-(4-aminobenzyl)aniline.

Fracture in Fiber Reinforced Polymer Composites

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Fractography is one of the most powerful tool for fracture analysis of composites. Fracture in fiber reinforced composites occurs in different ways depending on the matrix type and composite construction, as well as on the loading conditions. Using the fractography, valiable information could be obtained, such as cause of failure, initiation site, direction of crack propagation, fiber/matrix adhesion level, state of stress condition, matrix microstructural effects, *etc*.

In this work, some of the fracture characteristics and effects found in different fiber reinforced polymer composites will be presented, with main purpose to describe some of the basic fracture features.

Various composites, both thermoplastic (C/PP, C/PA6, G/PP, G/PPS, G/PEI) and thermosetting (hybrid C/PET/epoxy) were evaluated after loaded to failure, using SEM analysis. Composite samples were prepared by compression moulding and filament winding under the proper conditions [1,2]. Fracture surfaces were observed after the tensile test, using a Philips 501 Scanning electron microscope (vacuum Au/Pd alloy deposition of the samples in a Polaron sputtering apparatus was performed previously).

Based on the obtained SEM fractographs, the fracture surface was also examined with respect to fiber/matrix adhesion and the interphase effects. Characteristic fracture features for thermosetting composites (finger like, river markings, peel fracture) were found in C/PET/epoxy. Brittle and brush like fractures, fracture-crack propagation and delamination were registrated in multilayer thermoplastic composites.

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Phase Transfer Catalysis in Phosphorus-Containing Polymer Synthesis

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One of the most important classes of polymers obtained by the application of phase transfer catalysis (PTC) conditions is that of phosphorus containing polymers, especially polyphosphonates and polyphosphates. Polyphosphonates were synthesized by liquid-liquid (I-I) and vapor-liquid (v-I) interfacial polycondensation of bisphenol A (BA) with phenyldichlorophosphonate (PPD) and cyclohexylphosphonic dichloride (CPD). The main relationships in I-I and v-I interfacial polycondensations of the effects of reaction temperature on molecular weight and yield of the polyphosphonates have been studied and described in Table 1.

Table 1	. The	influe	nce	of re	action	tempe	erature	on	yield	and	mole	cular	weight	of the
р	olyph	nospho	nate	es ob	otained	' by I-I	and v-	l int	erfaci	ial po	olycol	ndens	sation ^a	

Temperature,°C	Yield, η (%)	Inherent viscosity, η _{inh} ^b (dl/g)	Mn	Mw				
I-I, $R = C_6 H_5$								
-5	75	0.92	8500	16810				
0	72	0.85	8400	16700				
10	60	0.55	7250	14300				
20	40	0.48	5130	9280				
40	15	0.10	-	-				
$I-I, R = C_6 H_{11}$								
-5	73	0.90	8400	15920				
0	70	0.80	8260	15510				
10	55	0.45	6800	11880				
20	38	0.40	4820	8800				
40	10	0.10	-	-				
v-I, $R = C_6 H_5$								
25	35	0.40	4100	6700				
60	60	0.85	8800	17000				
90	80	1.10	9230	17820				
v-I, $R = C_6 H_{11}$								
25	30	0.50	3800	5500				
60	58	0.72	8200	16800				
90	75	1.00	9000	17150				

 reaction conditions: 0,040 moles PPD and CPD; 0,040 moles BA; NaOH 1 M (0,090 moles); 50-70 minutes;

^b determined at a concentration of 0.5 g/dl, in tetrachloroethane, at 30° C

It is seen from Table 1 that some dependences in I-I polycondensations are analogous to the dependences in v-I systems, but also that some do differ: molecular weight increases with increase in the reaction temperature, in v-I polycondensation, and decreases with increasing reaction temperature, in I-I polycondensation.

Light-Scattering Studies of Dilute Aqueous Solutions of Carboxymethyl Starch

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Native starches are chemically modified to improve their properties. Carboxymethyl starch (CMS) is a very important starch derivative in which the -OH groups from the starch molecules are partially substituted by the ether group (-O-CH₂COOH). The advantage of CMS compared to native starch is that its sodium salts are water soluble, the solubility increasing with increasing degree of substitution (DS).

The properties of carboxymethyl starch as a polyelectrolyte were investigated in dilute aqueous solutions in this study. For that purpose, two CMS samples with similar DS but obtained by carboxymethylation of native starch from different plants (corn and potato starch) were synthesized. Starch carboxymethylation was carried out in two steps as described previously¹. The obtained Na salts of CMS were converted to the acid form and then washed with aqueous solution of 80 mass % methanol in order to remove salts present. Subsequently, the samples were dried and their humidity and DS were determined following a previously described procedure². Since the acid form of CMS is not soluble in water, the samples were neutralized with NaOH solution and then dried to the constant mass. The so prepared CMS samples were used for static light scattering (LS) measurements, which were performed with a FICA 50 photometer (λ = 436 nm) at 25 °C. The mass average molar mass, radius of gyration and second virial coefficient were determined for these two samples in aqueous NaCI solutions of four different concentrations.

The limiting viscosity numbers of the same CMS samples were also determined in aqueous NaCl solutions of the same concentrations as used for the LS measurements. The viscosity measurements were performed at 25 °C using a standardized Ubbelhode viscometer. The obtained results showed that both type of native starch and NaCl concentrations had large influence on the radius of gyration, second virial coefficient and the limiting viscosity number.

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Paracetamol Release Studies of pH-Sensitive Hydrogels

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The swelling behavior of pH-responsive hydrogels is very sensitive to the pH of the external solution. These gels may be made of homo- or copolymers, but the presence of acidic or basic groups is essential for the volume changes. The ionic group will ionize when the pH of the environment is above or below its pK value, causing the electrostatic repulsions between the equally charged groups in the network chains resulting in increased liquid uptake. The response rate of pH-sensitive gels depend on their composition and crosslinking ratio. The pH-sensitive or 'intelligent' hydrogels play a significant role in advanced drug delivery formulations [1,2]. Controlling hydrogels swelling properties is essential for their application as controlled release drug delivery systems.

This paper reports on the swelling properties and in vitro release of paracetamol, as a model drug, of the copolymer hydrogel based on acrylamide (AAm) and itaconic acid (IA) as a response to pH values of the external media and the changes of the gel composition. The copolymer hydrogels of AAm and IA, crosslinked with N,N-methylene bisacrylamide (MBA), were synthesized by radical polymerization at 60^oC, initiated with the redox couple potassium persulfate/potassium pyrosulfate (PPS/PyPS).

The swelling degree is strongly dependent on the pH of the buffer. At low pH the itaconic acid groups are not ionized so the swelling ratio is low and intermolecular complexation due to hydrogen bonding occurs, acting as physical crosslinks. As the degree of ionization increases, above the nominal pK_a values of IA (3.85; 5.44 [3]), increased hydrophilicity results in greater swelling ratios. On the other hand, the swelling degree depends on the network composition, i.e. the swelling degree increases with the increase of itaconic acid content.

The release profiles obtained under different experimental conditions show differences, indicating that the gel composition and environmental pH are the main variables influencing the drug release rate. The decrease of pH values of external media and itaconic acid content leads to the slower drug release rate.

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The Radical Copolymerization of Styrene and Di-2-Chloroethyl Itaconate

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With the ever increasing use of polymeric materials for various applications, the need to introduce specific functional groups into a polymer also increases. The introduction of functional groups may considerably change the polymer properties. The goal of this investigation was to synthesize the copolymer of styrene, a cheap and available monomer, and a comonomer that may be readily functionalized. Di-2-chloroethyl itaconate, DCEI, was chosen as the comonomer for this purpose. The kinetics of the radical polymerization of DCEI have been studied previously¹.



The copolymer samples were radically copolymerized in bulk at 60°C using α, α' -azobisisobutyronitrile (AIBN) as the initiator. The copolymerizations were taken to low yields, no greater than 10%. A series of bulk copolymerizations were performed with varying comonomer fractions. The corresponding homopolymers were also synthesized.

The mean molar masses of the obtained copolymers were determined by gel permeation chromatography. The samples were characterized by FTIR spectroscopy. The composition of the copolymer samples was determined by measuring the the refractive index increments of the copolymer solutions in 2-butanone.

The kinetic parameters were calculated based on these results and were found to be $r_1 = 0$ and $r_2 = 0.5$, with styrene being monomer 1. Such results may be explained by the stability of the propagating M₂ macroradical. The obtained results are in agreement with the results obtained at 50°C², with f₁ being the composition of M₁ in the comonomer mixture and F₁ the fraction of M₁ units in the copolymer.



Acknowledgement

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Preparation and Properties of Polydimethylsiloxane Surfaces Grafted with Acrylic Acid via Plasma or Ion-Beam Induced Graft Co-Polymerization

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Polymers are widely used as a biomaterial in the tissue engineering, biotechnology, medical implants, etc. Their interaction with leaving cells is of grate importance in this case.

Acrylic acid grafting is a possible way to turn the hydrophobic polymer surface into a hydrophilic one, which is a basic prerequisite for the cellular interaction. As an example, we describe here, haw acrylic acid grafted poly(dimethylsiloxane) (PDMS) surfaces could be prepared via argon RF (13.56 MHz) plasma or Ar+-beam induced graft co-polymerization. The chemical compound of the modified surfaces was controlled by X-Ray Photoelectron Spectroscopy. The surface tension and the relative contribution of the polar and disperse surface forces were estimated employing contact angle with polar (water) and non-polar (CH_2J_2) liquid measurements. The amount of the peroxide groups introduced onto the PDMS surface was measured via 1,1-diphenyl-2-picrylhydrazyl (DPPH) and the surface density of carboxylic groups was estimated by means of the Toluidine Blue O method. Human fibroblasts were used to investigate the cellular interaction of the modified PDMS surfaces.

UV Curing of Acrylic Pigmented Coatings

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In the last years the interest for UV-cured colored coatings have known an increasing development.

Addition of organic and inorganic pigments of various color may affect the UV curing performance of the photoinitiator. Pigments are competing with their light absorption properties against the photoinitiator. This can be understood in terms of scattering effects, film thickness, substrate type, amount of photoinitiator, pigment color and its particle size.

In this paper is studied the influence of the nature of pigment, particle size of the pigment powder and pigment content on the film pendulum hardness (PH). Koenig pendulum hardness was used as a quantitative method in evaluation of UV through-cure of the obtained films.

The formulation for UV curing contains: acrylic monomer: bisphenol A diglicyldyl epoxy diacrylat Photomer 3016 40T (Henkel), photoinitiator – *p*-methoxybenzoyldimethylphosphonate synthesized in laboratory, additive – triethylamine and pigments – white (TiO₂), red (cadmium sulphoselenide), green (TiO₂-NiO-ZnO) and blue (Al₂O₃-Cr₂O₃) at different particle size, d: d < 5 μ m, 5 μ m < d < 50 μ m and 50 μ m < d < 90 μ m and 5, 8, 12 and 15% pigment content. The film thickness was 120 μ m.

The efficiency of synthesized photoinitiator *p*-methoxybenzoyldimethylphosphonate was determined by differential scanning photocalorimetry method (DPC), using various amine as synergist additive.

The powder hardness of the pigment increases in order: white<red<green<blue.

It was observed that the PH of the pigmented film increases in the same order with pigment powder hardness, the hardest films were those blue.

Film PH depends both on pigment content and particle size. Dependences PH – pigment contain appear different function of particle size. It was observed, generally, an increase of PH, for each particle size, at 5 and 8% pigment content and a slowly decrease of PH at 12 and 15%. The best results were obtained when particle size was d < 5 μ m, because the photopolymerizable system was more homogenous and scattering effects were more diminished than in case when pigment particle size were bigger; thus, the photoinitiator was more efficient. Also, for particle size d < 5 μ m the films are more gloss and smooth.

Hyperbranched Acrylates in Dual-Curing Systems

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The aim of this work was to explore possibilities of use of hyperbranched polymers (HRP) in interpenetrating polymer networks (IPN).

IPNs are a combination of two polymers, in network form, of which at least one is synthesized and/or cross-linked in the immediate presence of the other without any covalent bonds between them. Most IPNs are heterogeneous systems comprised of one rubbery phase and one glassy phase which produce a synergistic effect yielding either high impact strength or reinforcement, both of which are dependent on phase continuity.

IPNs offer the possibility of combining in network form two otherwise non-compatible polymers with opposite properties. Similar to other multicomponent polymeric systems, the properties of the final product depend strongly on miscibility of the components.

In this case, IPNs based on hyperbranched polyesters have been investigated. All the IPNs consist of:

- 1. photocurable component, cross-linked by photopolymerisation of olefinic double bonds under UV-lamp, and
- 2. urethane component, cross-linked by the reaction of an polyol and the polyisocyanate. .

We used three types of hyperbranched polyesters in IPN samples:

- 1) Hyperbranched polyester which has 25% of hydroxyl groups modified by 3,5,5-trimethyl hexanoic acid (isononanoic acid) HRP(OH);
- 2) HRP(OH) which has 50% of hydroxyl groups acrylated HRP(A)₆
- 3) HRP(OH) which has 100% of hydroxyl groups acrylated HRP(A)₁₂.

HBP's were used as both, hydroxyl and C=C bearing polymers.

Fourteen IPN samples have been prepared and characterized by Dynamic mechanical analysis (DMA), Differential scanning calorimetry (DSC); Dielectric analysis (DEA) and Thermo gravimetric analysis (TGA).

As prepared, IPNs can be a good candidate for coating applications combining fast drying, excellent mechanical properties and good appearance.

Sorption of Benzene on Glycidyl Methacrylate Based Copolymers

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Macroporous hydrophilic copolymer adsorbents based on glycidyl methacrylate, GMA, are of great interest, since they possess suitable properties for separation of majority of classes of organic compounds. Their structure and chemical nature of the surface can be controlled by chemical transformation of reactive epoxy groups in GMA, which enhances polarity and specific interactions of the modified copolymer with polar adsorbates.

In this study, the adsorption of benzene on the macroporous poly(glycidyl methacrylate-coethylene glycol dimethacrylate), poly(GMA-co-EGDMA) and copolymer modified with ethylene diamine, EDA, poly(GMA-co-EGDMA)-en was studied by using inverse gas chromatography (IGC) under finite surface coverage conditions. Macroporous crosslinked poly(GMA-co-EGDMA) was synthesized by suspension copolymerization and modified by ring-opening reaction of the pendant epoxy groups with ethylene diamine. The specific surface areas of initial and modified copolymer samples were determined by the BET method from the low-temperature nitrogen adsorption isotherms (77 K) using a high-vacuum volumetric apparatus. Sorption properties of the copolymers were examined using a Hewlett Packard 5890 Series II gas chromatograph, with a flame ionization detector (FID). Varian Star 4.5 software was applied to collect the data. The FID was maintained at 523 K, the injector at 493 K, and the temperature was in the range 333-363 K. Dry nitrogen was used as the carrier gas (flow rate 24-28 cm³min⁻¹). Adsorbate amounts from 0.1 to 10 μ l were injected. The stainless steel columns (0.5 m × 2.2 mm) were packed with copolymer beads (particle size 150-500 μ m) and conditioned in a nitrogen stream for 24 h at 363 K. Relevant IGC results from the retention data were calculated by a program developed for the purpose.

The isotherms in the temperature range 333-363 K were used to estimate the surface area, the isosteric heat of adsorption and the adsorption energy distribution on the surface of copolymer samples. The adsorption of benzene on poly(GMA-co-EGDMA) and poly(GMA-co-EGDMA)-en were analyzed using the BET theoretical model. Both the initial and modified copolymer showed affinity towards benzene, as a result of specific interactions. The properties of the copolymer surface (porosity and chemical nature of initial and modified sample) govern the uptake of benzene. The data for specific surface areas obtained by IGC (S_a = 55.2 m²/g) and by the standard nitrogen adsorption method (S_a = 46.7 m²/g) agree reasonably well for poly(GMA-co-EGDMA). However, for poly(GMA-co-EGDMA)-en considerably higher value of specific surface area (S_a = 105.3 m²/g) was obtained from IGC data, compared with nitrogen adsorption method (S_a = 57.6 m²/g). The isosteric heat of adsorption for poly(GMA-co-EGDMA) and poly(GMA-co-EGDMA)-en approaches the constant value with increasing adsorbate loading. Chemical modification of the poly(GMA-co-EGDMA) with ethylene diamine significantly alters the shape of the functions isosteric heat of adsorption vs. surface coverage.

Composite Coating Polymer - Magnetic Powder for Magnetic Field Sensing

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The magnetic field acts upon the magnetic particles present in composite coating layer of the optical fiber in such a way that the action modifies the intensity of the light signal propagate trough optical fiber [1]. Composite material consisted of solution of poly (ethylene-co-vinyl acetate) – EVA in toluene and magnetic powder. Magnetic component of composite coating were powders of $SmCo_5$ and NdFeB. [2]. The primary conditions that a composite coating should satisfy are coating homogeneity and circularity, as well as thickness uniformity. The viscosity of the coating with dispersion depends on the: composition, temperature, concentration of polymer in solution and the concentration of the magnetic powder in the dispersion [3]. Dispersing a magnetic powder in a polymer solution also affects the viscosity of the system. Process parameters were optimized and optical fiber was coated with composite coating. Sensor's element on the basis of coated optical fiber with composite material was constructed and reaction to the external magnetic field was investigated. Under the applied magnetic field the sensor element shows sensibility on the magnetic field and reversibility of signal.



Fig 1. Change in intensity of light signal in external magnetic field of sensor's element with composite coating with (a) SmCo₅ and (b) NdFeB

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Biodegradable Poly(Ether-Ester) Copolymers with Different Hydrophilic Soft Segments

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Most synthetic polymeric materials are resistant to biodegradation causing a serious environmental problem. This environment pollution problem could be solved by using biodegradable polymers. Aliphatic polyesters are one of the most promising biodegradable materials because they are readily susceptible to biological attack. Many aliphatic polyesters have been extensively investigated as biodegradable materials and have found a large number of biomedical applications, such as carriers for the controlled release of drugs, bioresorbable surgical sutures, absorbable bone plates and some surgical fixation devices. One of the ways to improve the biodegradability properties of polymeric materials is by the incorporation of hydrophilic soft segments into the polymer chains^{1, 2}. At the same time, the introduction of the soft segments (e.g. polyether) leads to the formation of segmented block copolymers the mechanical properties of which can be tailored with variation of the type and content of the soft segments.

In this paper, the synthesis and characterization of poly(butylene succinate) copolymerized with poly(ethylene oxide) (PEO-series) and poly(tetramethylene oxide) (PTMO-series) as soft hydrophilic segments will be presented. The content of soft segments was varied from 10 to

50 mass% in both series. The molecular weights of the PEO and PTMO were the same (1000 g/mol). Copolyesters were synthesized by transesterification reaction in the bulk. The effect of the introduction of two different polyether soft segments on the structure and physical and thermal properties, as well as on their enzymatic and hydrolytic degradation was investigated. It was shown that the crystallinity and degradation kinetics could be tailored by the type and content of the soft segments.

¹H NMR spectroscopy was used to determine the composition of the polyesters. The composition of the polymers did not vary significantly from the composition of the reaction mixture indicating good incorporation of the soft segments into the polymer chains. The molecular weights of the polyesters were evaluated from solution viscosity measurements. The molecular weights were high enough to enable good filmability from the poly(ether-ester)s melt and solution. Thermal properties were investigated by means of DSC measurements. The melting temperatures and degree of crystallinity of the synthesized poly(ester-ether)s were lower than the melting temperature and degree of crystallinity of the homopolymer, poly(butylene succinate). Poly(ether-ester) based on poly(ethylene oxide), generally have poorer mechanical properties and oxidation instability during exposure to light under ambient conditions than those containing PTMO as the soft segments³.

The biodegradability of the poly(ether-ester)s was investigated in enzymatic degradation tests. The enzymatic degradation tests were performed in a buffer solution with Candida cylindracea lipase at 37 °C. The extent of biodegradation was quantified as the weight loss of the copolyesters films. Poly(ether-ester)s in both series showed higher weight losses than the homopolymer. The obtained results indicate that the biodegradability depends strongly not only on the degree of crystallinity, but also on the hydrophilicity of the chain backbone. Poly(ether-ester) based on PEO are more susceptible to enzymatic degradation, i.e. biodegradability properties are enhanced, compared to those containing PTMO. This behaviour is to be expected since PEO is more hydrophilic than PTMO.

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Synthesis of Polyaniline Doped with Phenylphosphonic Acid

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Conducting polymers has opened up new promising frontier in physics and materials chemistry. This new class of polymers known as synthetic metals combines the mechanical properties and processability of traditional polymers with electrical and optical properties characteristic to classical electronic conductors (metals).

Polyaniline (Pani) is one of this kind and seems to be the most studied partial because presents a variety of oxidation states and partial for the facility of synthesis and thermal stability.

The chemical polymerization of aniline was carried out in phenyphosphinic acid (APP) using ammonium peroxidisulphat as oxidant agent, at 0°C and 25°C.



The yield of the polyaniline was about 55-68%. The polymerization process required an induction time 8-10 times greater than in other acids (hydrochloric, sulphuric).

The density determined for polymer sample shows that the average density is 1,395 g cm⁻³ for PANI-salt and 1,203 g cm⁻³ for PANI-base.

Acid capacity of Pani depends on synthesis parameters and maximum value was 15.02 mechiv./g polymer.

Inherent viscosity of Pani was 0,662 dl/g at aniline/oxidant molar ratio >2 and 0°C.

The oxidation state function of synthesis parameters was between 0,553-0,625 and was evaluated from the UV-VIS and titration with $TiCI_3$ data.

The Pani synthesis was characterized by measurements of density, inherent viscosity, FTIR, UV-VIS and thermmogravimetric data.

FT-IR Study and Physical - Mechanical Properties of EVA-Wax Blends

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Waxes are critical to hot melt adhesives performance in terms of thermal stability and mechanical properties.

The thermal behavior of EVA with microcrystalline and polyethylene waxes have been investigated by infrared spectroscopy and physical-mechanical testing.

Infrared spectroscopy was used to follow the evolution of ratio of band intensities E_{730}/E_{720} with type and content of EVA –wax blends.

The tensile properties have been measured at two EVA/wax ratios: initially and after exposure at 175 and 200°C. A significant correlation was found among tensile strength at break / elongation and type and ratio of EVA / wax ratio.

Semiquantitative spectral information and evolution of physical – mechanical properties have been used to improve the behavior of EVA hot melt adhesives at work temperature.

Synthesis of Phosphonate-Based Polymers by the Michaelis-Becker Reaction

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Polymer-supported reagents are important in catalysis, organic synthesis, trace analysis and environmental separations.

In this work contributions to the synthesis of some phosphonates grafted on styrene-7% divinylbenzene copolymers through Michaelis-Becker polymer-analogous reactions are presented.

The functionalization polymer-analogous reaction is showed in Figure 1.



Figure 1. Synthesis of phoshonate-based polymers by Michaelis-Becker reactions.

The characteristics of phosphonates grafted on styrene-7% divinylbenzene copolymers are listed in Table 1.

No.	Phosphonate	G _F (mmoles/g)	η _F (%)
S1	(CH ₃ O) ₂ P(O)-	1.26	29.68
S2	$(C_2H_5O)_2P(O)$ -	1.27	31.25
S3	(C ₃ H ₇ O) ₂ P(O)-	1.29	33.28
S4	$(C_4H_9O)_2P(O)$ -	2.10	67.19
S5	$(C_8H_{17}O)_2P(O)$ -	1.51	54.68
S6	(C ₁₀ H ₂₁ O) ₂ P(O)-	1.36	39.06

Table 1. Characteristics of phosphonates grafted on styrene-7% divinylbenzene copolymers.

The functionalization degrees with phosphonate group are relatively high, ranging from 1.26-2.10 mmoles phosphonate group/g copolymer, ensuring an adequate concentration of active centers per mass unit of copolymer and being well suited for various applications.

Synthesis and Characterization of Poly(Ethylene Glycol)-Poly(D,L-Lactide-co-Glycolide)-Poly(Ethylene Glycol) Triblock Copolymer Modified with Collagen

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The aim of this work was a synthesis and characterization of poly(ethylene glycol)-poly(D,L-lactide-co-glycolide)-poly(ethylene glycol) triblock copolymer (PEG)-(PDLLG)-(PEG), and its modification with collagen. It was expected that collagen as a structural protein, with good mechanical properties, and good biocompatibility will provide both, mechanical and structural stability to tissues and organs. For this purpose poly(ethylene glycol)bis(carboxymethyl)ether and hydroxyl terminated poly(D,L-lactide-co-glycolide) were used. The synthesis itself consists of several steps: 1. transformation of the PEG carboxylic groups into more reactive acyl halide groups (CIOC-PEG-COCI), 2. coupling reaction with OH terminated PDLLG, 3. activation of PEG-tethered PDLLG with N-hydroxysuccinimide to produce a polymer more reactive to proteins and peptides, and 4. attachment of collagen to the PEG-PDLLG-PEG copolymer.

PEG, PDLLG, CIOC-PEG-COCI, PEG-tethered PDLLG, and NHS activated PEG-PDLLG-PEG were characterized by GPC, ¹H-NMR, and FTIR, whereas collagen modified PEG-tethered PDLLG was characterized by FTIR and solid state NMR.

Collagen covalently attached to a synthetic polymer through amide bonds, presents a new biomaterial convenient for a wide range of biomedical applications. Polymer devices were prepared using a solvent-casting technique, where a suspension of modified with collagen triblock copolymer in chloroform was poured on previously prepared PDLLG films. Cell growth experiments using fibroblasts were performed to observe the attachment and growth of cells on polymer-collagen matrices.

Sorption and Thermodynamic Properties of PVC/Poly(Alkyl Methacrylate) Blends

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Sorption and thermodynamic properties of a model polymer blend based on PVC/poly(alkyl methacrylates) were studied by inverse gas chromatography.

Retention volumes resulting from two organic solvents at infinite dilution (chloroform and dichlorethane) and different experimental conditions (temperature, concentration and blend composition) were used for calculating a large number of fundamental thermodynamic quantities such as: Flory-Huggins interactions parameters, $(\chi_{12}; \chi_{13}; \chi_{1(23)}, \chi_{23})$, weight-fraction activity coefficients at infinite dilution, Ω_1^{∞} , solubility parameters of solvents, δ_1 , polymer solubility parameters at infinite dilution of the solvent, δ_2^{∞} , the heat of solution, ΔH_s the partial molar heat of mixing, ΔH_m^{∞} and the heat of vaporization, ΔH_v . The values of these thermodynamic properties were affected by the presence of PMMA, PEMA and PBMA as second blend constituents.

Poly(alkyl methacrylates) showed strong specific interactions with the investigated solvents, influenced by the size of the alkyl group. The blends were found miscible in all range of compositions.

Also, chromatographic data were used for measuring diffusion and partition coefficients. Diffusion coefficients of 10⁻⁹ to 10⁻⁷ cm²/s and partition coefficients of 20 to 60 were calculated. These results were greatly depended by the concentration, blend composition and the nature of solvent. Sorption characteristics of all polymer blends were higher compared to those of pure homopolymers. The presence of poly(alkyl methacrylates) in blends caused increasing of diffusion coefficients when the alkyl group BMA was replaced by EMA or MMA.

Emulsifying Capability of Polymer-Surfactant Complexes

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Polymer-surfactant mixtures are widely used in practice in foods, pharmaceutical formulations, personal care products, paints, pesticides, etc. Water soluble nonionic derivatives cellulose like hydroxypropylmethyl cellulose (HPMC) is physiologically harmless and is preferred for use in the foodstuffs and pharmaceutical industry. The introduction of methyl and hydroxypropyl groups renders the cellulose molecule hydrophobic, and it thus has surface active properties so that HPMC can therefore be regarded as representative of the polymeric surfactant. In presence of small-molecule surfactant, sodiumdodecyl sulfate (SDS), the hydrophobic centers on the HPMC molecules are potential adsorption sites for surfactant molecules and HPMC-SDS complexes are formed. Therefore the HPMC-SDS interaction might have significant influence on emulsifying capability of complexes and on stability of emulsion.

In this paper the emulsifying capability of HPMC-SDS complexes as well as the influence of complexes on emulsion stability haw been investigated. Emulsions of sunflower oil (20%) were prepared in 1.0% HPMC solution and in presence of various concentrations of SDS. Rheologycal properties, particle size and particle size distribution of obtained emulsion were determined. Changes of emulsion stability, caused by HPMC-SDS interaction, are observed during two months.

The investigations show that the nature of HPMC-SDS interactions can influence particle size and stability of emulsion. Maximum stability and minimal particle size diameter has the emulsion obtained in solution of HPMC-SDS complexes with maximum viscosity, i.e. maximum interaction.

Synthesis, Characterization and UV Curing of Hyperbranched Urethane-Acrylates

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Hyperbranched polymers have attracted considerable and increasing interest during recent years. They are highly branched, tree-like macromolecules having large number of end groups. One possible application of hyperbranched polymers is their use in coatings due to their low melt and solution viscosities and large number of functional groups which can be chemically modified to adjust polymer properties (Tg, solubility, reactivity and rheological behaviour).

In this work, the synthesis and UV-curing of multifunctional urethane-acrylates based on aliphatic hyperbranched polyesters and polyethyleneglycol acrylate were invesigated. Hydroxy generations functional hyperbranched polyesters of different were synthesized bv polycondensation of bis-methylolpropionic acid and ditrimethylol propane using acidic catalyst at 140 °C. Hyperbranched urethane-acrylates were synthesized in two-step reaction: synthesis of an adduct from isophorone diisocyanate and polyethyleneglycol monoacrylate as a first step, and modification of previously synthesized hyperbranched polyol core with NCO-bearing adduct obtained in the first step. Obtained hyperbranched polymers consist of a hyperbranched polyester core, and linear grafts of polyethyleneglycol with acrylate end groups:



Their phisical and thermal properties were investigated and used to characterize the relationships between their structure and properties of cured coatings. Hyperbranched urethane-acrylates were mixed with hexanedioldiacrylate (20 wt.%) and photoinitiator (Irgacure 184, 4 wt.%) and cured with 80 W/cm metal halide UV-lamp. The curing process was followed by FT-IR spectroscopy. Viscoelastic properties of UV-cured polymers were determined by dynamic mechanical analysis. Tg temperatures of polymers and cured films were determined by DSC. Mechanical properties of UV-cured coatings (hardness, flexibility) and solvent resistance were also examined. Obtained coatings combine a high crosslinking density with flexible segments between crosslinks, which results in good compromise between hardness and flexibility and have the potential to be used in different UV-curing applications.

Swelling Behaviour of Poly(Ethylene Oxide) Based Hydrogels Obtained by Irradiation of Polymers in Aqueous Solution

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Hydrogels are defined as two- or multicomponent systems consisting of three-dimensional network of polymer chains and water that fills the space between macromolecules. Depending on the properties of the polymer (polymers) used, as well as on the nature and density of the network joints, such structures can contain various amounts of water in equilibrium.

A typical material applied for general purpose hydrogels is poly(ethylene oxide) (PEO). It is applied as a component of biomedical devices such as drug delivery systems, hemodialysis membranes, wound care products, dental and ophthalmic materials, elements of implants, constituents of hybrid-type organs etc.

In this study, gel samples were synthesized from aqueous solution of PEO - poly(itaconic acid) mixture and of a pure poly(ethylene oxide), as a reference gel, using gamma irradiation. Among various methods applied for the production of hydrogels, the irradiation technique has many advantages, as a simple, efficient, clean and environment-friendly process which allows combining the synthesis and sterilization in a single step.

The samples were characterized by IR spectra and thermal analysis. Swelling measurements were performed in various pH buffers in order to investigate the influence of small quantities of itaconic acid, which can impart pH sensitive swelling behaviour to the gels.

Rheological Behaviour and Processability of PVC/Poly(Alkyl Methacrylate) Blends

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Rheological behaviour of different PVC/poly(alkyl methacrylate) blends has been studied by determining the first material function. Experiments have been carried out under steady shearing conditions in a capillary rheometer.

Polymer blends followed the same power law relationship as that of pure PVC.

Processability tests have been performed on a Brabender Plasti-Corder PL-200 rheometer. The influence of processing temperature, shear rate and blend composition on fusion characteristics (fusion time and plasticizing energy) has been followed. Blend processability has been affected positively by the processing temperature and shear rate, but dominant influence has been shown by the blend composition. The addition of small amounts of poly(alkyl methacrylates) has significantly improved the processability of PVC. Blend's fusion time has dropped for 2-4 times, whereas the plasticizing energy was 30-60% smaller compared to that of pure PVC. Blend's plastograms lie between the plastograms of PVC and poly(alkyl methacrylates).

The pH-method, TGA and dynamic-thermal analysis have been used for heat and shear stability tests. Poly(alkylmethacrylates) have a role of a stabilizer even when they are added in a small amount in blends. TGA curves for pure PVC and pure poly(alkyl methacrylates) showed different mechanisms of degradation, whereas blends showed degradation behaviour between them.

PVC/poly(alkyl methacrylate) blends have increased elasticity and stress at break, but no significant changes in physical and mechanical properties have been noticed.

Synthesis of Thermoplastic Elastomers Based on Poly(Butylene Terephthalate) and Poly(Ethylene Oxide)-Polydimethylsiloxane

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Block copolymers, which belong to the class of thermoplastic elastomers, consist of two types of chemically incompatible segments: hard-crystalline and soft-amorphous segments. Thermoplastic elastomers combine the properties of chemically cross-linked elastomers, such as elastic recovery and low-temperature flexibility, with those of thermoplastic materials, such as impact strength and ease of processing (extrusion, injection moulding, etc.). Poly(organosiloxane)s were chosen as the soft segments in the thermoplastic elastomers because of their excellent thermal and thermo-oxidative stability, low glass transition temperature, low surface energy, ultraviolet resistance, good electrical properties, good biocompatibility and high permeability to many gases. Thermoplastic elastomers with soft segments based on poly(organosiloxane)s have recently been used for special applications, for example as biocompatible materials, gas separation membranes, elastomers, protective coatings, emulsifiers, etc¹.

In the present work, a series of thermoplastic poly(ester-ether-siloxane)s based on poly(butylene terephthalate) as the hard segment and poly(ethyleneoxide-dimethylsiloxane-ethyleneoxide), PEO-PDMS-PEO, as the soft segment, was synthesized. The PEO-block in the soft segment served as a compatiblizer between the hydrophobic PDMS and the hydrophilic PBT². Poly(ester-ethersiloxane)s were synthesized by a two-step catalyzed transesterification reaction in the melt, starting from dimethylterephthalate, 1,4-butandiol α,ω -dihydroxy-poly(ethyleneoxideand dimethylsiloxane-ethyleneoxide), M_n = 1100 g/mol. Tetra-n-butyl-titanate (2 mmol Ti(OBu)₄ / 1 mol DMT) was used as the catalyst, while N,N'-diphenyl-p-phenylenediamine (0.5 mass % in the reaction mixture) was used as a thermal stabilizer. The mass ratio of hard and soft segments was varied in range from 90/10 to 40/60. The composition and the structure of the synthesized poly(ester-ether-siloxane)s were determined by ¹H NMR and ¹³C NMR spectroscopy. The size of the copolymers was investigated by dilute solution viscometry and complex dynamic melt viscometry. The composition and structure of the soluble and insoluble fractions, obtained by chloroform extraction of the poly(ester-ether-siloxane)s, were identified by analysis of the ¹H NMR spectra. Extraction with chloroform confirmed the multiblock structure of both the soluble and the insoluble fractions.

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Nanoclay Exfoliation Effects on the Compatibilization with Polymer Matrix

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The authors studied the effect of the compatibilizing agents in polystyrene (PS) nanocomposites with:

• organophilised nanoclay by ion exchange and by ion-dipole interaction;

• organophilic nanoclay further modified with compatibilisers acting as exfoliating agents.

Two compatibilisers were used: copolymer (left photo) styrene-*alt*-maleic anhydride (PS-MA) and graft copolymer (right photo) polystyrene-*g*-polyethylene glycol (PS-g-PEG)

The effect of the exfoliation on the compatibilization with the polymer matrix was monitored by means of X-ray diffraction, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), melt-flow properties and dynamic-mechanical properties.

- Organoclay exfoliation diminishes the interactions of the alkyl-ammonium chains with the silicate, creating potential sites for the interaction with the polymer matrix. This effect is enhanced if the alkyl chains adopt an arrangement leading to an interlamelar distance larger than "bi-strate".
- The compatibilizing agents enhance the adhesion of the polymer matrix to the silicate; hence a better dispersion of the clay is obtained.
- Using exfoliated clay with PS-MA, a lamellar partially exfoliated / partially intercalated structure of the nanocomposite was obtained. These samples exhibited an even dispersion of the silicate in the polymer matrix and improved properties compared to starting material.

ATR/FTIR Spectroscopic Analysis of Emulsified Hydrous Epoxy System

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For the purpose of environment protection in coating products emphasis is placed on emulsions of epoxy resins and hardeners in water solution. The V1 and V2 systems based on water emulsions of epoxy resins were analyzed in this paper. The process of epoxy resin cross linking (EP 384W, EP 147W and EP 384W) with the chosen hardener (EH 623W) was monitored by ATR/FTIR spectroscopy. Fourier-transform IR spectroscopy proved to be a good method for monitoring and assigning of characteristic changes occurring during the cross linking process.
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Interface Shape and Solute Distribution during Crystallization from the Melt by Vertical Bridgeman Method

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In this study the influence of the solidification conditions on the microstructure and solute distribution was investigated. Solidification of six series of Al-Cu alloy was performed using Vertical Bridgman method.

According to the quantitative constitutional supercooling (CS) criterion [1], the critical rate for plane-to-cellular transition (R_{PC}) was calculated, and experimental values (R_{PC}^{exp}) were estimated. The critical microstructure corresponding to beginning of connection of cells is obtained at remarkable higher rate than the calculated R_{PC} [2,3].

According to the distribution of the solute along the sample, the effective distribution coefficient k_e was calculated [3].

From the CS criterion for R_{PC} and R_{PC}^{exp} and corresponding values of k_0 and k_e the following relation can be establish:

$$\frac{R_{PC}^{\exp}}{R_{PC}} = \frac{1 - k_0}{k_0} \cdot \frac{k_e}{1 - k_e}$$
(1)

which represents the line equation with the slope $n = \frac{1-k_0}{k}$.

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Figure 1. Correlation R_{PC}^{exp}/R_{PC} and $k_e/(1-k_e)$

Based on regression analysis, the value of R^2 =0.91758 was given and the coefficient od correlation *R*=0.958 was calculated.

This value shows very well alignment between parameters $\frac{R_{PC}^{exp}}{R_{PC}}$ and $\frac{k_e}{1-k_e}$.

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Pb_{1-x}Mn_xTe and PbTe_{1-x}S_x Alloys: Structural, Transport and Optical Properties

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The PbTe IV-VI compounds are narrow-gap semiconductors, with the band gap varying with composition from almost zero to 0.3eV. They can be used as infrared optoelectronic devices and thermoelectric materials in two-dimension quantum well systems. The effects of negative magnetoresistance, long-term non-equilibrium processes, the phonon dispersion anomalies in the high symmetry phase, and the low-temperature ferroelectric phase transition have been observed, too.

The different explanations have been proposed for it: in GeTe, SnTe and $Pb_{1-x}Sn_xTe$ the softening of TO-mode at the gamma point of the Brillouin zone, and in $Pb_{1-x}Ge_xTe$, forming the off-center ions. The off-centering effect means that impurity atoms are displaced from the regular lattice sites for about 0.5-1Å, forming the permanent dipole and changing the local conditions in the lattice.

 $Pb_{1-x}Mn_xTe$ and $PbTe_{1-x}S_x$ alloys are interesting materials for investigation in this field. In this paper we present the results of far-infrared reflectivity, Raman, X-ray, and Hall measurements of $Pb_{1-x}Mn_xTe$ (x \leq 0.12) and $PbTe_{1-x}S_x$ (x \leq 0.05) alloys. Measurements on these samples at different temperatures give us answers about Mn and S position in the lattice (off-centering), its clustering and ordering, as well as of influence of these processes on the crystal structure and properties. Also, we found that the phonons in $PbTe_{1-x}S_x$ show the two-mode behavior (each TO-LO mode pair of the end members degenerates to an impurity mode), while the $Pb_{1-x}Mn_xTe$ optical phonons have a intermediate one-two-mode behavior (LO-mode frequency shift continuously from PbTe to MnTe, while the other modes resemble the two-mode case). The model of phonon behavior based on Random Element Isodisplacement model, was applied. We obtained a very good agreement between experimental results and our numerical model.

Thermal Behaviour of Melt Spun Nd-Fe-B Alloy

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Thermal behaviour of melt spun Nd-Fe-B alloy with Nd low content was observed through phase transformations, for selected cooling rate and heat treatment regime.[1,2] The phase transformation and crystallization were detected by different investigation techniques: differential thermal analysis (DTA), X-ray diffraction analysis (XRD), thermomagnetic measurement (TM) and Mossbauer spectroscopic phase analysis (MS). Thermomagnetic measurement was done in the field 50 Oe with the temperature sweep of 4 K/min and supposed upper temperature limit was 1073 K.



Fig. 3 Mossbauer spectra taken before (a) and after (b) thermomagnetic measurements (A-Nd₂Fe₂₃B₃, B- α-Fe, C-Fe₃B, D-Nd_{1.1}Fe₄B₄, E-Fe₂B, F-FeB; X-belongs probably to the Nd₂Fe₁₄B phase).

In Figs. 1-2, the hysteresis loops before and after thermal treatment of thermomagnetic studies are presented. After first run of TM measurements, phases which are responsible for hard magnetic properties decompose which is prooved by hysteresis loop in Fig 2. MS spectra (Fig 3a,b) ilustrate the substantial difference between the state with optimized magnetic properties and after the decomposition induced by the TM measurment. Fig 3b exhibits the decay of the Nd2Fe23B3 phase and a dramatic increase of content of the α -Fe phase. This thermal decomposition will be the main reason for the quality loss of this hard magnetic material.

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Calculating the Thermodynamic Properties of the Ge-Ga Binary System

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The binary system Ge-Ga is one of the most interesting semi-conducting systems. In this paper thermodynamic properties, such as activity, coefficient of activity, partial and integral Gibbs mixing and excess energy for both constituents at three different temperatures, were calculated by experimental method of Oelsen calorimetry. The obtained results are shown in table 1.

Т	x _{Ge}	x_{Ga}	a _{Ge}	a_{Ga}	γ_{Ge}	γ_{Ga}	G_{Ge}^{xs}	G_{Ga}^{xs}	G^M_{Ge}	G^M_{Ga}	ΔG^{xs}	ΔG^M
К							J/mol					
1073	0	1	0	1	-	1	-	0	-	0	0	0
	0.0001	0.9999	0.0001	0.9999	1	1	0	0	-82165	-1	0	-9
	0.1936	0.8064	0.123	0.786	0.635	0.975	-4051	-226	-18694	-2148	-967	-5351
	0.3903	0.6097	0.289	0.532	0.740	0.872	-2686	-1222	-11074	-5630	-1793	-7755
	0.5903	0.4097	0.483	0.335	0.818	0.818	-1792	-1792	-6492	-9756	-1792	-7829
	0.7934	0.2066	0.718	0.139	0.905	0.673	-890	-3533	-2955	-17604	-1436	-5981
	1	0	1	0	1	-	0	-	0	-	0	0
1173	0	1	0	1	-	1	-	0	-	0	0	0
	0.0001	0.9999	0.0001	0.9999	1	1	0	0	-89822	-1	0	-10
	0.1936	0.8064	0.131	0.805	0.677	0.998	-3804	-20	-19822	-2115	-753	-5543
	0.3903	0.6097	0.304	0.561	0.779	0.920	-2436	-813	-11612	-5637	-1446	-7969
	0.5903	0.4097	0.505	0.349	0.855	0.852	-1528	-1562	-6663	-10266	-1542	-8139
	0.7934	0.2066	0.731	0.147	0.921	0.712	-803	-3313	-3056	-18698	-1322	-6288
	1	0	1	0	1	-	0	-	0	-	0	0
1273	0	1	0	1	-	1	-	0	-	0	0	0
	0.0001	0.9999	0.0001	0.9999	1	1	0	0	-97480	-1	0	-11
	0.1936	0.8064	0.142	0.815	0.733	1.011	-3287	116	-20659	-2165	-543	-5745
	0.3903	0.6097	0.327	0.598	0.838	0.966	-1871	-366	-11830	-5603	-953	-8033
	0.5903	0.4097	0.533	0.360	0.903	0.879	-1080	-1365	-6660	-10813	-1197	-8361
	0.7934	0.2066	0.768	0.154	0.968	0.745	-344	-3116	-2794	-19801	-917	-6308
	1	0	1	0	1	-	0	-	0	-	0	0

Table 1. Thermodynamic properties in Ge-Ga binary system at 1073 K, 1173 K and 1273 K

According to shown results, it is noticed negative deviation from Rault's law in Ge-Ga binary system, except for values x_{Ga} =0 do x_{Ga} =0.25 at 1273 K where it can be seen positive deviation from Rault's law. This means a good misciability of the components, especially at higher temperatures, except for values between x_{Ga} =0 do x_{Ga} =0.25 at 1273 K where gallium and germanium are not have good misciability. Coefficients of activity for both constituents are less than unity in whole concentration area. With increasing of molar content, coefficients of activity increasing at all three investigated temperatures. This pointed to the fact that deviation from Raul's law is less at higher temperatures. Obtained results for partial and integral excess and mixing Gibbs energies for both components also agreed with behavior of this binary system according to Rault's law. Partial molar Gibbs energy of mixing for germanium and gallium increase with content increasing and the negativity of this function also increases with temperature increasing.

Synthesis, Designing Structure and Formation Mechanism of Nanostructured Phosphorus Doped Tungsten Bronze Obtained by the Ultrasonic Spray Pyrolysis Method

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In our previous studies of polyoxometalates (POMs) of Keggin type we developed the process of doped bronzes receiving during thermally induced phase transformation of 12-tungstophosphoric acid (WPA) and its salts used as precursor [1,2]. The synthesized bronzes were obtained in the process of solid-solid recrystallisation of the anhydrous Keggin's anions.

The structural and conductive properties of the doped tungsten bronzes appeared to be well suited for application as cathode materials in secondary batteries and fuel cells.

With the aim to improve conductive properties of doped bronzes [3] we undertook new process of bronzes synthesis by ultrasonic spray pyrolysis method. In this paper the mechanism of droplet formation and its transformation into the phosphor wolframate sphere prepared by the process of ultrasonic spray pyrolysis using 20% a feeding water solution of the WPA atomised by ultrasonic atomizer with frequency 0,8 MHz will be discussed.

On the basis of theoretical models developed in the previous researches by V.Jokanovic et al. [4,5], all discrete values of particle diameters and frequency of appearance eg. quantitative number of each line in the size distribution spectrum were determined. Agreement between theoretically obtained basic structural parameters and experimentally determined values was confirmed.

Using IR spectroscopy and XRD analysis the phase composition of obtained spherical particles of phosphorous doped tungsten bronze was determined and compared with data from our previous research on the synthesis and caracterisation of doped tungsten bronze [1-3]. Besides this, the uniformity of distribution of ionic species W and P into phosphor wolframate particles is checked by EDS method.

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Microhardness and Morphology of Pulse Electrodeposited Ni-W Alloys

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The electroplating Ni-W alloy has been of considerable interest for its excellent wear and corrosion resistance even at high temperature. The Ni-W alloys were deposited electrochemically from ammonia-citrate electrolyte on a rotating disc electrode by direct and pulse current (at average current density of 70 mA cm⁻²). The effect of pulse deposition parameters, such as frequency (from 2.5 to 25 Hz) and ratio between pause and deposition time (t_p / t_c , from 0.2 to 5), on current efficiency, and composition, as well as on the morphology and microhardness of Ni-W alloys was investigated. The obtained results were compared with the corresponding values for direct current deposition.

The tungsten content in the deposited alloys was found to be from 11 to 25 mol %. The increase in the frequency and in the t_p / t_c ratio produced an increase in the tungsten content of the deposit, except for the case of the maximum value of the frequency and the pause to pulse ratio. On the other hand, increase in the frequency and the t_p / t_c ratio led to a decrease in the current efficiency. The broad XRD peak for alloy indicates very fine grained deposit. Crystal size, calculated from the Scherrer formula applied to the (111) peak, is about 5-6 nm. The size increases up to about 7-8 nm upon annealing. The lattice parameter of crystallite grains in the electrodeposited Ni-W alloy, calculated using the Bragg equation, is found to be larger than that of pure nickel, suggesting that the crystallite grains in Ni-W alloy is solid solution of tungsten in nickel. The appearance of weak diffuse peak centered at 96°, according to the literature¹, could be ascribed to the additional nanosized phases such as Ni₄W.



Fig.1 Microhardness of the deposited alloys

It should be noted that AFM images of the alloy surface show a periodicity higher than that calculated for the effective particle size derived Appearance of large from XRD pattern. aggregates, hills and valleys is most probably consequence of structural transitions the between crystalline and amorphous deposit.² Microhardness of obtained alloys is presented in Fig.1 as a function of the tungsten content. Increase in the tungsten content leads to an increase in microhardness of the alloy. After annealing at 450°C in nitrogen atmosphere microhardness increased due to the precipitation of very fine Ni₄W particles. The

electrochemical deposition by pulse current produced deposits with a finer grain size and lower porosity than that of the deposits produced by direct current, which may explain the higher hardness of the former.

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The Representative Particle of Flowing Copper Powder Electrodeposited by Reversing Current

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A model of the shape and surface structure of powder particles which permit the free flow of copper powder, in constant current deposition, was developed. From this model an apparent density of 2.2-2.3 g/cm³ was determined as the lower limit for the free flow of copper powder. On the other hand, powders obtained by reversing current electrodeposition can flow at considerably lower apparent densities. The aim of this work was to discuss this phenomenon.

The flowability of copper powder is mainly determined by the structure of the surface of the powder particles. If the surface structure of powders approaches the structure of the surface of bulk copper and if the shape of the partricles approaches a sphere, the friction in the powder mass is low and the flow of the powder is efficient. Besides, in these cases, the particle size distribution will not have an effect on the flowability of the copper powder, so non-sieved powders exhibit free flow. The model of the representative powder particle requires contact between the subparticles of the copper powder particle and in that way the behaviour of powders with large apparent densities characterized by free flow of non-sieved powders is explained, as illustrated in Fig. 1a. It can be seen from Fig. 1a that jamming of the particles is not possible and the a non-sieved powder obtained at 1600 A/m² can flow because of the structure of the particles.

On the other hand, as powders with considerably lower apparent densities, obtained by electrodeposition with reversing current flow can flow freely. It is known that powder particles, obtained at large current densities are very disperse but also that in pulsating overpotentrial and reversing current electrodeposition of metals, the parts of the metal surface characterized by a lower radius of curvature dissolve faster during the anodic period than the parts with a larger radius of curvature. In that way more compact structure are obtained. The powder obtained by reversing current flows regardless of the dendritic microstructure of the particles, as can be seen in Fig.1b. The surface structure or microstructure of the particles, does not allow the jamming of the particles and, hence, powders with considerably lower apparent densities than the critical for powders formed by direct current electrodeposition, can flow. A model of the surface structure of these particles which permits this flow was also developed.



Fig.1. Copper powder particles obtained at: a) 1600 A/m², apparent density 2.3 g/dm³, x1500 and b) reversing current deposition, amplitude current density 3600 A/m², cathodic time 1s, anodic time o.2s, apparent denisty 0.772 g/dm³, x2000.

Analysis of the Elastic-Plastic Bending of Shot Peened Sheets of AlMg4.5Mn Alloy

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Shot peening is an effective way of strengthening and pre-stressing elements for cars, aircraft, sheps, etc. The residual compression stress in the metal layers near the surface increases their lifetime.

To determine the residual stresses the deflection method has been applied and it is based on connection of models of residual stresses distribution depths, moment loading and elastic bending. The induction of residual stresses during shot peening is intensive. The elastic-plastic bending of sheet samples (Fig. 1.) can be modeled by applying the equation of an elastic line of a bend cantilever (Fig. 2.)

$$\mathbf{y} = \mathbf{a} \cdot \mathbf{z}_n^2$$
,

where: a – maximum of elastic-plastic bending;

 z_n – relative distance from the sample axis.

To define the residual stresses by deflection methods it is necessary to separate of elastic from plastic bending components. This separation is possible if the yield stresses are known. When successive layers of metal are removed from the shot-peened surface the stress distribution changes which cause sample to relax, resulting in decrease of elastic bending, while the plastic component remains unchanged.

Relation between fraction of elastic and plastic bending components depends on parameters shot peening process. For applied interval surface coverage from 60 to 90 %, of samples starting state, this relation changes from 0.37:0.63 to 0.1:0.9.



Fig. 1. Elastic-plastic bending of the shot peened sheet sample



Fig. 2. Bending line of the shot peened sample

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In this paper, by using automatic device QUANTIMET 500 MC, for the quantitative picture analysis and applying linear method of measurement through the example of AlCu15Mg3 and AlCu15Mg5 alloys, we have determined grain size (min, max and medium values), as well as relative standard measuring errors (RSE), dendrite arm spacing (DAS) and length eutectic (Le) and also distribution by size (histogram) and volume participation of α -hard solution and eutectic.

We have also studied the influence of grain-refining additives AITi5B1 for the same chemical composition of the aluminium-copper-magnesium alloy. It has been concluded that with the increase of titanium content, the mean value of grain size decreases. Titanium is added as grain refiner and it is very effective in reducing the grain size. If this results in a better dispersion of insoluble constituents, porosity and nonmetallic inclusions, a significant improvement in mechanical properties results. Grain size controls the distribution [1] of porosity and constituents, and for this reason the properties of the high-copper alloys are very sensitive to grain size.

In alloys containing high magnesium the average values of the DAS and grain size were found to decrease and we obtain a fine, uniform grain structure. Grain size and structure of dendrite and eutecticum depend on processing parameters [2], first of all on melt temperature and the solidification rate. Also, in alloys containing high magnesium the average values of the eutectic cell length and volume fractions of the eutectic were found to increase. Magnesium increases [3] the strength and hardness of the alloys, especially in castings, a decrease ductility and impact resistance.

Testing of properties of these materials included also measuring of hardness and determination of pressure strength. Hardness was measured by the Brinell method. Pressure strength of the samples was tested on an electronic cutter of 10 t. The changes in chemical composition of the alloy cause changes in the structure and these are reflected in the Brinell hardness and the compression strength. The hardness of the modified alloy is higher than the hardness of the alloy without any modification treatment. By increasing the content of magnesium the hardness and compression strength also increase.

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Composites

Optical Microscopy and Microhardness Characterization of Some Biovitroceramic Coatings (Composite Type) on Biocompatible Titanium

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The purpose of this paper is to characterize the biovitroceramic coatings (composite type) on biocompatible metallic substrates such as high purity and commercial titanium by optical microscopy and microhardness trials. The biovitroceramic layers belong to the oxide system: SiO₂-CaO-P₂O₅-R₂O (R=Na, K, Li) with additions of MgO, TiO₂ and B₂O₃. Reinforcing material of ceramic matrix is Ti powder added in different proportions. The metallic substrates (small plates and rods) were coated by an enameling procedure. All biovitroceramic coatings (composite type) titanium substrate couples followed a thermal treatment for phase crystallization. Titanium belongs to the biocompatible metals, being well accepted by the living tissue. But in time, titanium at the implant site is surrounded by a fibrous tissue that produces discomfort. The purpose of the covering the biocompatible metallic implants with biovitroceramic layers is to form a very strong bond between the covered implant and the bone tissue. At the contact between biovitroceramic layer and bone, a very thin hydroxyapatite layer is formed due to an ionic exchange. Because the biovitroceramic layers have poor mechanical characteristics we reinforced them with Ti powder thus obtaining a composite material. We chose Ti powder as reinforced material because the substrate material is made of titanium and so the expansion thermal coefficient of the ceramic material is lowered and close of that of titanium. The ceramic coating adherence to the metallic substrate is better when the two expansion thermal coefficients are identical or very similar. All the couples were examined by optical microscopy and Vickers microhardness trials. From Vickers microhardness trials made in vitroceramic layers we obtain information about the fracture toughness and brittleness. From Vickers microhardness trials made at the interface of vitroceramic layers - metallic substrate couple we obtain information about the adherence of the layer. A sample of biovitroceramic coating (ceramic matrix having the composition: $SiO_2 = 48$; CaO = 10; $P_2O_5 = 6.8$; $Na_2O = 7$; $K_2O = 7.5$; $Li_2O = 2.9$; MgO= 3.3; $TiO_2 = 1.3$ and $B_2O_3 = 13.2$ % wt. where 0.4 % wt. Ti was added) - titanium substrate is shown in Fig. 1.



Fig.1. Optical micrograph of a cross section in a biovitroceramic (composite type) coating – titanium substrate; the three light phases are titanium particles; with metallographic etching: 10 ml HF + 5 ml HNO₃ + 85 ml H₂O.

In our experiments we obtained couples having coatings composed by a ceramic matrix reinforced with titanium powder up to 8 % wt. Ti.

Composite Materials Based on Bentonite in Environmental Protection

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Nonwoven geotextiles are widely used for functions of separation, reinforcement, drainage, erosion control and moisture barrier [1]. The specially designed nonwovens and composites with nonwovens are gaining importance in environmental protection as filters, bio-barriers and geosynthetic clay liners (GCL). GCLs are made by bonding dry bentonite in powder or granular form between layers of two nonwovens. The bonding can be performed by sandwiching the bentonite between nonwovens by needling and/or stitching or the bentonite layers are adhered to nonwovens by water-based adhesive. The GCLs act as barriers, while bentonite component of GCLs acts as sorbent for pollutants. The polypropylene (PP) fibers are the most commonly used for production of nonwoven component of GCLs. Bio-based materials are seldom used in geotextiles mainly for temporary or short term applications.

In this paper the possibility of using hemp-based nonwovens in composite material based on bentonite was investigated. The main goal of this work was to study the influence of using hemp as component of nonwoven on capability of composite to remove heavy metals from solutions.

Two types of composite materials based on bentonite were synthesized. In the first type of composite the bentonite layer was embedded between two nonwovens solely made of PP fibers. The second type of composite contained hemp as component of nonwoven. The properties and quality of bentonite layer in both types of composites were the same. This layer consisted of chemically, physically, morphologically and texturally characterized bentonite powder (75-500 μ m) from coal mine "Bogovina", Serbia [2]. In both composites the mass ratio between textile and bentonite part of composite was 1:2. Hemp from Bački Brestovac, Serbia was previously chemically modified in order to obtain fine fibers used in synthesis of second type of composite. Needle-punched PP nonwoven "INTEX", Mladenovac, Serbia (m_A = 40 g/m²) was used for first type of composite was formed by alternating layers of hemp and PP. Both lower and upper nonwoven part of composite had only 30 mass % of PP. The die pressing on elevated temperature (170°C) enabled thermal bonding of hemp fibers and composite formation.

By using the obtained composite materials the efficiency of Pb²⁺ ion removal from solutions was measured. The solution of known concentration of Pb²⁺ was filtrated through investigated composites. The filtration area was constant for all experiments. The investigation process consists of four filtrations and one rinsing cycle. Different flow rates were implied in order to investigate the influence of contact time on sorptional properties of composite. The Pb²⁺ content in filtrate was measured by dropping mercury electrode using polarograph 757 VA Computerance-Metrohm in presence of acetate buffer. It was found that the amount of previously adsorbed Pb²⁺ ions does not affect composite, no leaching in filtrate was detected. Degree of Pb²⁺ removal exponentially decreases with the increase of flow rate. The efficiency of heavy metal removal by two types of investigated composites was compared and discussed.

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Charging Properties and Cycle Life of a Carbon Supported RuO_xH_y Composite

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Due to the large specific capacitance of the order of hundreds of Farads per gram,^{1,2} hydrous ruthenium-oxide is the most promising candidate for the application in electrochemical super and ultracapacitors. For the purposes of technological impact, the oxide redox pseudocapacitance is combined with double-layer capacitance of carbon blacks.³ The use of colloidal oxide dispersion for the impregnation of carbon blacks produces the composite material of excellent capacitive properties.⁴

In this work, the composite materials were produced from differently prepared RuO_xH_y sol by the impregnation⁴ of BP 2000[®] and XC72-R[®] carbon blacks, both from Cabot Corp. Differently aged sols, prepared by different procedures were used, while ultrasonically formed water suspensions of composite were applied onto Au disk with the aim to prepare an eletrode layer. The formed layer was covered by Nafion[®] to make it more coherent. Charging/discharging properties and changes in capacitive performances of carbon supported hydrous ruthenium-oxide with cycling was investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), in 1.0 mol dm⁻³ H₂SO₄.

The impregnation of XC72-R with a small amounts of oxide from colloidal dispersion prepared by forced hydrolysis of ruthenium-chloride, leads to about four-fold increase in capacitance, compared to the double-layer capacitance of carbon itself. It was observed that preparation conditions of electrode composite layer cause the changes in composite capacitive behavior with charging/discharging cycles, while the EIS measurements indicates the in-depth distribution of the capacitance within porous composite layer.

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Nanocomposites by Cationic "*in situ*" Polymerisation: the System Monomer-Clay-Lewis Acid

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Heterogeneous catalysis as direct synthesis of composites is one of the main fields of activity of the authors [1]. The polymerization initiated onto the surface originates in the heterogeneous catalysis and was in some extent systematically studied [2]. Natural silicates as reaction sites for the polymerization *in situ* were scarcely used in some radical systems [3] and in some Ziegler-Nata [4] systems.

Cationic heterogeneous polymerization is better explored on synthetic support [2,3,5]. An interesting system is ϵ -caprolactone initiated on a mica-type silicate [6].

This work presents the preparation of a layered silicate, its activation with a Lewis acid and the initiation of the polymerization of a series of monomers having different polarities. Resulting nanocomposites were characterized by means of electron microscopy, X-ray diffraction and thermal analysis (DSC and TGA). Reference samples were prepared by melt intercalation of the same polymer in a silicate with the same preliminary preparation, except its activation with Lewis acid. The analyses reveal that melt intercalation leads to agglomerates and to a composite with less improvement in properties. For the same silicate, the polymerization *in situ* favors the delaminating of the silicate with an extended intercalation of the polymer (in photo) between the layers of the silicate. Thermal stability is significantly increased for the samples obtained *in situ*.



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Examination of the Antibacterial Activity of Silver Coatings at the Carbon Material Surface

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Activated carbon is material which has porous structure and high adsorption capacity. Due to these characteristics, activated carbon has been used in water purification treatment, as the adsorbents for the removal of inorganic and organic pollutants (phenol, detergent, pesticide, hydrocarbons) [1]. However, during water purification process, bacteria preferably adhere to solid supports made of carbon materials. Bacteria may breed on the activated carbon, so that the activated carbon itself becomes the pollutant [2]. Silver is well known for its bacterial effects [3]. Therefore, it is assumed that activated carbon supporting silver have antibacterial effects.

The aim of this work was preparation of the different carbon materials with silver coatings and examination of their antibacterial behavior in the flow system. Two samples of granulated activated carbon (GAC) and two samples of carbon monolith (CM) were prepared, impregnated with similar amount of silver. Silver was spontaneously deposited at the surface of GAC emerged into AgNO₃ solution, and at the surface of CM by passing the AgNO₃ solution through the tube. First sample, of both GAC and CM, was rinsed from AgNO₃ residue. On other two samples the reduction of the residual AgNO₃ was achieved by chemical reduction with NaBH₄. GAC samples surface composition and silver particles are shown in SEM micrographs. Resistance to attrition of the activated carbon supporting silver was tested, and the results were compared with maximum silver concentration allowed in drinking water.

Antibacterial activity of these samples was determined using standard microbiological methods. Both tested carbon materials samples supporting silver, inhibited Escherichia coli grow. Antibacterial activity depends upon impregnation method. Chemical reduction of silver with NaBH₄ appears to be efficient method for impregnation of carbon material with silver, due to low amount of silver rinsed and good antibacterial activity.

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Obtaining and Characterization of Langmuir Blodgett Film from New Phthalocyanine Compounds

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Surface activity, including self-assembling properties as monolayers and multilayers at gas-liquid and solid-gas interfaces was investigated for some methalic phthalocyanine derivatives.

Phthalocyanine compounds with Cu and Sm, and various substituted hydrophobic and hydrophilic groups were investigated, in order to determine the monolayer forming and deposition Langmuir-Blodgett films behaviour. As expected, the copper phthalocyanine substituted with dodecyl hydrocarbon chain show the best monolayer behaviour at the air-water interface, forming a flexible and coherent film that can be deposited onto solid substrate.

For the more hydrophilic compounds, which form rigid films, or no stable film, the behaviour of the phthalocyanine compounds in their mixture with phospholipids and stearic acid was investigated. Some usual equations were used to fit the experimental data of bidimensional pressure isotherms at air-water interface for above simple and mixed systems with phtalocyanines. Observed surface pressure-area isotherms were of the simplest type, with no indication of phase transition or discontinuities, for the pure compounds and mixtures forming stable monolayers. Minimal molecular areas were determined from a serie of isotherm experimental determination at low compression rates, indicating that these systems have a large number of configurational states which are not capable of self-assembling quickly into a compact monolayer of highest density. Some models are proposed for the orientation of the phthalocyanine molecules at the air-water interface (for more compounds it appears that orientation at the water surface it is essentially flat.

Thin films from pure phthalocyanine compounds and their mixtures with long chain amphiphiles were obtained by deposition onto glass and silica solid surfaces. The monolayers at the air-water interface were transferred as Langmuir Blodgett films by using different techniques (Y and Z-type depositions, tilting method).

The composition and the degree of ordering in phthalocyanine films have been investigated using electron microscopy, UV-VIS spectroscopy and contact angle measurements. Examples of the mixtures phthalocyanine-long chain alkyl surfactants are excelent for fabrication of Langmuir Blodgett films, giving evenly deposited well ordered bilayer assemblies by Y type deposition. The homogenity property of the Langmuir Blodgett films deposited onto solid surface from monolayers in various states were investigated in order to determine the most suitable surface pressure of the monolayer to be used.

Particular attention has been given to films containing Sm derivatives, which is described as a compound with many potential applications in sensor devices.

The possibility to obtain highly ordered monolayers at the air-water interface in mixed systems with Sm phthalocyanine derivatives should appreciably extend the utility of the new Sm derivative in Langmuir-Blodgett films obtained with various transferred techniques.

Semiconducting Properties of Oxide Films Formed on Valve Metal Electrodes

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Valve metals and theirs anodic and thermal oxides have been widely investigated due to theirs applications in: chemical mechanical and air space industry. Theoretically the anodic and thermal oxide films formed on valve metals must be isolators. Practically they have the semiconducting properties due to existence of various surface defects, during the film formation /1,2/.

The semiconducting properties of anodic oxide films formed on valve metal electrodes Zr, Nb and Ti were studies in various concentrations of acid and alkaline solutions, using optical and photoelectrochemical methods. The oxides were grown under potentiostatic conditions, up to first sign of electronic leakage or breakdown. This sign strongly depends of type and electrolyte concentration, as well as valve metal utilized. For example the limit anodic potential for Ti in 1 M HNO_3 is 22 V, while for Nb in 1 M KOH is higher than 150 V.

For all investigated metals the films grow via a high field conducting mechanism and the film thickness increase linearly with applied potentials. Over the breakdown potential the film thickness begins to deviate from linear plot and at spark voltage the complete perturbation of film properties occurs.



By measurements of optical constants and band gap potentials of natural and anodic oxide films with various thickness, the big change in transparency and semiconducting properties have been shown. Catho-dic reduction inserts hydrogen into the oxide to a limited depth and the outer layer films formed is optically absorbing. Subsequent anodic oxidation of Zr and Nb removes the hydrogen and returns the film to its initial state monitored by strong and very sharp potentiodynamic anodic peaks. For Ti, at higher cathodic potentials the various hydrides are formed depending of utilized electrolyte. The refractive indices of all investigated metal oxides have been determined and it is shown that the conductivity of anodic oxide films increase from the formation of passive films to limit breakdown potential. The n-type and band gap of oxide films were determined by the

spectra measurements as shown on fig. 1. The surface defects accumulated on anodic oxide films at higher anodic potential were visually observed matallographic microscope, through various grains color

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Growth and Characterisation of Chemical Bath Deposited Zinc Sulphide Thin Films

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Zinc sulphide (ZnS) thin films are promising material for the manufacture of optoelectronic devices. Zinc sulphide could be used as light emitting diode in the blue to ultraviolet spectral region due to its wide band gap (3.7 eV), as reflector and dielectric filter because of its high reflective index (2.35) and its high transmittance in the visibil range, respectively [1]. Many techniques have been used to prepare metal chalcogenide films such as chemical bath deposition (CBD), sputtering, chemical vapour deposition and electrodeposition [2].

Zinc sulphide thin layers have been grown onto glass substrates by chemical bath deposition (CBD). According to our previous works, special CBD technique could be used in order to prepare mono-and multilayer metal chalcogenide thin films with variable thickness [3,4]. The aim of this work is to study the influence of different preparation conditions on thin film quality and, consequently, on some of structural and optical properties of mono-and multilayer ZnS thin films...

The deposition of zinc sulphide was performed at 85°C under continuous stirring, from chemical bath containing variable amounts of thiourea, zinc acetate, ammonia and sodium citrate. Prior the deposition stage, optical-glass platelets were degreased and ultrasonically cleaned in etanol-acetone mixture. ZnS/glass structures were annealed at 500°C in nitrogene atmosphere. Crystalline structure and optical properties were investigated by XRD, UV-VIS, FT-IR and luminescence spectroscopy.

The morpho-structural characteristics (fig.1) as well as the optical properties (fig.2) of zinc sulphide thin film are strongly influenced by growing and annealing conditions.





Fig. 2. Dependence of ZnS thin films thickness on deposition time (multi-layer technique)



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Electrophoretic deposition is a process where suspended solid particles are deposited directly from the stable suspensions/sols under the influence of an electric field. The electrophoretic deposition process allows control of the film thickness, uniformity and deposition rate, so it is well known, for many years, as a forming method for the films with various performances and for different applications [1-5]. Using this method for film production it could be recognized that the decrease in particle size decreases the temperature of sintering [6]. The use of sol-gel routes in ceramic processing has many advantages in comparison to conventional powder-based processing technique [7].

Boehmite water sol was prepared by precipitation method, starting from $AlCl_3 \cdot 6H_2O$ [8]. The characterization of boehmite powder, obtained from boehmite sol by drying at 90 °C for 48 h, was performed by IR spectroscopy and X-ray diffraction. The pH value of boehmite water sol was 3.82 and the solid phase content was 1.76 wt.%.

The influence of the deposition parameters on the electrophoretically deposited boehmite coatings on titanium from boehmite water sol was investigated. From the time dependence of deposition current density for constant applied voltage, it was observed that electrophoretic deposition of boehmite coatings corresponds to deposition of porous films [9]. The effect of applied voltage (1 -10 V) and deposition time (10 - 30 min) on the mass of boehmite coatings, at the room temperature, was determined by weighing the cathode before and after deposition process. It was shown that the increase in applied voltage over 6 V decreases the coating mass for longer deposition time (30 min). This behavior could be explained by the larger amount of evolved hydrogen on the cathode at higher voltages and for longer deposition times [3] and additionally, by poor adhesion of ceramic coating before sintering [5].

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EIS Characteristics of the Oxide Films Formed on Carbon Steel at High Temperature and Different Water Chemistry Conditions

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The corrosion tests have been developed and conducted at Institute for Nuclear Research (INR) in order to investigate the characteristics of the oxide films depending on the coolant chemistry.

The oxide films were formed by static autoclaving of the carbon steel samples in water at 260°C (5.1 MPa) and 310°C (9.8 MPa), for different periods of time under the following conditions:

- LiOH solution (pH=10÷11.5);
- AVT solution (demineralized water treated with cyclohexylamine and morpholyne);
- AVT + N₂ H₄ (hydrazine) solution, and
- AVT + HQ (hydroquinone) solution, their pH being 9.5-9.7.

The examination of the oxide films formed on the tested samples was done by using the EIS technique, metallographic microscopy and X-ray diffraction.

The experimental data allowed us to identify the influence of pH value and of the additive agents on the protective/no protective characteristics of formed films. The results emphasized the possibility to correlate the oxidation process parameters with the pH and with the presence of additive agents.

Chemical Nickel Coatings on a Steel Surface

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This paper presents procedure of the chemical nickel plating on the steel surface with the optimal working conditions.

Nickel coating can gives hard and smooth layers with good corrosion protection, and it is possible to obtain on the surface of different materials, by chemical process too. Chemical process has advantages over electrochemical process in being harder, having a higher resistance to friction, wear and very high corrosion stability, including possibility to depositing smooth layer on large and complicated profile and enables making layer on surface non-accessible for current.

Nickel coatings obtained by chemical method, with the sodium hypophosphite as the reducing agent, contain co-deposited phosphorus. The phosphorus gives better corrosion resistance, hardness, and adhesion on the surface, ductility, less porosity and another good property to coatings.

The experiments were carried out in the laboratory on the steel surface, with the acid solution. For the samples pretreatment it was used polishing by grinding, the chemical degreasing with strongly alkaline solution and the pickling in hydrochloric aqueous solution.

The optimal working conditions for obtaining nickel layer by the chemical process were:

•	the concentration of nickel	5.0 – 6.6 g/dm ³
•	the concentration of reducing agent	30 - 40 g/ dm ³
•	pH value	4.2 – 4.8
•	the temperature range	356 – 365 K
•	ratio of solution volume to area of metal surface	$0.7 - 1.5 \text{ dm}^2 / \text{ dm}^3$
•	filtering	permanently

The concentrations of nickel and reducing agent present in the solution were controlled with analytical method by titration. This solution is very stable and has high covering power it can have duration seven times change of whole nickel concentration. During the chemical nickel process it was made an insoluble compound nickel phosphite, which has been accumulated in solution and it can not be regenerated.

The chemical nickel process under those conditions deposits protective coatings with decorative effects, bright metallic gray colored coating, decorative and smooth layer, free from porosity, with good adhesion, ductility and acceptable mechanical-physical properties. On this layer it is possible to deposit any kind of metal coatings applying as the electrochemical as the chemical process.

Bioactive Glass-Apatite Coatings for a Titanium Implant

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Titanium and titanium alloy are widely used as materials for implants, because of their mechanical properties and nontoxic behavior. Unfortunately, metallic implants are bioinert, which lead to encapsulation by dense fibrous tissue in the body. As a consequence, non-appropriate stress distribution at the bone-implant interface appear, which can lead to interfacial failure and loosening of the implant.

In order to solve this problem, the metal implant could be coated with bioactive materials with good adhesion to metal and which could be also bonded interfacially to the bone.

The aim of this work is to investigate the synthesis of glass coating on Ti6Al4V alloys by the spray technique. In order to enhance bioactivity of the coating, hydroxyapatite particles were embedded on the coating. The influence of the glass to hydroxyapatite particle ratio on the morphology, adhesion and bioactivity of coatings were investigated

As starting materials, the bioactive glass in the SiO_2 -CaO-MgO-Na₂O-K₂O-P₂O₅ system, melted at 1500°C for 4 hours is used. The glass is previously pulverized in the planetary mill for 1 hour. The coatings are synthetised by spraying the glass and apatite powders on titanium Ti6Al4V alloy substrate and fired in dental furnace up to 830°C for 30 s. Coating is characterized by SEM and FTIR analyses.

It was found that the thick of coating and thermal treating make an important role on the formation and adhesion of coating to titanium substrate. Incorporating of hydroxyapatite particles into the coating enchance bioactivity of synthetised implant materials.

Some Possibilities of Electroplating Silver Coatings onto Aluminum

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The aim of this paper was to give contribute, also using some experimental experience in this branch through experimental work, in finding some electrolytes and optimum conditions for electroplating of final silver coatings. Besides, the chemical deposition of zinc and tin has been avoided since the copper coating was directly electroplated onto aluminum. Afterwards nickel and silver coatings were deposited on this copper coating from the commercial baths.

The chemical preparation of aluminum samples was performed in solutions (1-4): 1) degreasing solution 50% $Na_2CO_3 + 50\% Na_3PO_4 \cdot 10H_2O$; (5% aqueous solution), $t = 60 - 70^{\circ}C$; $\tau = 15$ min; pH=7,5; solution no. I for pickling: 20% NaOH + 2% NaF; $t = 70-75^{\circ}C$; $\tau = 2-5$ min; 3) solution no. II for pickling: HNO_3 (550ml/I) + H_2SO_4 (200 ml/I) + NaF (140 g/I); room temperature; $\tau = 5$ min; 4) bright dipping solution: HNO_3 (20%) + HF (10%); room temperature; $\tau = 5$ min. The copper coating was directly electroplated on chemically treated aluminum from the solution: $CuSO_4$ (55 g/I) + CH_2NH_2 - CH_2OH (100 g/I) + (NH_4)₂ SO_4 (30 g/I) + $Na_2SO_4 \cdot 10H_2O$ (75g/I) + Na_2CO_3 (3 g/I); room temperature; $j = 0,3 A/dm^2$; pH = 10,3. Afterwards nickel was deposited onto copper coating from the bath: $NiSO_4 \cdot 6H_2O$ (300 g/I) + $NiCI_2 \cdot 6H_2O$ (45 g/I) + H_3BO_3 (35 g/I); $j = 2 A/dm^2$; $t = 45-50^{\circ}C$, and finally the silver was electroplated from the bath: $Ag_{(met.)}$ (20-33 g/I) + $KCN_{(free)}$ (30-45 g/I) + K_2CO_3 (30-90 g/I); room temperature; $j = 0,3-0,5 A/dm^2$; specific aditives for brightness and ductility of coating with compulsory mixing of electrolyte. Structure characteristics of metallic coatings on aluminum were inspected by scanning electron microscopy (SEM) and scanning tunneling microscopy (STM).

Results of analysis show that metallic coatings with very good structural characteristics can get beside classical zinc procedure and at direct electrochemical deposition of metallic coatings on aluminum, at exact defined conditions: concentration of plating bath, electrochemical and technological parameters.

The structure of final coating of silver depends on the structure of basic copper coating i.e. the concentration of *NaF* in the solution. Analysing SEM microphotographs it can be concluded that the final silver coating follows the structure of the copper coating and that nickel intercoating plays very important role and has great influence on the structure of silver coating. In this paper structural characteristics of basic copper coating and final silver coatings examined with SEM (scanning electron microscopy) were shown.





Fig.1. SEM microphotographs of silver coating on the aluminum (undercoat of Cu and Ni). a) 2 g dm⁻³ NaF; *b)* 2.5 g dm⁻³ NaF. Magnification: x1500.

On the Pulverization Method for Photocatalytic TiO₂ Coating Deposition I. Structure and Face Composition

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A systematic study on the capabilities of the spray methods for TiO_2 coatings deposition is performed aiming to elucidate the effect of the: (i) type of the substrate, (ii) temperature of the heating of the substrate during the spraying, (iii) temperature and the time of the post-deposition annealing, (iv) chemical composition of the spraying suspension, (v) preliminary ultra-sound treatment of the suspension on the: (a) crystal structure (crystallites size), (b) morphology, (c) phase composition, (d) adhesion, (e) photocatalytic properties of the so obtained films.

It is believed that such a study may be useful for: (a) better elucidation of the effect of crystal structure and morphology of the films on their catalytic properties, (b) optimization of the preparation conditions, as to gain better performance of the final photocatalytic material.

Materials. TiO_2 (Degussa P-25) was used in all of the experiments. The microscopic slides, matted fused silica and stainless steel were used as substrate. Malachite green oxalate (Chroma) water solution was used as a model pollutant in the preliminary photocatalytic testing.

Deposition procedure. The device used is designed and constructed by some of the autors of the present report and is described elswhere. The pulverization regime was established in preliminary experiments and was kept constant through all the representative deposition procedures. The coating thickness was controlled by the number of spraying and was about 0.5 mg/cm². The suspension was prepared in methanol with (in some of the experiments) ethylene glycol (EG) or polyethylene glycol (PEG) with molecule mass 2000 or acetylacetone as additives. The deposition was done at ambient temperature of the substrate (silica), at ambient or 300 °C (glass) and at 100 °C (steel). The deposited films were annealed for 1 hour at 300 °C or 400 °C or 500 °C when no additives were added and at 500 °C when the latter presents in the starting solution.

Characterization. The crystal structure (crystallites size) and phase composition of the films were studied by X-ray diffractometry. Their morphology was estimated by SEM. The testing of the photocatalytic activity was done following the procedure described by other authors.

Results. About 50 films were produced varyingt the above described conditions. The results can be summarized as follow: (a) The deposition following the above described procedures causes a small (2-20 %) decrease of the TiO_2 crystallites size. (b) As can be expected the relative content of anatase is kept constant even when films on glass substrate is post-deposition heated at 500 °C. Some increase is observed at 500 °C heating of the films on silica and steel substrates but the difference is almost in the limits of the uncertainty of the method used for phase composition determination. (c) Post-deposition heating at 500 °C seems to be satisfactory for the elimination of the products of the thermal decomposition of the organic additives. (d) No significant effect of the substrate nature (glass or silica) and post deposition heating temperature (300 °C or 500 °C) on the films morphology is observed. The films are porous with strong agglomeration. (e) The preliminary treatment of the initial suspension by ultrasound disintegrator increases significantly the stability of the suspension, enhances the deposition procedure and ensures more uniform films with less expressed agglomeration. (f) The addition of PEG 2000 makes the coatings much more uniform and increases their porosity. (g) The addition of EG to the suspension makes the films even more uniform (comparing with the ones prepared in the presence of PEG) but little less porous. (h) The study of the photocatalytic effect and adhesion of the films is in progress.

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Electrical Resistance of Agrocellulose Textiles under Different Conditions of Humidity

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Since textile materials are dielectrics with usually very high electric resistances, which cause the unfavorable static electricity generation, it is very important to investigate the influence of external factors on their electrical behaviour. It is well known that textile material electric resistance strongly depends on humidity, and so on sample moisture content. Therefore the methods for determination the influence of humidity on textile materials electric resistance have been investigated. The special arrangement for determination of textile materials electric resistance, with a determined atmosphere in the measuring zone, which authors developed earlier, was used. The application of the equipment enables examining of the dependence of the textile materials electric resistance on the environmental humidity in regain moisture content in absorption as well as in desorption.

The arrangement was applied for electric resistance determinations of some hemp based samples having different constructions and raw material compositions.



Dependence of electrical resistance of cotton/hemp blend fabric on environmental humidity

A strong dependence of the textile materials electric resistances on the raw material composition and moisture content of the examined samples was observed.

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Application of QSAR and Other Computational Methods in the Field of Textile Dyes

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An outline of adsorption isotherms of several textile dyes on cotton fibre studied in our institute is presented. The experimental data obtained from the cellulose dyeing were fitted by linear/nonlinear regression analysis with the standard Nernst, Freundlich and Langmuir isotherms and the general multimodal adsorption model. Thermodynamic parameters (equilibrium constants, saturation concentration values) were derived by regression analysis. Adsorption models on cellulose are discussed. A review of QSAR/QSPR (Quantitative Structure-Activity/Property Relationship) for dye-cellulose fibre binding and calculations of pertinent (electronic, geometric and partition) properties of dye molecules is given. Reviewing of modern QSAR methods for dye-fibre adsorption is presented. Conclusions from these QSAR studies concerning the effect of structural features of dye molecules upon adsorption on cellulose fibres are discussed.

Properties of Alkali Modified Hemp Fibres

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Among traditional textile raw materials, bast fibres (especially hemp fibres) exhibit specific properties (high breaking strength and good sorption properties) and structural features that make them different from other fibres. Hemp fibres are ideally hygienic, antielectrostatic (low electric resistance), ultraviolet radiation-resistant, biodegradable, biocompatable, etc. Hemp fibres exist as technical fibres, consisted of a number of elementary fibres held together by pectinous gums. The pectins of the inner lamellae are encrusted with lignin, which makes it even more difficult to split the bundles into technical fibres. The methods for modification of hemp fibres, in order to make them finer, cleaner, soft and more suitable for processing on machines of higher efficiency than traditional hemp machines, are chemical, chemo-mechanical and mechanical methods [1-4].

In this paper, hemp fibres were modified chemically by alkali treatment. The progressive removal of the lignin, pectin and hemicelluloses, was carred out by the fibre bundles treating with 5% and 18% NaOH solution (1:50 liquor ratio), for 5, 10, 15 and 30 minutes, at room and boiling temperatures, and both under tension and slack. Such modified hemp fibres were washed with 1% acetic acid, and water, and dryed. The modified hemp fibres were caracterised by determining their chemical composition, fineness, mechanical and sorption properties.

Determination of chemical composition and investigation of physical and mechanical properties of modified hemp fibres indicated that fibres were finer (2-10 times), with a lower content of lignin (2,5-5,5%), increased flexibility, brightness and crease resistance as well as lower hairiness, with mostly unchanged mechanical properties. However, in some cases mechanical and sorption properties were improved (modification with 18% NaOH, under tension and slack).

The appropriate choice of procedure for determination of chemical composition and establishment of the completely new method for determination of breaking strength of bundle of hemp fibres contributed greatly to development of criteria and methods for evaluation of hemp fibre quality.

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Non-Wovens Based on Hemp as Acoustic Absorbers in Automotive Interiors

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Nonwovens provide a variety of functions in automobiles including passenger comfort, noise abatement and engine and interior filtration. The goal of this paper was to design materials that provide a quiet passenger compartment and automotive interior.

By using sound absorbing materials attached to various components such as doors, quarter panels, trunk sides and floors, headliners and others it is possible to reduce noise in automobile. In this paper several hemp-based nonwovens are tested in order to characterize there properties as noise absorbers that reduce the overall sound level in the passenger compartment.

The ability of a nonwoven material to absorb sound or unwanted noise in the passenger compartment of the vehicle is based on dissipation of the energy of the sound wave upon passing through the material and being redirected by the fibers, and also upon conversion of some of the energy into heat [1, 2].

The low cost, renewability, biodegradability and recyclability of hemp as the natural cellulosic fiber made it attractive as the material for a potential sound-absorbing nonwoven.

In this paper various blends of hemp-based nonwovens manufactured by hot pressing process ware tested for their ability to absorb sound energy. Hemp from Bački Brestovac, Serbia, was previously chemically modified by alkaline procedure in order to obtain fine fibers used in synthesis of composite. Second constituent of sound-absorbing composite was spundouce-spunbond thermal bonded nonwovens based on polypropylene ($m_A = 16 \text{ g/m}^2$). The nonwoven web of composite was formed by alternating layers of hemp and polypropylene (PP).

PP fibers in the hemp composites were used for thermal bonding. The specific mass and thickness were picked based on the normal practice materials used in vehicles. The amount of PP in composite varied between 10 and 30 mass% in order to establish the most efficient composition.

After processing the samples, each were cut into parts and inserted into the impedance tube for rank order absorption testing against commonly accepted levels for such "absorbent" materials. Testing was performed at various frequencies chosen to represent different types of noise in vehicles, such as low frequency vehicle structural noise and high frequency like wind or tire noise [1,2]. The amount of sound reflected by the sample was compared to the original wave.

In each of the hemp-based samples tested, the amount of absorption was recorded. The correlation between sample thickness and composition and absorption properties of composite was established.

Investigated nonwovens based on hemp are proved to be components that car manufacturer might use in cars to provide the quiet interior passenger compartment.

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Comparison of the Pin Method and Disc Method for the Estimation of Agrocellulose Woven Fabric Drapability

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Elasticity of woven fabrics is an important topic in various scientific textile researches, both from the theoretical and practical aspect. Studying the elasticity of clothing fabrics is becoming of importance when the estimation of their quality during wearing is concerned. During the exploitation, clothing fabrics are exposed to conditions of various mechanical forces that can provoke their deformation. These phenomena lead to the general aesthetic impression being disturbed. Because of that it is necessary to investigate the mechanical characteristics of fabrics under conditions that are the most approximate to the real conditions of fabric's usage.

Since textile surfaces, intended for clothing industry, during their exploitation are often exposed to the action of forces that provoke bending deformation, it is possible to say that bending is one of the most frequently investigated deformation of woven fabrics. These investigations are often realizing through the indirect indicators like wrinkling and drape. On the basis of the investigation of agrocellulose clothing fabrics drapability, the estimation of the fabric's surface appearance as well as the degree of it's elasticity can be monitored. It is also possible to have insight into the form stability of fabric and its dimensions.

Two methods, pin method and disc method, for the investigation of woven fabrics drapability are developed. Pin method is very simple for realization and efficient; it does not demand great financial investments. Constructed apparatus enables simultaneous determination of drape coefficient both in warp and in weft direction. Disc method, which requires more complicated apparatus with rigorous criterions in respect to the sample's illumination and some longer period of time for the realization of experiment, enables more detailed multiaxial information about bending of sample under it's own weight. Owing to more detailed insight in bending characteristics of investigated sample, disc method shows certain advantage in regard to the pin method. Keeping in mind existence of good correlation of the obtained results by the application of both mentioned methods, it might be concluded that pin method gives the reliable information about the investigated fabric's drapability in the case when disc method is not disposed.

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Thermodynamic Study of Direct Dye Adsorption on a Cellulose Substrate

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Dyeing is not a purely physical process like painting or other coloring processes involving the physical application of pigments. There are many difficulties encountered in controlling the physico-chemical changes that occur during dyeing. Therefore, the dyeing process was extensively studied, but it was not been satisfactorily explained yet. The results of dyeing measurements may be reported as sorption isotherms and the equations most widely used for describing the equilibrium sorption were proposed by Nernst, Freundlich and Langmuir.

Cellulose fibers can be dyed with more different categories of dyes (e. g. direct, sulfur, vat, fiber reactive and azoic combinations) than any other fiber types. Among these categories, direct dyes are widely used because of their relative ease of application and their favorable characteristics such as intense colors, hue, bright shades and fastness properties. Since benzidine – an intermediate largely used in the synthesis of direct dyes – was found to be carcinogenic, the benzidine dyes were prohibited and extensive research has been conducted to find alternative dyes. A number of approaches have been developed in order to identify suitable benzidine replacements. The conversion of these compounds to dyes, with similar dyeing properties to the benzidine based dyes is also of great interest. One such diamine is 4, 4' - diaminobenzanilide, an aromatic diamine which is also used in the plastics industries.

The aim of the present study was the experimental and theoretical study of the adsorption of three direct azo dyes on mercerized cotton fibre. The direct azo dyes were synthesized starting from 4,4' -diaminobenzanilide, which was used as substitute of benzidine. The coupling components were 2 -amino - 8 - hydroxy - 6 - naphthalensulfonic acid and 1 - amino - 8 - hydroxy - 3,6 - naphthalendisulfonic acid in the case of dye 1, a monoazo compound obtained by the coupling reaction of the diazonium salt of aniline with 1 - amino - 8 - hydroxy -3, 6 - naphtalendisulfonic acid and m - phenylendiamine in the case of dye 2. Dye 3 was synthesized using as coupling components salicylic acid and a monoazo compound prepared by the coupling reaction of the diazonium salt of 5 - nitroantranilic acid with 2 - amino - 5 - hydroxy - 7 - naphthalensulfonic acid. The dyeing was carried out at three different temperatures: 60°, 86° and 96°C and at a sodium chloride concentration of 4 g/L. The experimental data obtained from the dye adsorption process were fitted by linear regression analysis to the standard Nernst, Freundlich and Langmuir isotherms. For all the studied dyes, better statistical results were obtained in the case of Langmuir adsorption model. The characteristic thermodynamic parameters of the dyeing process, like: standard affinity, enthalpy and entropy were determined too.

Assessment of Some Comfort Properties of Hemp Based Textile Surfaces

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Although development of bast fibers for a long time was in the shadow of chemical fibers, in the past decade hemp has been the object of a great deal of attention. Owing to well known valuable features of hemp fibers, like physiological, hygienic, comfort and ecological properties, hemp has been traditionally grown for technical uses. Nowadays, hemp fibers are going through a period of renaissance by transforming these rustic fibers into different textile products of high added value. In order to estimate the transformation of hemp based yarns into comfort textile surfaces, an investigation of behaviour of woven and knitted fabrics during relaxation of compression (compressibility, resilience) was realized. Six samples of woven fabrics in plain and twill weave and four samples of weft knitted fabrics, with approximately equal value of mass, were used as experimental material. In order to monitor the behaviour of experimental material under 5-cyclic compression, the apparatus (TexTesT-306) for measuring the thickness of textile surfaces was used. The starting amount of loading, used for measuring the thickness of experimental samples, was 30g (thickness of sample without loading - JUS F.S2.021). After that the amount of loading progressive increased (170g, 420g, 670g, 1170g, 1670g). Absolute and relative value of compressibility, Δd , as well as the absolute and relative value of set, ΔS , were calculated from the following relations:

 $\Delta d_{abs} = d_0 - d_{1670}, \text{ (mm)}, \\ \Delta d_{rel} = [(d_0 - d_{1670})/d_0]100, \text{ (\%)},$

d₀ – starting thickness of sample, (mm),

d₁₆₇₀ – thickness of sample at maximal loading in first cycle, (mm);

 $\Delta S_{abs} = d_0 - d_5, \text{ (mm)}, \\ \Delta S_{rel} = [(d_0 - d_5)/d_0]100, (\%),$

d₀ – starting thickness of sample, (mm),

 d_5 – thickness of sample after the fifth loading-unloading cycle, (mm).

Imposed investigations showed that woven fabrics have less compressibility, but better ability of elastic recovery (set) in relation to knitted fabrics. Keeping in mind that characteristics of observed experimental fabrics approached to characteristics of other natural materials (cotton, flax), it was possible to conclude that investigated hemp based textile surfaces can successfully compete with other comfort clothing materials. Besides, it was shown that satisfied comfort properties of woven and knitted fabrics can be achieved by adjusting of their structure (weave, density), as well as by appropriate projecting of yarn structure.

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Insulin Sorption by Cation-Exchange Fibres Experimental and Modeling Studies

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Former results on obtaining of the insulin artificial store, in form ion-exchange fiber with controlled delivery of insulin, was showed possibility in obtaining fibrous insulin store with important quantity of bonded insulin, even reaching the amount of 800 mg of the insulin per g of fiber [1].

In this paper the mechanism and kinetics of the process insulin chemisorption from aqueous insulin solution, by cationexchange fiber was studied. On basis of experimental results a mathematical model of insulin chemisorption by fibers has been developed and presented in this paper. The model of the chemisorption process could be established in the relation to the change of the amount or concentration of the insulin joined to the fiber, dependence with the conditions and duration of chemisorption. Our study suggests that the current mathematical model of insulin chemisorption, may be useful in obtaining diffusion coefficient values and determining profile of the insulin concentration change in fiber[1-4].

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Sol-Gel SnO₂-SiO₂ Catalysts. Comparison with Impregnated Catalyst

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The application of SnO_2 in catalysis and also in the related field of catalytic gas sensors imposed to find new methods of increasing the surface exposed to gas adsorption, since the higher the exposed surface area, the higher the catalytic activity and the higher the electrical response (thus the sensitivity) to changes of (i)-the nature of adsorbed gases/reactants, (ii)-the coverage(s) of specific reactant(s). In this paper we report about structure and surface properties of some SnO_2 -SiO₂ systems prepared by sol-gel synthesis in two variants, i.e. in acidic and basic medium. The sol-gel catalysts were investigated by XRD, TEM, in situ ac electrical conductivity (differential step technique-DST) and catalytic activity (propylene oxidation) measurements and compared with a SnO_2/SiO_2 catalyst obtained by impregnating a SiO₂ support with the same amount (around 25%) of tin dioxide.

Synthesis and Characterisation of Manganese Oxide for Catalytic Purposes

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Manganese dioxide is well known for its high catalytic activity for ozone decomposition [1], CO oxidation [2], selective NO_x reduction [3] or CH_4 conversion [4] and consequently, for its utility for waste gases treatment.

The paper presents some of our results referring to the preparation and characterisation of manganese dioxide that is to be used as catalyst for ozone decomposition. In this purpose, different sorts of manganese dioxide were prepared from potassium permanganate and manganese nitrate, by using two different precipitation techniques namely simultaneous and sequential addition of reagents, respectively. The as-prepared $MnO_2 \cdot xH_2O$ precursors were fired at 500°C, for 1.5 hr in order to obtain MnO_2 samples for catalytic purposes.

Manganese dioxide samples were investigated by thermal analysis, X-ray diffraction, FT-IR spectroscopy, BET and particle size measurements. Catalytic activity was evaluated for ozone decomposition process and correlated with the physico-chemical characteristics of samples obtained in different preparation conditions (reagent concentration, thermal regime).

FT-IR and XRD spectra (fig.1) illustrate the difference between two manganese dioxide samples prepared in various conditions by the simultaneous addition techniques. The as-prepared samples possess high surface area and good catalytic activity.



Fig. 1. FT-IR and XRD spectra of some manganese dioxide samples prepared at room temperature (M4.C) and 60°C (M6.C)

Acknowledgements

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NiO-WO₃ Mixtures Prepared by the Sol-Gel Method

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Different variations of sol-gel techniqes are using nowadays to synthesize finely disperzed catalyst oxide powders, ceramics precursors as well as intercalate electrode materials for Li-ion batteries⁽¹⁾. It is reasonable to expect that the oxides, mixed at a practically molecular lewel, even in the very synthesis procedure, without an additional treatment, interact mutually and loss their individual characteristics. Such an behaviour was observed in this work on the example of NiO-WO₃ oxide mixtures.

The mixtures NiO-WO₃ were synthesized by sol-gel method in the following way: tungsten powder was dissolved in concentrated hydrogen peroxide to obtain polytungstic acid solution, and its concentration was determined on the basis of initial metal weight. Nickel nitrate hexahydrate was dissolved in pure water, and its concentration was determined by complexometric titration. These solutions were mixed in determined volume ratios to obtain the solutions with predetermined Ni/W molar ratios. A solution of citric acid was then added, to get the citric acid / nickel nitrate mole ratio of roughly ¼. The solutions were then heated to remove solvent, and upon, under permanent mixing, almost all water was evaporated, a very viscous transparent gel remained. The gel was heated in an open oven at a slowly rising temperature, until a combustion of citric acid happened. The heating at a constant temperature of 400 C was then prolonged for approximetely 1 hour.

The oxide mixtures were examined by x-ray diffractommetry, using Cu K_{α} radiation, and the figure below shows the resulting diagrams.



with the mole ratios 3:7, 5:5 and 7:3.

The diagrams in Fig 1 demonstrate clearly that the oxides NiO and WO_3 do not retain their individual crystallografic structure, but interact mutually and form new phases. NiWO₄ is already a known compound, which may be percipitated upon mixing aqueous solutions of nickel nitrate and sodium tungstate. Most probably this compound appears as a pure phase at oxide mole ratio 1:1, to which corresponds the middle placed diagram in Fig 1.

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Modified Mg-Al Hydrotalcite by Y, La, Gd, Sm and Dy: Highly Active Solid-Base Catalyst for the Cyanoethylation of Ethanol

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Introduction

The hydrotalcite-type (HT) anionic clays have been proposed as catalysts or catalyst precursors for many reactions of industrial interest like the fine chemical synthesis [1]. Our previous works have shown high activity and selectivity of mixed oxides obtained from Mg-Al HT in cyanoethylation of alcohols with acrylonitrile [2]. We report here the results of cyanoethylation of ethanol on HT – Mg_{0.75}Al_{0.23} and modified HT - Mg_{0.75}Al_{0.23}Me^{III}_{0.02} (Me^{III} = Y, La, Gd, Sm, Dy). The correlation between the concentration and strength of basic sites of the modified HT and their catalytic performances has also been investigated.

Experimental

The HT and HT – like samples were prepared according to the literature [3]. Mixed oxides catalysts were obtained by calcination of the dried HT under nitrogen flow at 733K for 5 hours. The catalysts were characterised by elemental analysis, XRD, FTIR, TPD of CO₂ and specific surface areas. The cyanoethylation reactions were carried out in a glass-batch reactor equipped with a condenser system, under stirring at 363K and a molar ratio $C_2H_5OH/C_3H_3N = 3/1$.

Results and discussion

The dried HT samples gave, after 5h reaction time, conversion of acrylonitrile to β -ethoxypropionitrile between 20-60%, the activity of the catalysts following the order: Dy<Al<Sm<Y<Gd<La which is in a good agreement to the increasing basicity of rare earth hydroxides. On catalysts obtained by HT calcination, conversion values were between 80 and 96%, with catalysts activities varying in the order:Dy<Y, La<Gd<Sm<Al. The catalytic activity was well correlated with the surface basicity of the samples determined on the basis of the irreversible adsorbtion of noninteracting acrylic acid (pK_a=4.2) and phenol (pK_a=9.9) and with the TPD of CO₂ data. The "memory effect" was studied for the Mg_{0.75}Al_{0.23}La_{0.02} catalyst and the results are shown in table 1. The activity of calcined and rehydrated sample after 3h of reaction increases and even overcomes the activity of dried HT. The rehydrated and recalcined sample has conversion values that are comparable with those of dried and calcined HT sample. The differences are due to hydration mode. These results show that the reaction is catalysed by weak Brönsted basic sites (OH⁻ grups) generated during rehydration. It may be concluded that the activity and basicity of HT Mg-Al in cyanoethylation of ethanol can be modified by partial replacement of Al with rare earth cations. The catalysts were found to be reusable without significant loss in activity.

Table 1. Acrylonitrile conversions on $Mg_{0.75}AI_{0.23}La_{0.02}$ (T= 363K: molar ratio $C_2H_5OH/C_3H_3N = 3/1$)

Treatment of the catalyst Mg _{0.75} Al _{0.23} La _{0.02}	dried	calcined	hydrated	recalcined
1) hydrated in Ar flow with H ₂ O	36.78	82.12	84.39	71.86
2) hydrated in CO_2 flow with H_2O	36.78	82.12	45.65	83.07
3) hydrated in air	36.78	82.12	80.63	78.05

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Olefin Metathesis on Cr, Ce, Zr Doped Mo-Mixed Oxides

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Introduction

This work presents results concerning the catalytic behaviour of Cr, Ce, Zr doped NiMoO₄/SiO₂ catalysts in the 1-octene metathesis reaction compared to that of the un-doped catalyst. The effect of doping on the physico-chemical properties of the catalysts is also investigated using XRD, FTIR and Raman spectroscopy, BET, SEM and TEM-EDX microscopy, and determination of acid-base properties by NH₃-TPD and CO₂-TPD. The concentration of NiMoO₄ in the supported catalyst was 39% wt. In the un-doped catalyst, the atomic ratio Ni:Mo was 1:1; while the doped catalysts were characterized by an atomic ratio Ni:Mo:D = 1:1:0.01 (D= Cr, Ce, Zr). Catalytic tests for 1-octene metathesis were performed in a conventional continuous flow apparatus in the temperature range 150-450°C using 0.5 g catalyst and 0.1 ml 1-octene/min flow rate.

Experimental results

In all XRD patterns the lines characteristic to β -NiMoO₄ along with lines characteristic to the α -NiMoO₄ were present. It was noticed that Zr doping lead to a lower crystallinity of the NiMoO₄ and Ce doping lead to the most intense lines corresponding to the β-NiMoO4. FTIR and Raman spectra did not present significant changes as a consequence of the doping, probably due to the low amount of the doping agent in the samples. The most significant differences in the physicochemical properties of the doped catalysts concerned the specific surface areas, the average size of the particles and the acid-base properties, as it may be seen from the data presented in table 1. For all catalysts, the highest selectivity for metathesis (i.e. the sum of the selectivities to C₂H₄ and 7-tetradecene) is obtained at 350°C. Besides the direct metathesis products some by-products obtained by metathesis of 2-octene and 3-octene are obtained (e.g. 2-C₄H₈ and 6-dodecene, and respectively 3-hexene and 5-decene). This fact correlated to the absence of 1-octene isomers in the reaction products leads to the conclusion that isomerization of 1-octene is a fast process and the isomers 2-octene and respectively 3-octene are totally consumed in secondary metathesis reactions between internal olefines, which take place faster than the metathesis of the terminal olefins. The selectivity to cometathesis was considered to be the sum of the selectivities obtained by cometathesis reactions (e.g. C_3H_6 and $6-C_{13}H_{26}$, $1-C_4H_8$ and $5-C_{12}H_{24}$, $2-C_5H_{10}$ and $5-C_{11}H_{22}$, $1-C_5H_{10}$ and $5-C_{11}H_{22}$. C_5H_{10} and $4-C_{11}H_{22}$). As it was revealed by TEM-EDX, doping the silica supported NiMoO₄ with Ce and Zr lead to an increase of the distance between the crystallografic planes characteristic to the β -NiMoO₄. It was assumed that this fact may be associated to the higher activity for metathesis presented by these catalysts.

Catalyst	BET S _{sp} (m ₂ /g)	CO₂-TPD μmolesCO₂/g	NH₃-TPD μmolesNH₃/g	Average size of particles			S _{metathesis}	S _{cometathesis}
				SEM	TEM (nm)	- 1-0 ₈ ⊓ ₁₆ (%)	(%)	(%)
				(µm)	(1111)			
NiMo/SiO ₂	84.3	78.1	4	77	100	78.6	26.4	14.2
NiMoCr/SiO ₂	93.0	63.4	8.5	83	104	99.9	36.2	10.1
NiMoCe/SiO ₂	118.2	53.9	3.8	98	136	94.9	53.0	6.1
NiMoZr/SiO ₂	107.8	47.9	12.8	90	110	99.6	80.6	17.4

Table 1. Physico-chemical characteristics of catalysts and their catalytic activity for 1-octene metathesis at 350°C.

Partial Oxidation of Ethanol to Acetaldehyde on Silver Catalysts. Effect of the Support on the Properties of the Catalysts

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Introduction

The vapor phase partial oxidation of ethanol to acetaldehyde over silver catalysts at 550°C is industrially established. The scheme of the reactions that can occur during the partial oxidation process involves the group of reactions [1], in which the primary reaction, i.e. partial oxidation of ethanol by air, as well as the reaction of ethanol dehydrogenation are responsible for the formation of acetaldehyde. Although extensive studies have shown that silver was superior to others catalysts when the partial oxidation with air was performed, the available information on the different types of supported catalysts and the favorable conditions for such catalysts are limited.

Objectives

The objectives of this investigation were to study the vapor phase partial oxidation of ethanol to acetaldehyde with air on mullite and silica gel supported silver catalysts and to determine the effectiveness of these catalysts when used with different supports. The goal was to find how the conversion changes with temperature in presence of a given supported catalyst.

Experimental

Mullite-M (S_{BET} =2.9 m²/g; V_P=0.75 cm³/g) and macro porous silica gel-SiO₂ (S_{BET} =27 m²/g; V_P=0.84 cm³/g) are used as supports for preparation of supported Ag catalysts. Catalyst samples were prepared using the impregnation method. After soaking in concentrated AgNO₃ solution and evaporating nearly to dryness, the samples were dried at 120°C, calcined at 700°C and finally reduced in hydrogen at 450°C. The content of silver in prepared samples was almost the same, 0,289 g Ag/g_{kat} (Ag/M) and 0,297 g Ag/g_{kat} (Ag/SiO₂). The catalytic reaction experiments were carried out in a vertical fixed-bed quartz reactor with preheating section within a temperature range of 410 to 650°C.

Results



The catalytic properties of the catalysts prepared is shown on ± Figs. 1 and 2. The obtained results (Fig. 1), show better conversion to main product for Ag/M sample 5 20 compared to Ag/SiO_2 sample. However, Ag/M conversion curve shifted to the higher are temperatures. The catalytic conversions to side products, CH₄, CO and H₂, are considerably higher for Ag/SiO₂ (Fig. 2).



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Tungsten (VI) Promoted Titania Photocatalysts

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This investigation is aimed to present fast, easy and simple procedure of preparation of titania photocatalysts based on TiO_2/WO_3 composites, to clarify the WO_3 content in case of different TiO_2 modifications used, and to illustrate the promoting role of the tungsten trioxide in the photocatalytic action of the so obtained materials.

The tungsten (VI) promoted titania photocatalysts were prepared from commercial TiO_2 brands (anatase from TRONOX or Degussa P25) and monoclinic WO₃ by solid-state synthesis. The initial charge consists of the thoroughly homogenized corresponding metal oxide powders of a 0.5, 2, 5, 7, 10, 25 and 50 WO₃ percentage. Thus prepared mixtures were thermally treated for 2 h at 200°C and 400°C. A series of samples was dried for 2 days at room temperature to make clear the influence of the drying temperature on the catalytic action of the composites.

The crystalline phase composition of the samples was characterized by X-ray analysis (CuK α source radiation, diffractometer Siemens). At the comparative XRD no solid solution Ti_xW_yO_z is observed – the components exist as separate phases. No changes in the position, width and intensity of the characteristic anatase and rutile peaks for the commercial TiO₂ brands and all the composite samples were observed.

The photocatalytic action of the samples was tested in photodegradation of commercial organic dyes in slurry under UV irradiation of ~ 350 nm (Sylvania 18W Black Light blue UV Lamp T8). The change in the dye concentration was determined by UV-VIS spectrophotometer (Jenaway, 320-1000 nm). As model pollutants the dyes Malachite Green Oxalate, Methylene Blue and Rhodamine B were used.

It is established that promoting with W (VI) leads to forced sorption rate and ability during the dark period, corresponding to the WO_3 content. The obtained forced sorption degree of the pollutant, as first step in the heterogeneous catalysis, assures more attractive start for the further TiO₂ photocatalysis due to kinetic reasons.

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Chemically Modified Aluminas for TLC Applications

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Alumina is an inorganic adsorbent widely used in thin layer chromatography (TLC) as an alternative for silica and polimer-based stationary phases. In order to increase the selectivity and efficiency of the chromatographic separations, the chemical modification of adsorbents with different organic compounds attached to their surfaces is a very useful method.

In this study, the unmodified active basic 90 alumina and chemically modified with 3-aminopropyltrimethoxysilane and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane by organosilylation reaction are presented. These stationary phases have been characterised by the Fourier transform infrared spectroscopy (FTIR), the nuclear magnetic resonance spectroscopy (NMR), the mass spectrometry (MS) and the thermoanalytical (TA) methods [1,2].

Using FTIR spectroscopy, the presence of modifier on alumina surface is well evidenced by the new weak bands that are observed in the $2800-3000 \text{ cm}^{-1}$ range due to the v(CH) vibrations of CH₂ and CH₃ groups. The bands evidenced in the 900-1100 cm⁻¹ range may be assigned to v(AIO) and v(SiO) of the newly formed AIOSi bridges after attaching of silane derivative onto alumina. To improve the sensibility of infrared method, the difference and second derivative spectra were also analyzed in order to find out the effect of the modifier on the alumina surface properties.

By ¹³C-CP/MAS NMR spectroscopy, the conformational properties of immobilized ligands were studied. The differences in the intensity of signals due to the variety of bonded silyl species show different grades of coverage of active basic 90 alumina. The ¹³C-CP/MAS NMR spectra of modified aluminas indicate a *trans* conformation of methylene groups from the chains of modifiers. The comparative study of mass spectra of chemically modified and unmodified samples shows the modifications of alumina surface with the corresponding chains of used modifiers. The results reveal that the silanization reaction of alumina with the trifunctional modifiers leads to ions which correspond to the structures: CH_2 -NH₂, CH_2 -CH₂-NH₂.

The thermoanalytical (TG, DTG, DTA) method gives quantitative information about the water removed by the desorption and dehydration processes (endothermal effect) and the elimination process of organic part (exothermal effect) of the studied stationary phases and data referring to the temperature ranges where the thermal effects take place. This method can be considered as a useful technique for the supplementary study of chemically modified stationary phases.

Based on our studies we conclude that due to the chemical modification according to the modifier the hydrophilic alumina surface decreased. The obtained chemically modified aluminas were tested as stationary phases for TLC at the determination of some compounds like dyes, benzopyrene derivatives, cations.

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Chemical Synthesis Route of Lithium Ferrite Structural and Magnetic Properties

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Lithium ferrite (LiFe₅O₈) a soft magnetic material with an inverse spinel structure is a promising material for applications in microwaves [1-4].

Nanoparticles of lithium ferrite have been prepared by two chemical synthesis methods: the thermal decomposition of polynuclear coordination compounds and the self-propagating combustion (a thermal decomposition of polynuclear coordination compounds *in situ*) The polynuclear coordination compounds – precursors:

 $\begin{array}{l} (\mathsf{NH}_4)_2[\mathsf{Fe}_{2.5}\mathsf{Li}_{0.5}(\mathsf{C}_4\mathsf{O}_5\mathsf{H}_4)_3(\mathsf{OH})_4]\cdot\mathsf{6H}_2\mathsf{O} \\ (\mathsf{NH}_4)_6[\mathsf{Fe}_{2.5}\mathsf{Li}_{0.5}(\mathsf{C}_4\mathsf{O}_6\mathsf{H}_4)_3(\mathsf{OH})_8]\cdot\mathsf{2H}_2\mathsf{O} \\ (\mathsf{NH}_4)_2[\mathsf{Fe}_{2.5}\mathsf{Li}_{0.5}(\mathsf{C}_6\mathsf{O}_7\mathsf{H}_{11})_3(\mathsf{OH})_4]\cdot\mathsf{2H}_2\mathsf{O} \\ [\mathsf{Fe}_{2.5}\mathsf{Li}_{0.5}(\mathsf{CO}(\mathsf{NH}_2)_7]\cdot(\mathsf{NO}_3)_8 \end{array}$

were characterized by chemical analysis, IR and UV-Vis spectra, magnetic measurements and thermal analysis.

Lithium ferrites obtained were characterized by XRD, IR spectra and magnetic measurements. The average particle size of these ferrites ranged between 10 - 30 nm.

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Spectroscopic Characterization of Copper / Cadmium Sulphide Heterostructures

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In order to obtain some metal / metal chalcogenide / glass heterostructures, studies referring to both cadmium sulphide and metal layer deposition have been initiated. UV-Vis transmittance and reflectance spectra (8° and 0° incidence) and X-ray diffraction patterns were used to characterize these films.

Thin films of copper onto optical glass support were obtained using two different techniques namely physical vacuum deposition (PVD) and chemical bath deposition (CBD). PVD was performed onto cold substrate, by metal thermal evaporation under 10⁻⁶ torr vacuum. CBD was achieved from solutions containing copper sulphate as cation source, hydrazinium hydroxide or formaldehyde as reducing agent and sodium-potassium tartrate as complexing agent. Physical vacuum deposited copper films are characterized by the sharp transmittance window observed at about 570 nm and the well formed cubic structure with average crystallite size of about 10 nm. Relatively larger crystallites, low crystallinity and high concentration of packing defects were observed in chemical bath deposited copper films.

Mono and multi-layer cadmium sulphide / glass films with variable thickness (up to 1200 nm) were prepared by CBD method. The films were deposited onto optical glass support from chemical bath containing thioureea, cadmium acetate, ammoniac and sodium citrate. Bath composition and the thermal treatment regime (air or inert atmosphere, temperature) determine the main layer characteristics influencing the optical parameters. The hexagonal crystalline structure of CdS films was evidenced by X-ray diffraction. The microstructural parameters i.e. effective crystallite mean size and the root mean square of the microstrains were determined by single X-ray profile Fourier analysis. By thermal treatment the crystallite distribution becomes more uniform and the root mean square of the microstrains decreases. The absorption coefficient and optical band gap have been calculated from the normal transmission spectra in the range 300 - 1100 nm.

Copper - cadmium sulphide heterostructures manufactured by the layers sequential deposition were stabilized by thermal treatment performed in inert atmosphere. Optical and structural properties were evaluated in order to illustrate the mutual interaction of CdS and Cu layers.

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Synthesis and Characterisation of Niobium Activated Yttrium Tantalate Phosphor

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Yttrium tantalate phosphors are used for the manufacture of X-ray intensifying screens for medical imaging applications. X-ray intensifying screens are generally used in conjunction with photographic films and serve to enhance the image formed on the film.

Niobium activated yttrium tantalate (YTaO4:Nb) phosphor has good X-ray absorption, emits in the blue region of the spectrum and is compatible with the blue sensitive radiological films.^{1,2} Yttrium orthotantalate crystallise in two main polymorph structures namely, the low-temperature monoclinic M-YTaO₄ phase and the high-temperature tetragonal T- YTaO₄ phase. In special synthesis conditions, a variant of the monoclinic structural arrangement, known as M-prime form (M'-YTaO₄ phase) could be prepared.^{3.} The M-prime yttrium tantalate structure is an efficient host for X-ray phosphors when activated with niobium or rare earth ions, in comparison with the monoclinic yttrium tantalate (M-YTaO₄ phase).

The purpose of the study is the synthesis of efficient niobium activated orthotantalate phosphor with $M'-YTaO_4$ crystalline structure.

The paper presents some aspects referring to the synthesis of YTaO4:Nb samples prepared by solid state reaction route.

The influences of different preparative factors such as firing regime flux nature, and activator concentration on phosphors optical and structural properties are investigated. Phosphor samples are characterised by spectroscopic methods i.e. photolumine-scence investigation, X-ray diffraction (XRD), and FT-IR.

The firing regime and flux nature influence mainly the luminescent properties (figure 1), particle size distribution and crystalline structure of the phosphor powders.



on luminescence properties

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SANS Study of Silica Xerogel Microstructure Synthesised Using Different Processing Conditions

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The purpose of the paper was to describe the appearance of certain developed microstructures, by small-angle neutron scattering (SANS) investigations upon silica xerogels obtained by using different processing variables. Starting from tetraethoxysilane, TEOS, as precursor, the samples were prepared by the alcoxide route. Using one or two steps acid and/or base catalysed, ultrasonically assisted and no assisted sol-gel process, silica xerogel samples were obtained. The SANS measurements were performed over a q (scattering vector) range from 0.005 to 0.37 Å⁻¹, providing structural information at length scales ($2\pi/q$) between approximately 1 and 100 nm. The measured small-angle scattering intensities of the investigated samples are presented in log-log plots (Figure 1 and Figure 2). The fractal dimension values of acid and base catalyzed sol-gel derived samples are consistent which those reported in literature [1, 2]. The sonicated acid catalyzed samples presents a peculiar fractal behaviour.



SANS measurements confirmed that pH and ultrasonic field have a significant influence upon the fractal behavior of the silica xerogels microstructure.

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Synthesis, Characterisation and Thermal Studies of New Oxovanadium(IV)-Copper(II) Complexes Containing Sulfide as Ligands

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The pharmacological and therapeutic agents available for the treatment of Wilson and Menkes diseases recently have been reviewed. Most of these pharmaceuticals are complexes of zinc or molybdenum which can act as ligands toward copper(II) ions. Also, $MOS_4^{2^-}$ and the oxy analogues, $MOO_xS_{4\cdot x}^{2^-}$, are involved as intermediates in the Cu-Mo antagonism that afflicts ruminants. $MOS_4^{2^-}$ is also clinically used for the removal of excess Cu from Wilson's disease patients. Only a few reports deal with V/Cu/S complexes¹⁴⁻¹⁹. These complexes were obtained from a reaction system containing thiovanadate in the manner used for Mo-S-Cu complexes. In most of these complexes, the structural motif of a four-membered heterocycle M_2S_2 was emphasised.

Our objective is to present in this paper the preparation of V-Cu complexes in which oxalate and sulfide anions and 2,2'-bipyridine or 1,10-phenanthroline act as ligands. As sulfide source, $Na_2S_2O_3$ and thiureea has been used and 1.10-phenantroline and 1,2-dipyridyl as ligands. The nature of the resulted compounds depend strongly on the copper(II) to vanadium and metal to sulfide ratio as well as on the nature of the used ligands. The nature of the obtained compounds has been established on the basis of elemental analyses, spectral properties and thermal behaviour.

Synthesis and Characterisation of Nanometric Ni – Cu – Zn Ferrites

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The usefulness of ferrites is influenced by the physical and chemical properties of the materials and depends on many factors including the methods of preparation, sintering or annealing conditions, the amount of constituent metal oxides, impurities or doping levels [1].

Recently, there has been a growing interest in low temperature sintered Ni – Cu – Zn ferrites for the application in producing multilayer-type chip inductors because of its better properties at high frequencies than Mn - Zn ferrites and the lower densification temperatures than Ni – Zn ferrites [2].

The present work studies the preparation of Ni – Cu – Zn ferrite nanometric powders by a sol-gel method in the systems 2 Fe(NO3)3 – x Ni(NO3)2 – y Cu(NO3)2 – (1-x-y) Zn(CH3COO)2 – AOH (where AOH = aminoalcohols like dimethylaminoethanol or triethanolamine, acting as chelating and also gelling agents and x = 0.8, y = 0.1 or x = 0.2, y = 0.1).

The precursors of ferrites have been characterized by chemical analysis, electronic and FT-IR spectra as well as TG / DTA analysis.

The polycrystalline Ni – Cu – Zn ferrite thin films have also been deposited from the above systems by spin coating method on Si / SiO2 substrates.

Structure and morphology of powders and films ferrite samples have been determined – as a function of annealing temperature – by FT-IR spectra , XRD and TEM.

The magnetic measurements of annealed powders and spin coated samples have been determined at room temperature. No significant difference of magnetic properties was observed by applying an external field along and perpendiclar to the surface of the film.

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Silicon Anisotropic Etching in TMAH Solutions

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Single crystalline silicon etches anisotropically with aqueous based hydroxides. Among various hydroxides, TMAH (tetramethylammonium hydroxide) solutions in water are used because they are CMOS compatible by their lack of alkali cations and because they are less aggressive towards SiO₂ mask materials than the widely used water KOH solutions, for example.

The aim of this work is to determine etching characteristics of TMAH solutions in terms of etching rates of different crystal orientations especially when etching rectangular convex corners in (110) oriented peg-like squares on (100) Si wafers. Deformation of the rectangular edges always occurs due to undercutting, which is unwanted effect in silicon micromachining when often perfect 90° convex corners are mandatory for good device specification.

The convex corner attack was studied on etching square patterns obtained by standard photolithography with thermally grown SiO₂ as masking material. All experiments were carried out on (100)-oriented n-type Si wafers, double-side polished, with resistivity of 5-3 Ω cm and thickness of 520 μ m. Squares were aligned along <110> direction.



Fig. 1. a. Picture of the masked square after 1 hour etching in 25 wt.% TMAH at 80 °C.



Fig. 1. b. Top view of an etched square with the definition of measured angles and undercutting (uc).

for applied etching conditions.

Based on these measurements, compensation patterns which contain directions of the fastest etch planes (in this case <520>) could be elaborated for the formation of convex corners in (100) oriented silicon.

Acknowledgements

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The etching process was carried out at 25 wt.% TMAH solution in water at temperature of 80 °C in a thermostated vessel (temperature stabilization \pm 0.5°C) with reflux condenser to prevent change of solution composition. During etching wafer was in horizontal position, and solution was electromagnetically stirred with 700 rpm.

Etching rate in <100> direction was determined as $R_{<100>}$ = 0.44 µm·min⁻¹ and etching rate of masking material SiO₂ (thermally grown at 1150°C in water saturated atmosphere) was 1.28·10⁻⁴ µm·min⁻¹. On Fig. 1. is a picture taken from reflected light microscope in phase contrast mode ("Epival-Interphako" from Carl Zeiss) of one of squares with initial dimensions of 500·500 µm² after etching for 1 h. The slowest etched plane was (111) (R_{<111>}≈0.04 µm·min⁻¹).

During the course of etching convex (peg-like) structures slow planes decrease in length and fast increase in length – so the convex corners have symmetry of the planes with maximum etch rates.

We obtained following results for angles in convex corners: α =135.2° and β =135°. These measured values could best be matched with the <520> directions as shown on Fig 1.b, for which α should measure 136.4° and β =133.6°. Knowledge of tightly packed lattice plane that cross the wafer surface at the <520> direction needs determination of angle between this plane and (100) plane of silicon. On Fig. 1. b. is also shown undercutting (uc) which was dependent on the etch depth (ed). The relative undercutting (uc/ed) was typically 5

Determination of the Mn(II) Electronic State in Kaoline Nanostructure

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Based on the actually known data about the kaolinite-illite clay resources in Vojvodina region a kaolinite model system was synthesized to investigate the influence of some metal ions on the kaolinite nanostructure. It is well known that pillaring process of polyhydroxy cations in the clay structure increases the basal plane dimensions, influencing thus its nanostructure. Ordinary impregnation of kaolinite with transition metal ions causes an increase of the basal layers, even at so high temperatures as 900°C. However, the natural kaolinite structure is destroyed during the heat treatment by formation of new components such as mullite, β -cristobalite, α -quartz, etc.

In view of the above the layer structure of kaolinite was studied by XRD and DRS methods. The data collected by the DRS method showed that Mn(II) ions in the basal plane are present in the tetrahedral and octahedral structures (spinel structure). The XRD analysis data confirmed the influence of the metal ion on the nanostructure, characterized by the changes of the basal plane dimensions. Incorporation of Mn(II) ions increased the d-space between the tetrahedral oxygen layers from 7.15 Å to 8.18 Å. In the kaolinite with Mn(II) ions the d-values for $3Al_2O_3 \cdot 2SiO_2$ and MnO were 5.42 and 2.70 Å respectively, giving thus the overall d-space of 8.12 Å.

A previous investigation showed that Mn(II) ions accelerate the polymorphic transformations of metastable alumina and decrease the temperature of their transition to more stable forms. The observed phenomenon was explained in terms of a catalytic mechanism, taking into account the Mn(II) electron configuration [d⁵ (Mn²⁺)] and the Jahn-Teller effect.

Considering the above facts, the electronic states of Mn(II) ions in the polymorphic transformation of alumina after its thermal treatment (900[°]C, in the air atmosphere) were determined. Based on the positions and intensities of d-d transition maxima, the spinel structure was established, followed by the appearance of partial octahedral band splitting of Mn(II) ions as a consequence of the Jahn-Teller effect.

Further, the energies of the electronic levels in the synthesized kaolinite model system were calculated. It was established that the Mn(II) environment is of octahedral and tetrahedral type. Experimental values of the crystal-field splitting parameter 10 D_q served to calculate the ionization potential H_{dd} and the constants of partial population s, p and q of the d-level in Mn(II). Finally, the energies of electronic levels were calculated and the most probable scheme of MO for this system has been proposed.

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Preparation of ^{99m}Tc-C₆₀(OH)_X and Its Radiochemical Studies

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Introduction

The biological behavior of Fullerene derivatives shows their considerable potential for medical application. Previous work suggested that Fullerenes have successfully reacted with organic molecules which bond to the outside, leaving the cage intact¹⁾. Also, diameter from 0.71nm (C₆₀) to about 0.84nm (C₈₄) is large enough to be able to contain a variety of atoms of different sizes. Such characteristics would be especially useful in biomedical applications where radiolabelling of biological molecules and pharmaceuticals have been used extensively for medical imaging and therapy²⁾. In order to investigate the biodistribution and metabolism behavior of fullerol, quickly and conveniently, we present possibilities for its labelling with ^{99m}Tc (T_{1/2}=6.02h, E_y=141keV), which bond to the outside, leaving the cage intact.

Results and dictions

Polyhidroxilated, water soluble fullerol $C_{60}(OH)_{20}O_2H_2$ used in these studies, was synthesized by procedure complete substitution of bromine atoms from polybromine derivatives $C_{60}Br_{24}^{3)}$ in alkaline media⁴⁾. Fullerol is dark brown powder substance soluble in water. FTIR ($C_{60}(OH)_{20}O_2H_2$): 3430, 2924, 1697, 1635, 1399,1037, and minor peaks on 855, 670.

Pertechnetate, (${}^{99m}TcO_4$), was eluted from ${}^{99}Mo/{}^{99m}Tc$ generator (produced in Vinca Institute of Nuclear Sciences, Laboratory for radioisotopes) and reduced to lower valent state by stannous chloride method. The mixture of aqueous solution of fullerol, stannous chloride and ${}^{99m}TcO_4$ was allowed to react in boiling water for 40 min. Radiochemical yields for three different mixtures (fullerol-stannous chloride ratio 2:1; 5:1 and 10:1) were determined by paper chromatography using Whatnan 1 and ITLC-SG chromatography paper strips (1.5x15cm), developed in acetone and 0.9% saline. The strips dried, and the radioactivity was measured by using (NaI) γ -counter. The analysis of our radiochemical studies show that percentage of ${}^{99m}TcO_4$ are depend on fullerol-stannous chloride ratio and increase from 3.4% to 11.6% in SG-0.9%saline system, from 3.3% to 40% in SG-acetone system, from 4.5% to 18.3% in Whatnan 1-acetone and 5.5% to 44.2% in Whatman 1-0.9%saline system. Comparing these data with data we have got at the same conditions for free pertechnetate, (${}^{99m}TcO_4$), conclusion can be that ${}^{99m}Tc$ was bonded to the outside of the fullerol cage. The method we used can not separate labelled fulleroll from ${}^{99m}TcO_2$, which is usually impurity in the process of labelling with pertechnetate.

Conclusion

Radiochemical yield of labeling fullerol with pertechnetate was not enough for other investigation, but protein binding and lipophilicity measurements indicate probably the biological behavior of labelied fullerol.

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Mathematical Modeling of Steel Slab Solidification by the Isothermal Method

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In this paper the mathematical modeling of the steel slabs solidification was presented. For this purpose the isothermal method was applied. The mathematical modeling of the steel slabs solidification is related to the stationary part of the continuous casting process.

The solidification process of the steel slabs has been followed through the growing up of the shell thickness along the tighter side of the slab. The isosolidus surface to the longitudinal slab's cross-section was mathematically described using the function of Green. The solidus, liquidus and two-phase areas were determined by the isothermal method. In such way, three-dimensional show of the isosolidus surface was obtained.

The results obtained by the isothermal method were presented with the shape and the size of the isosolidus area - solidus curves to the longitudinal slab's cross-section as well as the shell thickness of the steel slab. This results were compared with similar results, obtained by the numerical methods, and satisfying precision was achieved.

Temperature Field Determination in the Steel Slab Solidification Process by the Numerical Method

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A subject of this work is temperature field determination in the solidification of the steel slab by the numerical method. Estimation of the temperature in precisely determined points into formed net on the transversal cross-section was done on the base of known temperatures on the contour of this cross-section. Calculation of the temperature was performed by the finite-difference method, using Gauss-Seidel method.

Thermophysical parameters – specific heat, coefficient of heat transfer and density, were inputted into mathematical model as temperature dependences, instead as constants, which contributed to increase of model's precision.

Temperature field on the slab's transversal cross-sections by the temperatures estimation was obtained. Connecting the points with temperature solidus and temperature liquidus, the solid, liquid and two-phase areas in the solidification process of the steel slab were determined.

The temperature field in the solidification area of steel slabs directly influences on slab's forming and its quality. Thus, it can be used for quality analysis of produced steel slabs.

Studies on Yttrium/Gadolinium Oxysulphide Phosphor

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Under UV and X-ray excitation, terbium activated oxysulphide phosphors shows bright green luminescence related to the rare earth ion presence. Due to the high phosphor efficiency, the material is used in the manufacture of X-ray intensifying screens for medical diagnosis [1]. Phosphor utilisation depends on powder characteristics and luminescent properties that are regulated during the synthesis stage [2].

The paper presents some of our results referring to the synthesis of terbium activated yttrium/gadolinium oxysulphide phosphors were prepared by solid state reaction route [3]. The influence of flux amount and composition as well as the sulphuring agent concentration on phosphor morpho-structural characteristics and luminescent properties was investigated in order to prepare efficient luminescent powders for X-ray intensifying screens.

Homogeneous synthesis mixtures of oxide precursors, flux and sulphide suppliers were fired (1200 °C,4 hrs.) and washed. Samples were characterised by luminescence measurements, particles size distribution and X-ray diffraction spectroscopy (XRD).



of Y_2O_2S :Tb (5 %); sulphurising agent- flux ratio: S: Na₂CO₃ : Na₄P₂O₇=6:2:x YOS31 (x = 0,125); YOS34 (x = 0,200);YOS35 (x = 0,085)

Photoluminescence spectra of Y₂O₂S:Tb (noted YOS) or Gd₂O₂S:Tb (noted GOS) consist in many narrow emissionbands whose relative intensitiesdetermine the luminescence performances. The ratio of the four main emission bands i.e. 485 nm $({}^{5}D_{4} \rightarrow {}^{7}F_{6})$, 545 nm $({}^{5}D_{4} \rightarrow {}^{7}F_{5})$, 585 nm $({}^{5}D_{4} \rightarrow {}^{7}F_{4})$ and 620 nm (${}^{5}D_{4}\rightarrow {}^{7}F_{3}$) depends on activator concentration, sulphide supplier amount flux and composition and concentration synthesis mixture (fig.1). The composition influences also the microor macro-structural particle parameters and size distribution of the green emitting Xray phosphor.

Acknowledgements

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Influence of Tartaric Acid on Al(OH)₃ Crystallisation from Caustic Soda Solution

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Crystallization of Al(OH)₃ from caustic soda solutions is important part of Bayer process of Al₂O₃ production because the phenomena that occurs during this process influence on the physicchemical properties of precipitated Al(OH)₃. Phenomena are nucleation, agglomeration and crystal growth. Nucleation present formation of new small particles and cause the decreasing of grin size of precipitated Al(OH)₃. Agglomeration is sticking together of small particles.

Especialu important is investigation of agglomeration and $AI(OH)_3$ crystal growth as the basic factors of increasing grain size of precipitated $AI(OH)_3$.

In this paper we have investigated influence of tartaric acid on the nucleation, agglomeration and $Al(OH_3 \text{ crystal growth from caustic soda solutions}$. Crystallization is carried from sinthetic solutions and industrial seed, obtained from alumina Plant in Podgorica, is used. All experiments were carried out at the temperatures of 60-75 $^{\circ}$ C, caustic soda concentrations of 130-150 g/l and mass ratio of 1.05. Seed ratio was 1 and concentration of tartaric acid 20 mM.

Obtained results have shown that tartaric acid influence inhibitory on the all phenomena of $AI(OH)_3$ crystallization from caustic soda solutions. Besides, it is observed that the of change of all mentioned phenomena with change of temperatura and caustic soda concentration, in the presence of tartaric acid, is the same as in the case of crystallization from pure caustic soda solution. Namely, nucleation process is increased with decrease of temperature and caustic soda concentration while agglomeration and $AI(OH)_3$ crystal growth processes are increased with increase of temperature and decrease of caustic soda concentration.

Phase Composition Synthesized Powders Obtained by the Neutralization of Sodium Aluminate Liquor

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Activated alumina is alumina with good adsorption characteristics, having specific surface area more than 350 m²/g. High specific surface area and good adsorption characteristics of the activated alumina can be obtained by thermal activation of aluminium-hydroxide powders, which can by synthesized by different technique.

In this work aluminium-hydroxide powders have been synthesized by neutralization of sodiumaluminate liquor with sulfuric acid, under different conditions. The aim of this work was to investigate the influence of different processing parameters (such as: caustic module, concentration of sodium-aluminate, neutralization temperature and time of dosing sulfuric acid) on the phase composition of as-synthesized powders. Amorphous aluminium-hydroxide and boehmite particles have been obtained by neutralization process of sodium aluminate at pH=8.5-9.5., whereas at pH=10-12 the as-synthesized powder consists of amorphous aluminium-hydroxide and bayerite particles. It is shown that the specific surface area and adsorption characteristics of activated alumina depend strongly on the phase composition of as-synthesized powder.

Thermodynamic Study of the Formation of Solid Ti in Thermal Plasma

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Thermal plasma, as high temperature mixtures of atoms, molecules, ions and electrons are nowadays widely used for the synthesis of high purity ultra fine powders (in size range of 10-100 nm) of silicon, boron, aluminum etc., oxides, nitrides and carbides [1]. A reactants, introduced into thermal plasma evaporates and, depending on the temperature, partially dissociates into atoms and ionizes, producing ions and electrons. The formation of the molecules and radicals stable at high temperatures also occurs. These species are transported to the reaction zone where, under definite temperature, the desired gas product can be formed. By rapid cooling (quenching) of such system, under controlled conditions, a saturated or supersaturated vapor can be formed and the formation of ultra fine (solid) particles can be achieved.

Titanium is the ninth most abundant element (0.6% by mass) in the Earth crust. It was found in the meteorites and in the sun. Some lunar rocks contain high concentrations of the titanium dioxide. Pure titanium is lustrous, white metal with low density, high strength and excellent corrosion resistance. Titanium and titanium alloys are used in air and space crafts, where strengths, low weight and resistance to high temperatures are important. Titanium metal is considered to be physiologically inert and because of that it is very much used in medicine technique.

Titanium production in plasma reactor has been theoretically and experimentally investigated [2,3]. Problems in production of solid titanium are due to the possibility of the formation of other solid titanium containing compounds instead of or together with solid titanium.

In this paper we consider the formation of atomic titanium at high temperatures in thermal plasma. This process is investigated theoretically by computing the equilibrium composition of the gas mixture containing titanium and chlorine (titanium as reactant is assumed to be in the form of titanium tetrachloride) with argon and of the mixture involving also hydrogen beside mentioned elements. The calculation is performed for temperature range between 500 and 6000 K and for the total pressure in the system of 1 bar and 0.5 bar. Use is made of the fact that thermal plasma is a plasma in (local) thermodynamic equilibrium, which makes possible the theoretical determination (by employing Gibbs free energy data for the compounds present in the system and assuming that the equilibrium of the system corresponds to its minimum energy state) of its equilibrium composition. From the calculated compositions of the investigated gas systems the temperature zones with saturated and/or supersaturated vapor of Ti and another species like TiCl₂ and TiCl₄ were determined and the possibility of the formation of solid Ti was analyzed.

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A New Procedure for Obtaining Calcium-Sulphate α -Hemihydrate on the Basis of Waste Phosphogypsum

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During technological procedure of phosphoric acid production by action of sulphuric acid on phosphoric acid, in dependence of H_2SO_4 concentration, as well as of reaction temperature, dihydrate and hemihydrate may be formed as a product. In the conventional procedure for phosphoric acid production, the conditions are actually selected for dihydrate to be formed (temperature below 80°C and sulphuric acid concentration of 25 wt.%), which would absorb all impurities by its large crystals and which could be easily filtered out on rotation filter:

Thus, by the conventional "wet" procedure, phosphogypsum is already prepared as waste material, because with the majority of absorbed impurities, approximately 20 wt.% of uranium and even up to 85 wt.% of radium-226 isotope pass into phosphogypsum. Considering that, phosphogypsum is a predicted waste and is disposed in deposits. Investigations, conducted in this paper, showed that waste phosphogypsum-dihydrate represents a burden which even must not be kept in deposits because of its large quantity in relation to the main product – phosphoric acid, as well as because of great impact of a phosphogypsum deposit on the environment.

In order to perform transformation of phosphogypsum dehydrate into α -hemihydrate at least 98°C temperature is needed, while it has been found that the transformation takes place with highest rate within the temperature interval between 150°C and 160°C. At higher temperatures, little is obtained by increasing the reaction rate, while at lower temperatures large reactors are needed to provide a complete transformation.

The procedure of the transformation is, carried out with 28 wt.% water solution of sulphuric acid which had been heated to the temperature of 90°C. Phosphogypsum was added to the solution and the resulting emulsion has been vigorously stirred. After phosphogypsum addition, barium sulphate was added also with continual stirring, until the temperature reached 85°C. Then the mixture was cooled. After cooling, it was filtered and separating the solid from the liquid phase. After drying and calcination, grinding of the purified phosphogypsum was carried out by laboratory mixer to the particle size mainly between 100 and 200 μ m.¹

By the proposed procedure, calcium-sulphate dehydrate is transformed into a far purer α -hemihydrate which, with its physic-chemical characteristics, approaches natural gypsum and contains additional components which enable formation of small-grain phosphogypsum which may be utilised in construction industry.²

Test installation, given in this paper, is automated and designed in such way to be operated by only one person. Because of the simplicity of the process and short conversion time, of about 3 min, starting and terminating of the process is measured by minutes instead of hours, with the capacity of 1.8 t/h.

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Hydrothermal Synthesis and Structure of a Novel Organically Templated Zincophosphate

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Introduction

An enhanced interest in inorganic solids with extended structures is mainly based on their application in the catalytic, sorption and separation processes. Thus, many synthetic efforts have been directed towards preparation of novel structural features. Crystallization of these solids generally proceeds under hydrothermal conditions in the presence of organic amines (or quaternary ammonium salts), which exhibit a critical structure-directing (template) role. Here we report on the synthesis and structural characterization of a zincophosphate templated by 3-methylamino-propylamin (MPA).

Synthesis

The compound was synthesized hydrothermally from a mixture of zinc acetate dihydrate, phosphoric acid, and MPA. The crystallization at 120 °C during 10 days yielded a colorless rod-like crystalline product as a single phase. The product was characterized by ICP, SEM, FTIR, TG/DSC analyzes as well as by single crystal structure determination.

Results and disucssion

The compound crystallizes in the monoclinic Pc space group with the unit cell parameters a=11.8920(2) Å, b=5.13180(10) Å, c=12.3063(10) Å, β =98.1250(10)°, where each asymmetric unit contains two crystallographically distinct tetrahedrally coordinated Zn atoms and three P atoms. One P atom has four oxygen atoms bridging to adjacent Zn whereas others are in addition bonded to terminal OH groups. The macroanionic [Zn₂P₃O₈(OH)₄] framework consists of zincophosphate layers separated by monoprotonated MPA cations (Figure 1). Thermal investigations show that the compound is stable up to 300°C when decomposition of organic species occurs. This event affects structural features of the zincophosphate lattice.



Figure 1. Schematic presentation of zincophosphate layers with intercalated diamine molecules

The Influence of Surface-Active Agents on Magnesium Trihydrate Carbonate Crystallization

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Introduction

The purpose of the present paper is to find a theoretical explanation concerning the implication of surface-active agents in the magnesium trihydrate carbonate crystallization.

Experimental and Results

The MgCO₃·3H₂O crystals are obtained by precipitation of Mg(HCO₃)₂ solutions in presence of surfactants.

The influence of the surface-active agents on the growth rate and the shape of crystals were studied. The interpretation of the experimental data was associated with the results of the electrostatic potentials calculations on the crystal faces.

The MgCO₃·3H2O crystals are acicular-shaped. The crystalline habitus is characterized by measurements of crystal dimensions on microphotographies.

In order to evaluate the effect of the surfactants, the method of the cakes humidity determination has been also applied.

Electrostatic potential calculations demonstrate a big difference of V values on the different faces being in the 1:4.5:35 ratio (Table 1), in agreement with the acicular shape of crystals.

		-		
Face	Plane type	Vobtained	V "mean"	
040	Even	2.4569	2.45675	
UAC	Odd	2.4566		
000	Even	0.0693	0.06945	
OBC	Odd	0.0696		
	Even	0.3058	0.0050	
UAB	Odd	0.3058	0.3058	

Table 1. Values of the electrostatic potential on different crystal faces

The rather large anions of the surface-active agents will bind preferentially to the face with the highest V, and hereby, lowering the crystal increase rate along the axis perpendicular to this face.

Conclusion

 $MgCO_3 \cdot 3H_2O$ crystals grow, in absence of surface-active agents, as acicular crystals, in accord to the high imbalance (1:4.5:35) of the electrostatic potential along the main crystalline faces (OBC:OAB:OAC).

The anionic surface-active agents bind preferentially to the face with the highest electrostatic potential (the OAC face), thus reducing the lengths : width (L/w) imbalance to about the half of value.

There is therefore an agreement between the experimental data (crystal dimensions, humidity of cakes) and the calculated values of the electrostatic potential on the faces of the growing crystal; these are reciprocally balancing, confirming the implication of surface-active agents in the $MgCO_3 \cdot 3H_2O$ crystallization mechanism.

Magnesium Carbonates Processed Under Different Technological Variants

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Introduction

The paper presents a synthesis of the original contributions concerning the magnesium carbonates formation from $Mg(HCO_3)_2$ solutions, as a step within the processing of basic magnesium carbonate and magnesium oxide of dolomites by carbon dioxide leaching methods.

Experimental and Results

The kinetic curves of the $Mg(HCO_3)_2$ solutions decarbonating process, performed under different experimental conditions, as well as the impact of technological parameters upon the magnesium carbonates structural characteristics are presented.

The system temperature is responsible for the formation of a certain magnesium carbonate: the magnesium trihydrate carbonate results in the temperature range of 14 to 54.3°C, as well-developed acicular crystals; the basic magnesium carbonate, precipitated over the mentioned temperature (until 100°C), is weakly crystallized, mostly amorphous, of small sizes. The pronounced differences in the shape and the size of the obtained carbonates particles have significant technological implications, which are decisive even for the flow sheet establishment.

The system stirring under different variants was performed by mechanical means (blade stirrer, shaker bath), intense air bubbling, respectively activation in ultrasonic field. As the differences in the stirring intensity of the $Mg(HCO_3)_2$ solutions bring differentiations in the crystals sizes, this is considered a decisive parameter in the control of the particles sizes.

Small admixtures of surface-active agents at the decarbonating of $Mg(HCO_3)_2$ solutions led to good filterability of precipitates, the reducing of filter cakes humidity and the preventing of crusts formation on the decarbonator walls.

The characterization of the two magnesium carbonates, investigated by different techniques (XRD, FT-IR, SEM), had put into evidence the presence of $MgCO_3 \cdot 3H_2O$ and respectively $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$.

Conclusion

By the directions which are identified, the paper opens important practical ways for the obtaining of some magnesium compounds (carbonates, oxides and derivatives) with imposed properties (particles size, partial hydrophobic surfaces). As technological advantages, less energetic consumptions and improvements in equipment operation are to be mentioned.

Toward Crystalline Covalent Solids: Crystal-to-Crystal Dihydrogen to Covalent Bonding Transformation in Sodium Borohydride - THECN and Sodium Borohydride - THBCN

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The hydric-to-protonic interaction, or dihydrogen bonding, between negatively charged hydrogen atoms of M-H (M=metal) bonds and conventional proton donors has been extensively studied since 1944[1]. With characteristics similar to those found in classical hydrogen bonding, this unconventional interaction can influence reactivity and stereoselectivity in solution[2]. In the solid state, dihydrogen bonds have the ability to direct crystal packing, thus finding utility in supramolecular synthesis[3]. O-H...H-B hydrogen bonds have been employed in the construction of novel extended structures with various topologies[4]. More interestingly, some of these systems can react topochemically in the solid state, releasing hydrogen and exchanging the weak O-H...H-B interactions for strong B-O covalent bonds, to form ordered, extended covalent materials[4].However, due to the cumulative shrinkage of the B-O distances during decomposition, these topochemically assembled solids have poor crystallinity. Jackson and Custelcean[4a] suggested two strategies to circumvent this problem. We now describes dihydrogen-bonded systems that satisfies these geometrical criteria, leading as a result to crystalline covalent products, in a crystal-to-crystal thermal decomposition.

N,N',N"-trikis-(2-hydroxyethyl)-triazacyclononane (THECN) or N,N',N"-trikis(orto-hydroxybenzyl)-triazacyclononane(THBCN) and sodium borohydride form a 1:1 complex, which precipitate as a white crystalline solid from ethanol. Single crystals suitable for X-ray crystallography were obtained by slow diffusion of hexane in a solution of these complexes in acetonitrile. The triazacyclononane adopts a conformation with all hydroxyethyl or hydroxybenzyl arms oriented towards the same face of the azacrown ring, encapsulating the Na cation. Solid state decomposition of these complexes, induced by heating under an inert atmosphere results in complete elimination of hydrogen, as indicated by the FT-IR and B solid-state MAS NMR spectra of the resulting materials. The solid- state decomposition product exhibits high crystallinity, as indicated by microscopic examination, which showed good transparency to polarized light for the decomposed crystals. The reaction appears to be crystallographically homogeneous. That the solid-state decompositions of these complexes are a single-phase transformation is also supported by X-ray diffraction analysis, which shows a gradual shift of the diffraction pattern as the reaction progress. The final covalent products exhibit high crystallinity, in agreement with the microscopic observations.

In summary, we report here crystall-to-crystall dihydrogen to covalent bonding transformations of these two complexes. Judicious engineering of dihydrogen-bonded crystals permits transfer of crystallinity to the covalent products resulting from their solid-state decompositions. Further elaboration of the dihydrogen-bonded building blocks, described herein may ultimately lead to low-temperature, rational construction of extended crystalline covalent solids.

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Separation of Tungsten and Rhenium Possibilities and Realisation

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In chemical properties the pair ¹⁸⁸W/¹⁸⁸Re is a close analog of the pair ⁹⁹Mo/^{99m}Tc. Therefore, the methods applied in the separation of ^{99m}Tc can be used for the preparation of high quality ¹⁸⁸Re. The choice of the method depends on the specific activity of the parent radoisotope. Due to the high specific activity of ⁹⁹Mo obtained in uranium fission, the column chromatography based on alumina as the adsorbent and saline solution (0.7% NaCl) as the eluence, is the method of choice. In the case of ¹⁸⁸W/¹⁸⁸Re it can be applied only when high specific activity of the parent radioisotope is on disposal because of the low adsorption capacity of alumina for anions. Suficiently high specific activity of ¹⁸⁸W can be obtained only in the high flux reactors (about 10¹⁵ n cm⁻²s⁻¹) enabling the reaction ${}^{186}W(2n,\gamma){}^{188}W$ to take place. For the separation of ${}^{188}W$ of low specific activities several methods can be applied. They are in many items similar to those developed to avoid uranium fission utilizing $(n,\gamma)^{99}$ Mo produced in medium/low flux research reactors. There are several advantages of such an approach. Instead of the production in only a few now existing high flux reactors, a large number of these machines with lower neutron fluxes can also be used. The enriched or even natural tungsten targets can be used, thus considerably reducing the costs. One of the common procedures is extraction, usually employing methyl ethyl ketone (MEK). The obtained rhenium solution is of high radiochemical purity and of high purity of inorganic ions. Thus, the production of rhenium solutions of high specific activity is possible. Another approach is the development of so-called gel generators. However, due to the advantages of the chromatographic generators many attempts were made in their development. Alumina is an inorganic adsorbent, resistant against radiation and microbial contamination. Saline solution is compatible with most uses of the separated rhenium. However, a procedure of the concentration of rhenium in the eluate should be introduced. It should remove all salt and the common metal impurities. Then ¹⁸⁸Re-perrhenate is taken up in low volume reagents required or radiolabeling. The paper presents the discussion on several aspects of the separation prosesses used in ¹⁸⁸W/¹⁸⁸Re generators. The results in the development of the chromatographic generator in the Laboratory for Radioisotopes (Vinča Institute of Nuclear Sciences) are shown.

The Effect of Mechanical Activation on the Synthesis of Ce₂Si₂O₇

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According to the literature data, if the solid state reaction between oxide powders was used for $Ce_2Si_2O_7$ preparation, only the low temperature polymorph of $Ce_2Si_2O_7$ (A – type) could be obtained by annealing the high temperature modification (G – type) of Ce₂Si₂O₇. The sluggish phase transition was found to occur at 1274°C. However, we have obtained in the present study the low temperature modification of Ce₂Si₂O₇ by heating the mechanically activated mixture of the oxide powders CeO₂ and SiO₂ (quartz). Also, mechanical activation has accelerated the synthesis of Ce₂Si₂O₇ due to better homogenisation of the mixture, particle fragmentation and lattice defects formation in the starting oxides. Mechanical activation of the mixture with composition corresponding to Ce2Si2O7 stoichiometry was performed in high energetic vibratory mill 2, 15, 30, 60 and 120 min. Activated mixtures as well as the non-activated ones were heated in an Astro furnace in an argon atmosphere at different temperature, from 1200 to 1550°C, for 1 hour. Microstructure characterizations of the activated mixtures and phase identification were done using X-ray powder diffraction (XRD) analysis and Scanning electron microscopy (SEM). It was found that well crystallized quartz became amorphous during 60 min milling of the mixture, while the crystallite size of CeO₂ decreased rapidly from 140 nm to 20 nm and its lattice distortions attained maximum in 30 min activation. XRD phases analysis showed that in non-activated mixture, heated at 1200, 1300 and 1400°C, predominantly the other cerium silicate, Ce_{4.67}(SiO₄)₃O was formed. However, at 1550°C the reaction between oxides was completed, resulting in high temperature polymorph of Ce₂Si₂O₇ with monoclinic structure. On the other hand, heating of the 60 min activated mixture at 1300°C produced only the tetragonal low temperature modification of Ce₂Si₂O₇ (I.t.). Activation of the mixture during 15 min provided formation of high temperature form of Ce₂Si₂O₇ (h.t.) at 1400°C. A few of relevant XRD patterns are shown in the Figure 1.



Figure 1. XRD patterns of mixture heated at 1300 °C, non-activated (a), 60 min activated (b) and heated at 1400 °C, 15 min activated (c)

Symposium B

The Greening of Chemistry: Pursuit of a Healthy Environment and Safe Food

INVITED LECTURES





The four phases of alchemy from Johann Daniel Mylius' Philosophia reformata, Frankfurt 1622

Semiconductor-Mediated Photocatalyzed Degradation of Chlorothalonil in Aqueous TiO₂ Suspensions

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Environmental pollution and destruction on a global scale have drawn attention to vital need for totally new environmentally friendly, clean chemical technologies and processes, the most important challenge facing chemical scientists in the field of green chemistry. Strong contenders as environmentally harmoniums catalyst are photocatalysts that operate at room temperature and in clean manner, while applications of such safe photocatalytic systems are urgently desired for purification of polluted water and decomposition of offensive atmospheric odors as well as toxins, NOx and chlorofluorocarbons on a huge global scale.

The use of semiconductor photocatalyzed degradation of organic and inorganic substrates as a method of treatment of wastewater pollutants is currently attracting considerable attention. Earlier studies have shown that a wide range of organic substrates can be completely photomineralized in the presence of TiO₂. A wide variety of pesticides are nowadays introduced into the water system from various sources, such as industrial effluents, agricultural runoff and chemical spills. Their toxicity, stability to natural decomposition and persistence in the environment has been the cause of much concern to societies and regulating authorities around the world.

Most aromatic molecules undergo photocatalytic degradation when irradiated in the presence of suitable semiconductors. The most commonly used catalyst is TiO_2 (cheap, non toxic and abundant product). The initial step of the transformation is the formation of electron-hole pairs in the semi-conductor particles when irradiated with light or energy higher than the band-gap. Photocatalytic degradation occurs through a multi-step process involving the attack of the substrate by radical species, among which the [•]OH radical is recognized to be the most powerful oxidant. In most cases the final stoichiometric oxidation of organic carbon to CO_2 is achieved. However, the evaluation of the mineralization degree achieved for the organic pollutants after treatment is necessary. If only partial degradation is envisaged, toxicity assessment of treated water becomes necessary.

The photocatalyzed degradation of the biocides chlorothalonil and dichlofluanid has been investigated in aqueous suspensions of titanium dioxide under simulated solar irradiation. The primary degradation of the micropollutants follows a pseudo-first-order kinetics following the Langmuir-Hinshelwood model. In our conditions total disappearance of chlorothalonil and dichlofluanid was achieved in 90 and 20 min respectively whereas the mineralization of organic carbon to carbon dioxide after 240 min of irradiation was found to be 100% for chlorothalonil and 78% for dichlofluanid. The evolution of heteroatoms (Cl, N, S, F) followed by ion chromatography showed a mineralization into chloride, nitrate, sulfate and fluoride anions respectively. In addition Microtox bioassay (*Vibrio fischeri*) was employed in evaluating the ecotoxicity of solutions treated by photocatalysis. Photocatalytic intermediates detected during the degradation of biocides were identified by GC-MS techniques. Based on this byproduct identification a simple degradation and decarboxylation leading to the mineralization of the starting molecules.

Green Chemistry: Chemical Processes Reducing Toxic Byproducts Released in the Environment

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A recent assessment of the sources of Persistent Toxic Substances in the Mediterranean Region, has evidenced that most of the industrial sources of this contaminants are the result of a low level of technological implantation of the Chemical Industry in the Region.

The Sustainability of the Chemical Industry in Europe and in the Mediterranean Region at large, strongly depends on the greening of their industrial practices. Therefore, the Chemical Industry at large faces a critical challenge to adapt and renew their production practices to take into consideration the Sustainibility Paradigm.

In my presentation, I will give an overview of the industrial sources of PTS in the Region, the current deficits in this area, as well as new promising developments on Cleaner Production. Experiences in the Mediterranean Region will be the main focus of the presentation.

Phytoremediation Potential of Some Plants for Nickel-Contaminated Soils

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Phytoremediation is a new low cost alternative technique for remediation of contaminated soils from heavy metals that are emitted by ferrous and nonferrous mining and extracting processes. This is based on the ability of some plants to accumulate very high concentrations of metals from soils and thus providing the basis for a remediation of the contaminated sites. This technique as an emerging branch of natural biotechnology, has several advantages compared to the sophisticated physicochemical techniques of soil remediation. It is not only environmentally friendly and low cost but furthermore plants can accumulate metals to such levels that the mineral recovery maybe feasible even in conventional smelting or refining processes.

The aim of this paper is to present for the first time data of the wild plants species growing in nickel-containing serpentine soils in Albania, in order to identify the nickel-tolerant and hyper-accumulator species that could be used for phytoremediation and phytoextraction purposes.

In this work, the potential of many plants to accumulate nickel has been investigated in order to identify the species which offer the best phytoremedial potential for nickel contaminated soils in Albania. Field surveys have been made in five nickel-containing sites in order to identify the nickel tolerant species that have spontaneously grown in contaminated soils. Atomic Absorption Spectrometry measurements were carried out on 145 different plants collected. 16 of them were identified as having an hyper ability to accumulate nickel since they contained more than 10 000 mg Ni per kg (DW). Seven taxa are of Alyssum genus and one of Bornmuellera genus of Cruciferae. The taxa showing the highest accumulation of this metal is Alyssum murale var. chlorocarpum with 28 600 µg/g or 2.86% and Alyssum markgrafii O.E. Schulz with 23 700 mg/kg or 2.37%. In order to optimize the phytoremediation and phytoextraction processes further biological and chemical studies were carried out to determine the parts of the plants that accumulate the highest amount of nickel and the best biological cycle during which they accumulate the highest amount. The results show that the greatest accumulation of nickel occurred in the leaf material (2.86%) and the least in the roots (0.43%). The investigation of the biological cycle of the genus Alyssum showed that: (1) the seeds germinated between 5° C to 30 ° C and more in 25 ° C; (2) 62.9 % of seeds germinated at A.m. var. chlorocarpum; (3) the emergence is almost continue from March to April; (4) the anthesis occurs from May to July; (5) the ripening of the fruit takes place 30 days after flowering; (6) the dissemination of fruits occurs from September to October.

The above-mentioned results are obtained for the wild species that grow spontaneously in nickelcontaining soils. However, the cultivation of selected Alyssum genotypes in the conditioned soils can lead to adequate hyper-accumulation of metals in the plants in order to make feasible the recovery of the metals from these plants. Some of the soil conditions that increase the accumulating ability for nickel and it phytoextraction might be a low pH of the soil (at a range of 4.5 to 6.2), low exchangeable calcium concentration and relatively high magnesium concentration and the addition of ammonium-containing fertilizer and chelating agents.

Due to these special characteristics it is reaffirmed that Alyssum murale var. chlorocarpum, as a nickel hyperaccumulator, is the most promising plant to be used for feasible phytoremedation and phytoextraction purposes.

Environmental Sampling: A Tentative Assessment of the Associated Uncertainty

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Experience has shown that the difficulties in developing a common information data-base on the quality of the environment are caused by a lack of harmonized monitoring procedures. Indeed the use of standard operating methodologies from sampling to chemical analysis can help to obtain reproducible and comparable values and represents a prerequisite for a reliable interpretation of measurement data. However, the harmonization of both sampling and analytical procedures is not sufficient because the quality needs to be measured. A parameter to assess their quality is the uncertainty. This is a measurable parameter based on the evaluation of statistical distribution of a series of measurements described by standard deviations and variances. Therefore, the comparability between measurements should be found in sampling procedures and protocols associated with realistic estimates of uncertainty, rather than in the repeated use of the same protocol.

In the last years a large effort has been made to improve the analytical techniques and to reduce the sources of uncertainties during the laboratory operations so that the measurement uncertainty is usually well characterized and controlled by laboratory quality assurance and quality control procedures. On the contrary, uncertainty associated with sampling and sample treatment is not yet fully considered. In fact, the principles to assess the uncertainty associated are rarely applied despite the requirements of international rules such as the ISO/IEC 17025 on the competence of testing and calibration laboratories. Samples collected by using different sampling methods and designs might produce different measurement values, even if analysed by the same sophisticated analytical technique This because many uncertainty components such as the sampling strategy, the 3D spatial variation, the sample handling and its pre-treatment, the sample type and the related stability have to be considered. Therefore, the total variance (S_{tot}) can be defined as the sum of at least four main components, i.e. the variance of sampling (S_s), the variance of sample treatment/reduction (S_t), the variance of analysis (S_a) and the spatial variability(S_{sp}). This gives: S_{tot} = S_s + S_t + S_a + S_{sp}

In the recent years few studies, in particular on soil, have been carried out. Sampling intercomparison exercises confirmed the contribution of different sampling protocols and devices to the variability of the final analytical data. Now, if a reference sampling on a selected area is performed by an intensive sampling and by a single operator using the same device and following a defined pattern and protocol, a well-characterized reference site can be obtained. In such a way the element/compound concentrations in the different sample locations can be known as well as the related uncertainties in analogy to the reference materials used in the analytical field. Selected compounds can also be added and homogenised in soil so that a synthetic reference material for sampling is obtained. Therefore, the reference site becomes a natural matrix reference material for sampling, well characterized in terms of spatial/time variability and the subjectivity in sampling procedures, that was found to be the main source of data availability, properly limited.

Photodegradation of Pesticides and the Application of Bioanalytical Methods for their Detection

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The information provided by well established and highly sensitive and selective, but time consuming analytical techniques, is frequently obtained too late to enable active control of processes in environment or industry. It therefore become apparent, that fast information with just 10 % uncertainty is much better than the information with less than 1 % uncertainty but provided too late. To ensure better quality control, qualitative methods of analysis are regaining importance. Since they are rapid, simple and inexpensive, they provide a valuable tool for screening of large numbers of samples. This approach is based on accurate identification of "positive" or "negative" samples with respect to the presence of unwanted compounds such as pesticides or other toxic substances. Such compounds are usually detected in just a minor fraction of all samples, and are further analysed by conventional quantitative methods such as HPLC, GC/MS etc..

Application of highly sensitive techniques such as thermal lens spectrometry (TLS) offers some interesting advantages in qualitative analysis, which were recently exploited in some novel methods for detection of organophosphate and carbamate pesticides and studies of their photodegradation, as well as for quality testing of foodstuffs including vegetables, fruits and fruit juices. High sensitivity and low sample volume requirement of TLS is particularly favourable in the case of flow injection analysis (FIA), where it enables reliable measurements before the analytical signal is completely evolved, and therefore increases the sample throughput. High sensitivity of the technique also enables detection of minute amounts of toxic and other substances in concentrations well below the regulatory limits. TLS provides LOD for cumulative concentration of organophosphate and carbamate pesticides below 1 ng/mL paraoxon equivalents as achieved by FIA-TLS. For this purpose the TLS was hyphenated with a bioanalytical method based on acetyl-cholinesterase (AChE) inhibition in a FIA system. The FIA technique enables on-line oxidation of organophosphates present in thiono form (parathion, malathion...), which do not inhibit AChE, as well as the regeneration of inhibited enzyme.

The described method was applied to monitor the efficiency of different photodegradation processes of pesticides such as malathion, diazinon, coumaphos, and azinphos-methyl under laboratory and environmental conditions, with particular emphasis on the toxicity testing of degradation products. Presentation will also cover the results and analysis of a large scale testing of the FIA-TLS bioanalytical method, which includes comparative analysis of several hundred samples from fruit juice production. The main focus were the matrix effects and their influence on the reliability of results, which was found strongly affected by the differences in pH, content of sugars, electrolytes etc. These parameters can vary significantly even for samples, such as fruit juices from the same kind of the fruit, depending on the microclimatic conditions and stage of growth. The matrix effects were reduced and the performance of the method was improved by calibrations with matrix-matched standards.

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GMO Challenge for the 21st Century

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As every new step in a science and in the practices, genetically modified organisms confused almost everyone. Are these products from 20th century, as a historical step, safe for humans and nature? Will it cause some changes in the environment, if we consume and deposit it in our body? For now it is still unknown. From this point of view genetically modified organisms present a challenge for the 21st century.

During the past couple of decades, molecular methods have been developed to clone genes and transform or transfer them into living organisms, including plants and animals resulting in what we commonly call Genetically Modified Organisms (GMO's), or Genetically Enhanced Organisms (GEO's).

In plants, particular genes have been identified, cloned and transferred into particular parental lines that have then been used as gene donors or carriers in backcross breeding programs. New inbred lines or parental lines often referred to as Genetically Modified Lines (GML) are then used in the development and production of Genetically Enhanced Hybrids (GEH) or Genetically Enhanced Products (GEP) that are then purchased by farmers and used for production of grain or plants for use in animal or human feed or food.

Answer today a package of new steps relating to seed purity. These include:

- pressing for concerted international action to seek new legal standards for seed purity;
- testing of seed imports;
- and working with the industry on a Code of Practice.

These measures build on the current consultation on the importance for labelling of seeds.

It is basically important for GM to have a data base, and it will be organized, and we hope this data will give some answers to many questions. On the level of EU there is an official body responsible for it. In our country there is a project based on it. But this project includes, beside GMO testing food, the analyses of soil and data relating to cross pollination.

On the basis of facts mentioned above we can say that there is no GMO present in food in one small area in Novi Sad. Our goal is to spread our work across the whole region of Vojvodina, not as a protest against GMO, but simply because we would like to know what will happen in a future. This is a question for all of us.

Thirty Years of Environmental Research of PCBs and DDTs at Ruđer Bošković Institute, Zagreb, Croatia

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At the beginning in early seventieths by using C-14 labelled DDT, investigation the sorption of DDT on various marine sediments was performed. The results were published in Bull. Environ. Contam. Toxicol. and Water, Air, Soil Pollut. After development GC analysis these investigations were continued on the distribution of DDT and Aroclor 1254 in laboratory-grown marine phytoplankton. Separation of PCBs from chlorinated insecticides on silica gel micro column was especially important taking into account that in this time the most laboratory performed GC analysis by using filled columns. Results of this investigation were published in Journal of Chromatography. During 1973 -1975 inside Project COST 64b, investigation of the possibilities of concentrating hydrocarbons and chlorinated hydrocarbons from water samples were performed. In that period a lot a work was done about the analytical problems of analysis polychlorinated biphenyls and chlorinated insecticides in water. 1980 we have published work: Picer, N. and M. Picer (1980), Evaluation of macro reticular resins for the determination of low concentrations of chlorinated hydrocarbons in sea water and tap water, J. Chromatogr. 193: 357-369. This paper was until 2000 one of the most cited analytical work in Croatia. Even from 1973 mussels samples were collected from various areas in the Adriatic Sea and analysis of PCBs and chlorinated insecticides were performed until nowadays. Sampling and analysis PCBs and chlorinated insecticides in sediment and fish samples began in middle of seventies. It means that monitoring of PCBs and especially DDTs in the Adriatic Sea in Rudier Boskovic Institute has very long tradition and surely is the longest on the Mediterranean Sea and due available data, maybe the longest in the World. It is very important to stress that all these samples were analyzed from a single analytical group (mostly by the same analyst), using a uniform methodology, which was very successfully intercalibrated during numerous international intercalibration exercises. Namely, based on the frequency of participation and the quality of the data reported, the IAEA has issued a list of selected laboratories around the Mediterranean for trace organochlorine compound analysis. Of the 56 laboratories from 14 Mediterranean countries that participated in the intercalibration runs to determine chlorinated hydrocarbons in marine samples, six were selected for excellent analytical performance. Among them, only the laboratory from Rudjer Boskovic Institute, Zagreb and the Institute of Marine Biology, Venice, Italy, published most data on chlorinated hydrocarbons in the Adriatic Sea.

The burning or damaging of industrial and military targets in the Former Republic of Yugoslavia resulted in the release of a large number of chemicals into the environment. European Commission experts of the fifth framework Programme (Call Identifier ICFP501A2PR02) have been recognized these problems and approve the proposed investigations under Contract APOPSBAL ICA2 - CT2002-10007. M. Picer from Rudjer Boskovic Institute is scientific coordinator of the Project. Nowadays the Project has been carry out in 12 institutions from Croatia (3 institutions), Serbia and Montenegro (3 institutions), Slovenia, Bosnia and Herzegovina, Kosovo, Austria, Czech Republic and Greece. In the presentation on the Congress detailed description of the Project with some investigation results will be described.

Atmospheric Pollution of Athens by PM10 Particulate Matter: Mass Concentration of Inorganic and Organic Pollutants

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The determined inorganic and organic chemical composition of airborne particulate matter sampled in Athens at 2 sites during 2 separate month-long intensive campaigns, one in winter, the other in summer were used to study seasonal variations in chemical composition. Fractionartion in three major particle size categories was effected using either High Volume Samplers or Dichotomous Stacked Filter Units (particles > 10 μ m; between 10 and 2.5 μ m and particles < 2.5 μ m). As traffic emissions were anticipated to be a key source, each pair of sampling sites in Athens, comprised of a city centre roadside site (chosen to represent traffic influence + urban background), and a city centre site away from any major roads (selected to represent urban background). This facilitated evaluation of the contribution of traffic emissions to air pollution.

Also, the determined inorganic and organic chemical composition of particulate matter and their size distribution, emitted by a variety of known combustion sources of particulates were used to apportion specific emission sources *e.g.* diesel and gasoline-fuelled vehicles; oil-fired domestic heating *etc.*

Finally, inverse modelling was validated using the above results and an air pollution management software package is been modified to apply to 5 other European cities.

The above work is part of the European research programme 'SAPPHIRE'.
How Levinthal's Paradox Can Be Used to Improve Microbiological Determinations

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From various folding pathway of thermally denatured human and bovine serum albumin (used as model molecules) as well as of gelose (used for microbiological determinations), mixtures of different conformers were obtained by various cooling procedures. The main effect of heat on the conformation of the albumine (which in the narrative state takes such a conformation that prevalently has the polar residues of amino acids oriented towards the outside of the molecule and the non-polar ones toward inside) is supposed to consist in the redirection of the amino acid moieties, involving a change in the hydrophilic-hydrophobic balance. A sequence of conformational modifications is assumed to result from different refolding processes of thermally denatured albumin. Because of the large number of freedom degrees of the macromolecule, this leads from the largely featureless ensemble of denatured conformers to structure modified to different extends compared with the native albumine. In this way, the capacity of the protein to interact or bind with other species can be gradually modified, as it was well observed in its chromatographic and electroforetic properties, spectral results concerning the associations with and bromphenol blue, interferometric evidence of self-association of protein eosin macromolecules, kinetics of oxidation by hydrazyl radicals and from the Drude equation for anomalous dispersion, apparent helix content of various conformer mixtures were obtained. Some of these results were applied in order to improve the standard microbiological method for the determination, at 37°C, of mesofila aerobica bacteria, allowing different refolding time in the last stage of gelose sterilization process.

Green Chemistry: Designing Chemistry for the Environment

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Green Chemistry is not different from traditional chemistry inasmuch as it embraces the same creativity, and innovation that has always been central to classical chemistry. Green chemistry merely pursues those same ideals with additional considerations to those incorporated into the design and implementation of chemistry historically.

Green Chemistry focuses on the designing, manufacture, and use of chemicals and chemical processes that have little or no pollution potential or environmental risk and are both economically and technologically feasible. The principles of green chemistry can be to all areas of chemistry including synthesis, catalysis, reaction conditions, separations analysis, and monitoring.

The history of protecting human health and the environment has been a constant striving to minimize risk by reducing exposure and intrinsic hazard. Green Chemistry has sought to shift environmental protection from merely addressing the conditions of risk to changing the inherent nature that causes the risk.

The chemical industry releases billion tones of chemical waste each year to the environment. Industry then spends billion per year in waste treatment, control, and disposal costs. The challenge of chemists involved at all stages of chemical design, manufacture, and use is to make incremental changes that, when summed, will achieve significant accomplishments in the design of new products and processes that are less polluting and hazardous to the environment.

This paper presents the current research efforts and recent results of leaders in the field of green chemical synthesis and processes. The projects described cover a range of topics that are broadly applicable to the chemical industry as well as to the chemical education. In order for the Green Chemistry to reach its potential, government, industry and academia need to work together for the needed research and the development of this new area.

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Structural Elucidation of Biologically Active Substances and Metabolites by HPLC-MS/MS

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MS-MS Techniques

MS/MS coupled to HPLC is a powerful tool for the selective and sensitive detection of analytes. Compounds can be ionized either by atmospheric pressure chemical ionization (APCI) or by electrospray ionization (ESI), mainly forming $[M+H]^+$ ions. For specific and sensitive detection the MS/MS operates in the selected reaction monitoring mode (SRM).

The presentation will deal with the following three classes of substances: pesticides, antibiotics and natural products from fungi.

Pesticides

Some pesticides are a racemic mixture and in many cases only one enantiomer exhibits biological activity. Therefore the application of the pure active compound results in a fifty percent reduction of the contamination of the environment. It is generally accepted that chemical degradation is a non-chiral process, while biodegradation may result in enantioselective degradation. We performed degradation experiments with *R*-Metalaxyl, *S*-Metalaxyl and the racemate. The concentrations of the parent compound as well as the primary metabolite were monitored by RP-HPLC and confirmed by LC-MS. Additionally, the enantiomeric distribution of Metalaxyl was studied by chiral HPLC. The results obtained with two soils revealed that there was not only a difference in degradation kinetics but also in chirality.

Antibiotics

Antibiotics are used to treat infectious diseases in livestock. The animals absorb most of the compounds quickly but they excrete the compound after some days or weeks with excretion rates of 50-90% of the applied amount. The respective antibiotics are trapped in the manure, some undergoing microbial metabolism, and are brought with the manure to the fields. Antibiotics can also be released into the environment by excretion of human pharmaceuticals. There is a growing concern that the intensive use of antibiotics leads to resistance of bacteria that infect humans.

Our study focused on the determination of antibiotics in the agricultural environment and sewage sludge. The soil analysis was performed by an accelerated solvent extraction (ASE), manure and sewage sludge were analyzed by liquid/liquid extraction, followed by a clean-up on a 2000 mg diol-SPE cartridge.

A simple and rapid method for the determination of salinomycin and tiamulin in pig manure, soil and sewage sludge was established using diol-SPE and APCI-SRM analysis. Recovery rates of 75-100% for the compounds did not depend on concentration. Limits of quantification were in the low μ g/kg range. In the tested samples, tiamulin was found at concentrations of 43 μ g/kg in manure and 0.7 μ g/kg in soil.

Natural products

HPLC has pioneered the structural elucidation of new polar components of natural origin. Examples will be given for *Cortinarius orellanus*, a deadly poisonous fungus, and *Melanogaster broomeianus*.

Overview of Perspectives for the Destruction of Toxic Chemicals and CWA According to the Chemical Weapons Convention

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Necessity for the destruction of toxic chemicals (waste) along with destruction of chemical weapons and chemical warfare agents (CWA) in accordance with provisions of the Chemical Weapons Convention (CWC) signed by majority of the countries in the international community has been a great challenge for research and development in modern and environmentally safe techniques for the destruction.

In the article, modern techniques and the perspectives in the area of the destruction of CWA are presented.

Discussion is given on destruction of chemical weapons, especially on classification and characteristics on several methods of CWA destruction, as follows:

a) Destruction regarding temperature conditions [1, 2]:

- high temperatures (incineration, plasma torch, molten metal)
- medium temperatures (pyrolysis, supercritical and wet air oxidation, hydrogenation)
- low temperatures (metal oxide catalysis, silver II oxide electrolysis, dry HCI)

b) Destruction regarding reaction state or medium of the reaction [2-5]:

- incineration (combustion diagnostics)
- reactions on well characterized metal and metal oxide surfaces (surface chemistry)
- reactions in solutions (mechanism in supercritical water, with or without oxidizing agents, GC reactors, redox catalysis combined or not with photolysis semiconductor)
- organised assemblies and dispersions (phase transfer catalysis, micelles, vesicles, emulsions)
- biodegradation (using molds, fungi, bacteria) and direct enzyme interactions (DFPase, peroxidase, or immobilized cell systems for multi-step catalysis...)

Special emphasis is given on methods of destruction used in the destruction activities conducted under the provisions of CWC in States Parties of the CWC - possessors of Chemical Weapons.

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New Developments on Dimethyl Carbonate Chemistry

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Dimethylcarbonate (DMC) is a valuable methylating reagent which can replace methyl halides and dimethylsulfate in the methylation of a variety of nucleophiles and phosgene in carboxylatiin reactions. It couples tunable reactivity, and unprecedented selectivity towards mono-*C*- and mono-*N*-methylations (>99% at complete conversion). It is a prototype example of a *green reagent*, since it is non-toxic, made by a clean process, it is biodegradable, and it reacts in the presence of a catalytic amount of base thereby avoiding the formation of undesirable inorganic salts as by-products. Depending on the reaction conditions, DMC can be reacted under plug-flow, CSTR, or batch conditions. Other remarkable reactions are those where DMC behaves as an oxidant. The high selectivity in methylations is due to the double reactivity of DMC which reacts on its hard centre (the carbonyl group) with harder nucleophiles and on its soft one (the methyl group) with softer nucleophiles. Recently achieved selectivity with nucleophiles on N, O, S and C will be given.

Activation of DMC on acidic catalysts like zeolites and the related reaction mechanism will be reported as well.

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Remediation of Heavy Metals in Toxic Solid Industrial Waste and Polluted Soils: An Integrated Approach of Technologies

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The management of toxic solid industrial wastes and of polluted soils (especially those contaminated with heavy metals) nowadays can be considered as an emergency issue and as an serious environmental threat. For this purpose, various treatment technologies have been suggested and applied, presenting promising results. In this paper an integrated approach, regarding also the possibility of recycling certain pollutants, such as lead, will be presented. Hydrometallurgical, thermal and materials science aspects, as well as (in situ) stabilization (applying as additives for example natural or synthetic phosphates/apatites) and vitrification methods, have been successfully examined. The toxicity of final (stabilized or vitrified) products was evaluated by applying standard leaching tests, i.e. the DIN 38414 S-4 method and the Toxicity Characteristic Leaching Procedure (TCLP). The obtained results indicated that the initially highly toxic waste was transformed into a non-toxic vitrified product, which can be safely disposed or reused (for instance as construction material), due to the fact that the measurements of lead concentrations (the major pollutant in this case), following the (TCLP) leaching of stabilized products were found to decrease substantially from almost 2,500 mg/L (before treatment), to less than 1 mg/L (after the application of appropriate treatment). As a result, an overall treatment scheme can be suggested, incorporating various technological aspects.

ORAL PRESENTATIONS





Alchemical symbols used in the 17th century, from Basil Valentine's Last Will and Testament, London, 1671

Determination of Prolyn in the Lichens Usnea hirta

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Recent investigations have shown that some lichen metabolites may have an important role in protecting thalli from the dangerous toxic action of free radicals produced by oxidative stress exposure. Oxidative stress in lichens may be caused by many agents, including high light levels in the habitat, SO₂ pollution and herbicides, which transfer electrons from various transport systems to oxygen, producing superoxide radicals.

Examining different stress conditions in plants, researchers, were facing increased content of prolyn. This occurrence is proven in stress cases provoked by drought. It is proven that increased quantity of SO₂ influenced quantity prolyn to increase in experimental condition.

Investigation of stress condition of autochthonous lichen type Usnea hirta (L.) Web. in Wig from Kopaonik region distributed to Vranje localities was done in the 2002/2003 year.

The aim of this work was to determinate the quantity of amino acid prolyn in lichens Usnea hirta, having in mind air-pollution factors, acid rains, and abiotical factor during the exposition of Kopaonik samples in Vranje localities.

The quantity of amino acid prolyn is determined using Troll and Lindslay method. The quantity of prolyn is measured using spectroscopic method by standard curve.

Examination showed increased level of of prolyn in Usnea hirta influenced by action of airpollution, acid rains and abiotical factors during the exposition of lichens. Values of prolyn are distributed by following order: Bunuševac > Suvi Dol - (E - 75) > Zlatokopačka petlja - deponija > Vranje - center.

Serbia Danube River Enterprise Pollution Reduction Project (DREPR)

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The Project is carried out under The World Bank – GEF Investment Fund for Nutrient Reduction in the Black Sea/Danube Basin and coordinated by the Ministry for the Protection of Natural Resources and Environment – Republic of Serbia.

The section of the Danube that flows through Serbia and Montenegro (SM) is 588 km long of which about 138 km constitute the state border with Croatia and about 213 km with Romania. The Danube's largest tributaries, Drava, Sava and Tisa, empty into the Danube on Serbian territory increasing its flow about 2.5 times. Other significant tributaries that empty into the Danube on SM territory include Velika Morova, Tamiš which comes from Romania, and Timok which constitutes parts of the SM-Bulgarian state border. SM is one of the largest contributors to the Nitrogen (N) and Phosphorus (P) pollution of the Danube River. The Danube Water Quality Model developed in support of the Transboundary Diagnostic Analysis for the Danube River, estimated SM's annual discharges at 72000 N t/y and 7000 P t/y, representing 13% and 14% of total loads, respectively. These values place SM third in N discharges and second in P discharges among the 13 countries of the Danube River Basin. The National Review on SM identified wastewaters from livestock farms, industrial enterprises, notably fertilizers, agro-processors and breweries, as the largest source of N and P in SM's Danube Watershed. The Project will aim at increasing the prevalence of environmentally friendly practices among polluting enterprises in the Danube Basin of the Republic of Serbia. The Project covers several components:

Component 1. Regulatory Reform and Capacity Building. The project will support legal reforms that target the reduction of enterprise nutrient pollution, and support SM in its goal to gradually harmonize its environmental laws and regulations with those in the EU *aquis*.

Component 2. Investment in Nutrient Reduction. Investment support will be provided to fertilizer factories, agro-processors, notably slaughterhouses, and livestock farms that are nutrient pollution hotspots. Eligible activities supported under the project will include cost effective advanced waste management and wastewater treatment, process improvements, and proper manure and on-farm nutrient management practices which will reduce nutrient discharges into the Danube river system. Monitoring of reduction in nutrient discharges will also be carried out under this component.

Component 3. Awareness Raising and Replicability Strategy. The project will carry out public information campaigns at the national and local levels to raise public awareness on nutrient containing waste management and water pollution, and their impact on public health, economy and ecosystems. The project will also institute on a pilot basis a "Public Environmental Information Sharing Scheme" in which information on pollution emissions from industrial enterprises and their potential impact on public health and the economy would be shared with the public in an easily interpretable manner.

The Formation of Potassium Magnesium Phosphate Hexahydrate in Aqueous Solutions. Alternatives for Phosphorus Recovery from Aqueous Media

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Phosphorus recovery from wastewater is becoming very urgent. Recovery in the form of fertilizers is an attractive oprion resulting in savings of raw materials. Crystallization of free inorganic orthophosphate in the form of a salt incorporating besides phosphate important plant nutrient metals, such as potassium and magnesium.

In the present work, we have investigated thw formation of the pottasium magnesium phosphate hexahydrate (KMgPO₄.6H₂O) in supersaturated solutions. Both spontaneous and seeded growth studies were done in unstable and stable metastasble solutions respectively at 25°C. The experiments were done using the free drift and pH-stat methods. In all experiments the initial pH was adjusted to 8.50.

From the kinetics analysis the induction times were measured for the unstable solutions which was inversely proportional to the solution supersaturation with respect to $KMgPO_4.6H_2O$. In the low supersaturation range, seeded growth experiments were done. Both during spontaneous supersaturation and in the seeded growth studies the rates increased with increasing supersaturation. The morphology of the crystals did not vary significantly although aging effects were observed. On the basis of the kinetics analysis it was suggested that the precipitation of $KMgPO_{4.6H_2O}$ tales place by a surface controlled mechanism.

Strategy to Greener Analytical Chemistry

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An overview of the strategies to greener analytical chemistry is presented. An ideal green analytical procedure should be implemented without reagents or, in a more realistic approach, by employing only non-toxic chemicals. A new concept of green analytical chemistry is based on reagentless procedures, replacement of hazardous chemicals, strategies for waste minimization as well as on-line waste treatment. Automation, employment of solid-phase reagents and miniaturization are highlighted as alternatives for waste minimization.

Green chemistry does not only apply to the production and use of chemicals, but also to areas such as analytical methodology. While this might be thought of as involving small amounts of materials, there is a definite need to apply the principles of green chemistry here too. This overview analyses some of the current trends in greening analytical chemistry. All current procedures could become more environmentally being if the amounts of the reagents were considerably reduced. This task can be readily attained downscaling the manifold components and possibly arranging them in a single device. This resulted in the application of the concept of micro total analytical systems (μ TAS) to chemical sensors and flow analysis. The central idea of μ TAS is to arrange all the steps of sample processing in a single device of a few square centimeters.

Green analytical chemistry is in its initial stage of development but there is a clear trend towards fast and consistent growth. Analytical methods with high performance but which are not environmentally friendly tend to be unacceptable and this will stimulate the development to a greener analytical chemistry but there is a long road to go and the potentialities have not been fully exploited. This also holds in the context of education in chemistry. The replacement of old experimental practices by attractive procedures exploiting available instrumentation will result in the immediate reduction of wastes as well as develop an essential environmental conscience for the future.

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Distribution of Heavy Metal Contents of Urban Soils in Parks of Belgrade

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Soils in urban environment, particularly in parks or green areas near roads, have a direct influence on public health not related with production of food. This is due to that they come easily in contact with humans and are transferred to them, either as suspended dust or by direct contact (1). Furthermore, even though urban soils are rarely used for food production, they receive higher than normal loads of contaminants from traffic and, in heavily industrialized cities, industrial activity.

Most of the urban parks in Belgrade are built close to major roads or industrial areas, where they are subject to many potential pollution sources, including vehicle exhaust and industrial emissions. The present work is the result of a preliminary sampling campaign, aimed at obtaining some knowledge of the distribution of the contents in heavy metals and ascertaining whether some pollution is likely to exist in some green areas of public use in Belgrade. Cadmium, Cu, Pb and Zn were chosen for this study because they are good indicators of contamination in soils because they appear in gasoline, car components, oil lubricants, industrial and incinerator emissions.

Soils from 11 urban parks in Belgrade were sampled to reflect the different land use and traffic conditions. Composite samples were obtained by mixing sub-samples from three random points within about 1m² in each sampling site. At each sampling point, the top 10 cm layer of the soil profile was taken using a stainless steel trowel. Heavy metals were extracted in triplicates by 0.1 M HCl and by digestion with aqua regia. Selective soil samples were also analyzed for potential chemical speciation by a sequential chemical extraction method (3). The extracts were analyzed for examined metals by AAS.

The obtained results indicate that urban soils in Belgrade have elevated concentrations of Pb, Zn and Cu. The parks with high metal concentrations are located in urban districts and industrial areas, indicating that the major contamination sources in these soils are traffic emissions and industrial areas. The most Pb in soil probably came from exhausts of vehicles since leaded gasoline is steel in use in Belgrade. Using reference values given by the Québec Ministry of Environment (4) it was shown that those green areas closer to the urban center and industrial areas present contents in Zn, Cu and particularly Pb that often exceed the acceptable limits for residential, recreational and institutional sites.

The chemical partitioning results show that Pb, Cu and Cd are mainly in the exchangeable and carbonate/adsorbed phases while Zn is largely associated with Fe-Mn oxide and organic fractions. Considering the first 2 extraction steps, the exchangeable and carbonate/specific adsorbed phases, the relative mobility and bioavailability of heavy metals in urban soils decrease in the following order: Cd > Pb > Cu > Zn. The high exchangeable Pb in urban soils needs further investigation for its ecological and health implications.

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Behaviour of Imidacloprid in the Environment

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The use of fitopharmaceutical compounds is one of the most important domains because it has to ensure very high standards concerning protection of human health, protection of the nature and non-target organisms and lifeless nature. It is necessary to submit all the documents in the step of registration from the field of ecotoxicology and behaviour in the environment. As the consequence of the additional steps in the procedure of registration, by the end of July 2003 it was cut off almost 300 active substances from the list of all registered compounds. These compounds should be replaced in the future by new ones. In Slovenia it was withdraw from the list of insecticides 30 compounds, from the group of organophosphates 8. These compounds will be replaced with new ones, such as neonicotinoids.

Neonicotinoids are relatively new systemic insecticides, which are chemically alike nicotine – toxin, preset in tobacco. Similarly as nicotine, neonicotinoids act on the nerve system. They irreversibly block acetylcholine receptors. The affinity for the binding is expressed much stronger at insects as it is expressed in mammals.

Imidacloprid is one of the most applied neonicotinoid and it was registered for the first time as insecticide in USA in 1994. Because of the new mode of action which controls many insects, already resistant to other insecticides and because of its excellent systemic properties which enable also different techniques of application, imidacloprid is today on the market in more then 120 countries for the protection of more then 140 different sorts of crop.

The aim of our research was to study the degradation of neonicotinoids in the environment. In our investigations we monitored the degradation of imidacloprid and the formation of its metabolites in water, soil, and on chicory. Pesticide was added to the samples in the concentration range from 0,1 ppm to 10 ppm and were periodically analysed in the 35 days period. For the isolation and detection we have used classical analytical methods, such as solid phase extraction and liquid-liquid or solid-liquid extraction, in combination with liquid chromatography coupled with DAD detector. The results have shown high persistence of imidacloprid in soil. The monitoring of imidacloprid in water has shown, that the degradation process was much faster in the presence of sunlight as in the dark. We found out that imidacloprid degradation on the chicory was not complete within 7 days, and its concentration exceeded the MRL value prescribed in Slovenian legislation (partially due to its presence in the technical product).

POSTERS



Alchemical Symbols

The Four Classical Elements:



Earth Cold and Dry. Melancholy.

Water Cold and Wet. Phlegmatic.

A

Air Hot and Wet. Sanguine.



Fire Hot and Dry. Choleric.

Processes:

------ Precipitation

Sublimation

Caput Mortuum

The Three Principles:



Salt. The Contractive force in Nature. Crystallisation, condensation.



Sulphur. The Expansive force in Nature. Dissolution, Evaporation.



Mercury. The Integrative force, interweaving and balancing that of the Salt and Sulphur. Circulation. Dynamic equilibrium.



← Previous page: The water-bath furnace from Geber's Works, London 1678

Contents of Polychlorinated Biphenyls in Adipose Tissue of the Human Population of Vojvodina (Serbia)

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PCBs are mixtures of synthetic organic chemicals with the same basic chemical structure and similar physical properties ranging from oily liquids to waxy solids. Due to their non-flammability, chemical stability, high boiling point and electrical insulating properties, PCBs were used in hundreds of industrial and commercial applications including electrical, heat transfer, and hydraulic equipment. Because of their high persistence, and their other physical and chemical properties, PCBs are present in the environment all over the world. The International Agency for Research on Cancer and the Environmental Protection Agency classify PCBs as a probable human carcinogen. Acute effects of PCB exposure in humans were documented following ingestion of contaminated rice oil in Japan in 1968 and Taiwan in 1979. Long-term studies of the more than 2,000 people who were exposed during these events revealed increased mortality due to PCB intake. A positive association was established between PCB dosing and acute liver damage. Human fetal exposures of PCBs are associated with neural and developmental changes, lower psychomotor scores, short-term memory and spatial learning effects, and long-term effects on intellectual function.

In this paper the content of PCB residues in human adipose tissue was determined by gas chromatography (GC/ECD). Samples of adipose tissue (2 g) were collected from 21 vascular and abdominal surgery patients of both genders and different age. PCBs were extracted from the samples with the mixture of chloroform:methanol:water (2:2:1) purified with concentrated sulfuric acid. The following PCV congeners were detected in all human samples: PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180. The average content of total PCB was 0.55 μ g/g, and the most abundant were congeners PCB 138, PCB 153 and PCB 180, representing 86% of total PCB burden of human adipose samples. It was observed that the higher content of PCBs was detected in the adipose tissue of women; however, there is no statistically significant correlation between age and gender of the patients and the PCB concentrations in their adipose tissue.

(3)

Silver Electrolyte Regeneration

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The Moebius method for silver electrolytical refining process was used in the Anode Slime Treatment Plant in Bor. Nitrous acidic solution of silver nitrate is used as electrolyte. Main ingredient is copper in anode metal from non-precious metals, and when its content in electrolyte has limit value of 50 g/l, it is necessary to carry out regeneration of silver electrolyte.

The scope of work was an investigation of the most efficient method for regeneration of silver electrolyte, that is silver and copper separation from saturated silver electrolyte.

The most used previous methods of silver deposition from acid solutions were methods of silver cementation or methods of Ag and AgCl deposition (by the use of NaCl or HCl) after what the elementary silver is obtained by additional processes of dissolution and reduction.

Upon detailed investigations in laboratory conditions in Copper Institute Bor and industrial conditions in the Anode Slime Treatment Plant in Bor, a method of selective silver deposition was developed from saturated silver electrolyte by the use of sodium sulphite and its complete separation from present copper ions in electrolyte.

Main advantage of selected methods is recovery of elementary silver in one stage reaction.

By reaction of silver deposition with Na_2SO_3 , Ag_2SO_3 is formed, per reaction 1.

$$2AgNO_3 + Na_2SO_3 = Ag_2SO_3 \downarrow + 2NaNO_3$$
(1)

 HNO_3 reacts with Na_2SO_3 in strong acid solutions with separation of SO_2 which acts as reducent and leads into deposition of elementary silver, what is given in reactions 2 and 3.

$$Na_2SO_3 + 2HNO_3 = 2NaNO_3 + SO_2 + H_2O$$

$$(2)$$

$$Ag_2SO_3+SO_2+H_2O=2Ag+H_2SO_4+SO_2\uparrow$$

Described procedure was tested in laboratory conditions (Copper Institute Bor) and industrial conditions (Anode Slime Treatment Plant in Bor) and the similar results were obtained regarding to the degree of silver deposition and quality of the obtained silver powder.

The advantages of selected method are:

- Fast, simple and economical method
- Recovery of silver in powder in one-stage of reaction
- High degree of reagent selectivity
- High deposition degree of silver >99.99 %
- Obtained silver in powder is of commercial quality (99.9 % Ag).

Status of Some Microelements in a Calcareous Chernozem Soil after Long-Term Application of Mineral and Organic Fertilizers

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Elements that are needed by plants in small amounts for their growth and development are known as microelements. However, they can be toxic to plants when present in high concentrations. Their content and distribution in soil depends on various factors. Long-term fertilization is one of the factors that can have significant influence on status of microelements in soil.

The purpose of this investigation was to determine the effect of long-term application of mineral and organic fertilizers (beef manure and cornstalks) on the content of iron, manganese, copper and zinc in a calcareous chernozem soil. For this purpose soil samples were taken from an experimental field of the Maize Research Institute in Belgrade. These samples were taken with an auger from two depths: 0 to 20 and 20 to 40 cm. There were six variants in the experiment and one of them was the control, i.e. variant without application of fertilizers. Total content of the investigated microelements was determined by atomic absorption spectrophotometry (AAS) after digestion of the samples with nitric acid and hydrogen peroxide. AAS was also applied for the determination of available Fe, Mn, Cu and Zn. This was done after the extraction of the soil samples with a 0.005M solution of DTPA. The analytical data obtained in this investigation were subjected to statistical analysis (analysis of variance and Isd test).

On the basis of the results obtained the following important conclusions could be drawn. Total contents of the investigated microelements were in the following intervals: 32216 – 47616 mg/kg (for iron), 817 – 953 mg/kg (for manganese), 16.8 – 21.5 mg/kg (for copper) and 83.3 – 95.0 mg/kg (for zinc). These contents are within usual values for normal agricultural soils. Long-term application of mineral and organic fertilizers did not cause significant changes in the total content of manganese, copper and zinc. However, total content of iron increased significantly under the influence of beef manure application. This can be attributed to the fact that beef manure contains appreciable amounts of this microelement. There are no statistically significant differences between two soil layers with respect to the content of the investigated microelements.

When obtained results for the content of available Fe, Mn, Cu and Zn are compared with corresponding limiting values used for the method of soil extraction with DTPA (classification according to Ankerman) the following can be said. Relatively low values were found for available iron in all investigated soil samples. All experimental variants have high contents of available manganese and copper. The content of available zinc is medium in all variants where organic fertilizers were applied. However, it is low in the control and in the variant where only mineral fertilizers were applied. Comparison of variants with fertilizers and the control gave the following results. The contents of available zinc and copper increased significantly in all variants where organic fertilizers (beef manure and cornstalks) had been applied. Application of beef manure (alone and in combination with mineral fertilizers) caused statistically significant increases in the availability of iron and manganese. Statistically significant differences were found between two soil layers with respect to the content of available manganese and zinc. Higher values were found in the first soil layer.

At the end it can be concluded that the investigated organic fertilizers had positive effects on the fertility of calcareous chernozem soil. In other words, they contributed to the increase in the availability of the investigated microelements. None of these elements was present in the amounts that could be a problem for the environment. Investigations of this kind should be preformed on other important soil types in our country.

Characterization of Components Obtained during the Processing of Three Rough Rice Cultivars

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During processing of rough rice into white rice (polished rice) through a series of operations, hulls and bran are obtained. Rice is number one food crop in the world. However, from recently rice and its structural parts are utilized for production of value-added products. Oil rich with antioxidants, very good adsorbents for removing metal ions and gases, and edible films could be obtained. Further processing of rice by-products depends of their composition.

Therefore the present study is focused on the characterization of the rough rice, hulls, bran and white rice of three the most abundant rice cultivars in Macedonia, Monticelli, Prima Riska and P-76/6.

The solubilization potentials of the proteins fractions (albumins, globulins, prolamins and glutelins) of all components and gelatinization behavior of white rice were evaluated .

The Bacterization of Maize Seeds in the System of Environmental Preservation

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The biological nitrogen fixation is a safe mode of substitution or supplement of mineral nitrogen fertilizers to protect the environment from pollution and direct and indirect degradation of soil. Our previous investigations with liquid inoculums, consisted of pure strains lowered the mineral N fertilizer for 30%.

This trial continued the examination of the strain variants: Azotobacter chroococcum (1), Azospirillum lipoferum (2), Klebsiella planticola (3) and the combinations: variants 1+2+Bacillus megaterium+Azotobacter vinelandi+Bacillus subtilis (4), 1+3+Bacillus megaterium+Azotobacter vinelandi+Bacillus subtilis (5), with five rates of mineral N fertilization ranged from 0-120 (Δ 30) kg ha⁻¹. At the end of vegetation the number of active microorganisms and the yield of maize kernel was examined (ZP SC 677, Table 1).

Among five combinations of mineral N fertilization, two were the most favourable: at 60 N kg ha⁻¹ the better yield was associated with higher number of active micro organisms, except combination 1, but at 90 N kg ha⁻¹, in variants 2 and 3 was realised the maximal yield.

	N fertilizer		Bacterization variants				
	(N kg ha ⁻ 1)	Control	1	2	3	4	5
Total number of	60	418	306	231	766	423	451
microorganisms (10 ⁷ ha ⁻¹)	90	49	365	221	171	452	281
Number of	60	30	44	50	61	60	55
<i>Azotobacter</i> (10 ⁷ ha ⁻¹)	90	22	60	61	37	19	24
Maize vield (t ha ⁻¹)	60	10,26	11,46	10,88	11,67	11,36	10,90
	90	10,96	11,37	11,39	11,92	12,18	11,07

Table 1. The most favourable influence of bacterization and N fertilizer application on number of active microorganisms and maize yield

Combinations of bacteria (variants 4 and 5) were more favourable than pure strains as in number of active microorganisms and the realised yield, especially 4, with 20 and 11% of higher yield, compared to control.

The applied bacterization lowered the mineral N-fertilizer input down to half amount, with obtained of high yield – economic effect, without disturbing of microorganisms in soil – environmental effect.

Control of Trace Ion Pollutants in Ultra-Pure Water

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One of the primary concerns of all power plants is to ensure that the high-purity water used for power generation is of sufficient quality to maintain plant chemistry parameters. Ion chromatography (IC) is a fundamental technique for monitoring water quality with respect to corrosive ions. Anions, cations, transition metals and silica can be monitored in raw water, demineralizer influent/effluent, process steam, boiler feed water, boiler blowdown water, high and low pressure steam condensate and condensate polisher water. The measurement of trace level of ionic impurities throughout the power generation process is critical in identifying and preventing corrosive conditions in many power plant components. Corrosive ions, such as sodium, chloride and sulfate can bi minimized by continuously monitoring their respective levels and maintaining levels as low possible. Control of these impurities provides valuable information regarding the source of contamination, the likely rates of contaminant build-up, and probable rates of corrosion and timely data during the start-up and shut-down of power plants [1].

Ion Chromatography has become an important technique for the determination of ionic species. Anions in the part-per-million and part-per-billion range can be analyzed easily with direct injection. For the determination of low levels of ionic impurities in the low part-per-billion or part-per-trillion levels, sample preconcentration is usually used. Typically, the analytes of interest are preconcertrated on a small precolumn in order to "strip" ions from a measured sample volume. This process concentrates resulting in lower detection limits. However, preconcentration method has several disadvantages compared with a technique high-volume direct injection which is applied in this work.



Figure 1. Block diagram of a suppressed ion chromatography system

In this paper, an ion chromatographic method was developed for the determination of inorganic anions and cations at trace levels (sub- to low μ g/l levels) in power plant water samples. In this method, samples were injected using a high-volume direct injection technique (large sample loop volume up to 1300 μ l). The analyte ions were separated on a selective ion-exchange column using high-purity mobile phases: carbonate/hydrogencarbonate eluents for anions and methanesulfonic acid for cations, and detected using the suppressed conductivity detection method. The method detection limits for most analyte ions in ultra pure water ranged from 0.1 to 1.0 μ g/l (ppb) [2,3].

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Lipase Production from *Penicillium* sp. Oil 1. Fungous Isolate and its Application in the Ester Synthesis Reaction

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Lipase hydrolyses triacylglyceride to fatty acids and glycerol. Incomplete hydrolysis gives a mixture of mono- and diacylglycerides along with the end product of the reaction. The hydrolysis reaction is reversible, which means that lipase (under adequate conditions) can also catalyze the fat and oil synthesis reaction from free fatty acids and glycerol /1/.

Lipase are used in the production of fats with exactly defined physical and chemical features, for acylation of carbohydrate substrate by application of organic solvents and for the synthesis of biodegradable biological tenside, with special physical and chemical properties /1-3/.

To produce the enzyme a *Penicillium* sp. OIL1 fungous isolate was used, which was obtained from the air. The enzyme activity was determined by the amount of released salicylic acid from acetylsalicylic acid (aspirin) /4/ or by the amount of succinic acid released from dimethyl succinate. The salicylic acid was assayed in form of FeCl₃ complex, and the free carboxylic acid by titration with 0,1 M NaOH in the presence of phenolphthalein indicator.

The cultivation of fungous *Penicillium* sp. OIL1 isolate was made on solid nutrient medium with sunflower oil and Tween 80 at 28°C.

The syntheses esters of benzoic acid and *sec*-butanol, and fructose and fatty acids in *terc*-butanol, with lipase in fungous *Penicillium sp.* OIL1 biomass are performed in reciprocal shaker at various temperatures (28, 30 and 38°C).

The highest production of enzyme lipase was obtained by cultivation of fungous *Penicillium* sp. OIL1 on substrate with sunflower oil and Tween 80, for 76 days with 4 inoculations. After treating the fresh fungous *Penicillium* sp. OIL1 biomass with buffer and acetone, enzyme activity in biomass was 569 U/g. It was found that the enzyme from fungous *Penicillium* sp. OIL1, that hydrolyzed esters, operated at the phase barrier and that it belonged to the lipases group. The enzymatic synthesis of esters was investigated with damp and dry fungous *Penicillium* sp. OIL1 biomass as the enzyme preparation. With damp biomass in the synthesis esters of benzoic acid and *sec*-butanol, the degree of benzoic acid conversion was 11.3%, while with dry biomass this conversion degree was 35% at 28°C. The fatty acids conversion degree in the process of fructose ester synthesis at 30°C with dry biomass was 42.9%, while at 28°C, a fatty acids conversion degree of 64.7% was achieved.

In the above experiments, the fungous *Penicillium* sp. OIL1 biomass played the role of an immobilized enzyme, i.e. immobilized cells of microorganism, where the water content in the system was decreased, favoring the esterification reaction. Also, the effect of phosphate and acetate buffer, and the concentration polyvinyl alcohol on lipase activity was investigated, as well as residual lipase activity after the enzymatic syntheses.

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Determination of Biotin in Sugar Beet by the Microbiologic Method

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A modified microbiological method (Danielsen and Eriksen) was used for quantitative determination of biotin in pressed juice of sugar beet sweet chops. The working micro-organism was the yeast Saccharomyces cerevisiae.

The essence of the method is to sow a solid nutritive base (defined composition, biotin-free for a certainty) with suitable amount of the yeast, to pour it into the petri boxes and to impress 8 holes. Standard solutions of D-biotin should be inserted into 4 holes, and in the rest of the holes (4) – series of specially prepared dilutions of the pressed juice of sugar beet sweet chops examined. Diameter of the growth zone will increase with the increase of the amount of biotin, since biotin is an essential growth factor of Saccharomyces cerevisiae.

The amount of biotin in the examined sample is calculated (μ g/100g) by displaying the diameter of the growth zone in the function of the D-biotin concentration and the the pressed juice of sugar beet sweet chops concentration in semilogarithmic diagram.

11 sorts of sugar beet were examined in 6 repetitions, in 2 vegetation periods (August and September).

Values varied from 0.44 to 1.50 μ g/100g of pressed juice of sugar beet sweet chops (in August) and from 0.57 to 2.90 μ g/100g of pressed juice of sugar beet sweet chops (in October).

Detection limit of the method is 0.5 ng/cm³ and reproductivizy is about 96%.

The results were statistically treated and the analysis of sort essay variance in seeing the amount of biotin in sowing periods gave statistically highly significant indicators (F-relation and LSD test). It means that the biotin amount depends upon the sort of sugar beet and the vegetation period.

The Glutathione and Thiolics Status in Maize Seedlings Originating from Low Viable Seeds, Influenced by 2,4-D

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The seed ageing is closely related to increased activity of free radicals and the consequence is the lost of germination ability and production of seedlings retard in growth. On the other hand, the low doses of 2,4-D stimulate germination and growth¹. The antioxidants are responsible for trapping of free radicals and the keeping of conditions for growth achieving². Therefore the aim of experiment was to study the stimulative influence of 2,4-D on the changes in content of antioxidants such as: - SH groups of low-molecular proteins (S_{thiol}) and glutathione (reduced-GSH and oxidised-GSSG forms) in maize seedlings, originated from low viable seeds.

The seeds of two maize hybrids (H1 and H2) were submitted to accelerate ageing during 9 days and then used to determine germination capacity. The filter paper towels as germination substratum were soaked in distilled water (control) and $5x10^{-9}$ mol 2,4-D (treatment). The uniformly grown seedlings were separated into plant (root+shoot) and seed rest and then used to determine the content of S_{thiol}, GSH and GSSG (as monomer) by method of de Kok³.

The initial seeds of both hybrids had lower content of S_{thiol} , but mainly more GSH and GSSG (Table I). The majority of S_{thiol} , GSH and GSSG were finding in the seed rest (the place of prolonged synthesis *de novo* and/or reversible redox exchange).

		H1			H2			
		S _{thiol} (nmol)	GSH (nmol)	GSSG (nmol)	S _{thiol} (nmol)	GSH (nmol)	GSSG (nmol)	
	Seed	26	132	216	133	116	174	
Plant	Control	82	22	20	65	24	42	
	Treatment	130	122	47	71	37	56	
Seed	Control	119	107	127	70	134	16	
rest	Treatment	116	131	78	63	92	28	

Table I. The influence of 2,4-D on changes of thiolic-S, GSH and GSSG (presented as monomer)

The 2,4-D treatment in comparison to control increased germination of H1 and H2: from 87.7 to 94.7% and from 77.5 to 79% and plant growth: from 50.3 to 65.9 mg and from 50.1 to 61.3 mg respectively. This might be the result of changes in content of GSH and GSSG in course of increased GSH in both: plant (82%) and seed rest (18%) of H1, as a result of GSSG reduction (dropped to 38%). Despite of GSH rise (35%) in H2 plant, there is drop of GSH to 31% and the increase of GSSG to 43% in its seed rest. Additionally, the S_{thiol} increased in plant of both hybrids (H1-37% and H2-8%), but dropped to 23 and 11%, respectively.

According to the results, it could be supposed that in the examined hybrids the reversible redox equilibrium³ was shifted to reduction in H1 and to oxidation in H2, resulted in higher, i.e. lower germination increase and growth as response on 2,4-D stimulation.

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Water Consumption Reduction in Chemical and Petrochemical Plants

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The paper shows how the optimization of water circuits in a large fertilizer plant lead to reduced water intakes and decreases the waste water quantity returned into the environment. An intensive operating program of the cooling circuits combined with a better condensate recovery and a proper treatment of wastewaters could reduce the raw water intake up to 60 % from the actual intake. Consequently, the waste water discharge may be decreased with at least 35 %.

The raw water from the freshwater source (river) is settled and clarified, then is used as cooling agent, raw material for the demine-ralization plant, and as process water (fig. 1 & 2). The cooling systems are once-through and open circulating.

By analyzing the presented facts and figures of the plant, several solutions have been outlined:

- it is possible to operate the cooling circuits at 3.5 cycles instead of 1.2 -1.5. Thus, less makeup water is necessary and the blowdown could be also reduced;
- the water used as cooling agent in once-through circuits can be used as makeup water for the cooling towers, together with the boilers' blowdown and with the wastewaters from the demineralization unit;
- the condensates from urea and ammonia plants could be directed to the deminera-lization unit, polished in order to retain the iron and silica, and recycled to the boilers. Thus, less demineralized water and subsequently clarified water would be necessary, the plant's effluent being simultaneously reduced;
- the final homogenization basin can be transformed with minimal effort in a final decanter, in order to reduce the suspended solids [mainly CaF₂ and Ca3(PO4)₂] evacuated into the river.

With minimal investment costs, an old fashioned water system from a large fertilizer plant can be updated in order



Figure 1. Utilities section before modernisation: 1- clarified water; 2 - demineralized water; 3 - boilers blowdown; 4 - cooling towers blowdown; 5 - wastewater final mixing point.



Figure 2. Utilities section after modernisation

to reduce fresh water consumption and waste water discharge, both achievements being benefic for the environment.

Decolorization of Sugar Beet Pulp with Hydrogen Peroxide

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The increased consumption of dietary fibers with common food not only can improve digestion and the elimination process, and benefit in the treatment or prevention of diet-related chronic disorders, as it was emphasized in numerous papers. Increased dietary fiber intake could be achieved by changing dietary habits, increasing the consumption of high fiber foods, and by the help of consuming fiber-fortified foods and fiber supplements. Fiber fortification of common food is an advantageous. Consumers remain by local dietary habits, but the producers have to find proper ways for supplementation. As a result, it has become a dominant claim to incorporate dietary fibers in an adequate amount into daily meals. As bread is a constituent part of all typed of human diets, it is a convenient food for correcting a variety of disorders. Bread can be enriched with various fibrous materials. Related to different fiber sources implemented in bread, several problems arise, like: adverse effects on crumb color and texture, low volume, not appetizing appearance etc. Sugar beet pulp is a valuable fibrous supplement, but adverse effects on crumb color are not negligible, so procedures by which this influence can be diminished are beneficial. The decolorization of the sugar beet pulp has been examined by hydrogen peroxide. Applied concentrations of the hydrogen peroxide's liquor were 5, 10 and 20 [g/l]. The influence of the hydrogen peroxide on the color of the fiber has been examined at temperatures of 30°C, 45°C and 60°C. The exposure to peroxide lasted up to 12 [h]. The best decolorization effects were at the pH 11. At that pH value a significant reduction of color accompanied with increased water

retention capacity was achieved. Water retention capacity of no treated and decolorised beet pulp is 620[%] and 1400 [%], respectively. These changes are more expressive at higher temperatures as a result of the changes in the composite and structure of the fiber.

Functional Group Manipulations Using Supported Potassium Ferrate under Microwave Irradiation

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Functional group manipulation is of great interest to synthetic organic chemist, and introduction of new and mild catalyst for these conversions under eco-Friendly conditions still remains of great importance. Prompted by stringent environment protection laws in recent years there has been increasing emphasis, on the use and design of eco-friendly reagents, solid and solvent free conditions [1]. There has been considerable attention in the creation and development of ever green and solvent less methodology in organic methodology[2] dictated by stringent environment protection laws.

Organic solvents are not only expensive but are often flammable, toxic and environmentally hazardous.

Microwave irradiation in organic synthesis is a useful technique nowadays [3-5]. Dry media using microwave thermolysis have attracted much attention, because it omits the use of hazardous and relatively expensive organic solvents and the reaction can be conducted in open vessels [6].

Potassium ferrate (K_2FeO_4) is a sixvalent iron compound which can be easily and economically prepared by oxidizing ferric nitrate with sodium hypochlorite and the subsequent treatment with potassium hydroxide [7]. It has been recently used by P. Laszlo and coworher fear oxidizing organic sub in non aqueous media [8].

Reagents adsorbed on mineral supports have gained popularity in organic synthesis due to their selectivity, ease of manipulation [9] and especially suitability to be placed in a microwave oven [10].

Association of ferric salts with zeolite [11-13] under microwave irradiation in solvent free conditions had been pioneered in our laboratory. Armed with these experiences, in this communication we wish to report that sold supported potassium ferrate can be efficiently used for functional group transformation such as oxidation, oxidative deprotection of acetals and ketals, oxidative deprotection of silyl and THP-ethers, regeneration of carbonyl compounds from their oximes semicarbazones, and phenylhydrazones in solventless system. Use of microwave irradiation has accelerated these reaction drastically.

In conclusion the use of nontoxic potassium ferrate permits several useful transformations in organic synthesis. The advantages of these methods are mild eco-friendly conditions, short reaction time, easy workup and high yields. We belive these procedures will find their places in organic methodologies.

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Sonochemical Removal of Cyanide lons from Wastewater

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Inorganic cyanide salts are often used in metallurgical industry (metal surface treatment) but also in mining industry (gold extraction). All these activities consume large amounts of water and water effluents always contain cyanide, which must be treated before disposal to the nature environment.

Sonochemistry, the application of ultrasound to chemical systems, is known to produce localized cavitations, acoustic streaming and other energetic phenomena. The enormous local temperatures and pressure together with extraordinary cooling rates and free radicals formation can provide a unique medium for leading chemical reactions under the extreme conditions. The researches related to physical and chemical effects of ultrasound had known a powerful development in the last decade with important impact in different area of science: chemistry, medicine, environmental protection and others. Nevertheless, the physical, chemical and biological consequences of ultrasound irradiation as well as the mechanism of acoustical cavitations phenomena are still not completely elucidated.

The authors present some experimental methods of cyanide remediation from wastewater by: 1) the combination of ultrasound irradiation with usual oxidants like hydrogen peroxide, oxygen, chlorine and 2) sonoelectrodestruction of this pollutant.

The work conditions are indicating in table 1.

Work condition	Observation		
Sonochemical destruction of cyanide with air.	With and without air bubbling.		
Sonochemical removal of cyanide	Influence of hydrogen peroxide		
with hydrogen peroxide.	concentration.		
Destruction of cyanide	Dimension film influence on reaction rate		
in film sonooxidation.			
Sonoelectrochemical removal of cyanide	Influence of electrodes.		
from wastewater.			

Table1.

Possibilities of Processing Magnesium and Magnesium-Alloy Scrap

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Magnesium is among the lightest of all metals. Due to its light weight and with additional alloying with other non-ferrous metals and rare earth superior mechanical properties could be achieved such as ductility, mechanical properties, castability and etc. This fact contributes increasing of the variety of applications of this metal. If magnesium application continuous to grow at the rapid pace that it has in past few years, then this growth could have significant effect on quantity of generated magnesium scrap. As a result of this increase in scrap generation companies worldwide are planning new magnesium recycling plants or expanding existing capacities.

This are the first testing of possibilities of recycling of scrap based on magnesium in Serbia and Montenegro. Great deal of magnesium scrap is generated during die-casting of magnesium-alloys, high-grade scrap, so called Type 1. Type 2 of magnesium scrap is oil-contaminated scrap.

For Type 1 examination was performed in laboratory scale (on Faculty of Technology and Metallurgy, Belgrade) and industrial scale (Foundry of magnesium factory "Bela Stena", Baljevac on Ibar). Type 2 of magnesium scrap was tested only in laboratory volume on TMF, Belgrade. Tested scrap was from France, provided by company COMESIM.

Experimental research of Type 1 included examination of following technological operations:

- Mechanical preparation, separation of goaf parts,
- Chemical preparation, separation from left over goaf oxide part with treatment with 5% H₂SO₄ solution,
- Rinsing and drying,
- Smelting of prepared scrap in induction furnace.

With this kind of treatment metal extraction efficiency rate was 45-90%. Lower metal extraction rate of 40-45% was achieved in industrial testing scale, because of the lack of necessary equipment for scrap preparation.

Examination of Type 2, oil-contaminated scrap included investigation of following parameters:

- level of oil-contamination, 16.9%,
- preparation of solutions for oil removal, water solution of DBS, NaOH, water glass,
- time of oil removing process, 5-10 min,
- temperature of oil removal, 60°C.

High level of oil removal was achieved, more than 90%, which allows metal extraction efficiency rate about 92%.

Accomplished results show that this kind of scrap could be processed in our country with our technology, of course with suitable equipment from projected technological solution.

Casted ingots of MgAI5 alloy could be used for making Mg-powder used in metallurgy of iron and steel. This plant is unique in this part of Europe.

The Reduction of Energy Consumption during the Fluidized Bed Drying of Biomaterial

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Drying is known as an intensive energy customer. Energy consumption in the drying processes is generated by: drying agent heating and drying process.

In powdery biomaterials case, due the temperature restrictions imposed by the nature and structure of the material, it is recommended that drying process to be operated without material heating above a critical temperature. Also it is necessary that biomaterials drying to be realized in intensive conditions to reduce considerably the solid particle – drying agent contact time. Such an intensive method is the simple or modified fluidization (by inert add, mechanical mixing, oscillations use) [1]

In drying fluidized bed case the energy consumption will be reduced by eliminating the transporter elements heating, the heat loss being smaller, adjusting the energy consumption for the developing of the fluidized state.

We propose the reduction of the energy consumption the realizing a drying process of powdery biomaterials, due their characteristics, in two stages:

- Fixed bed stage; due the initial moisture of the powdery biomaterial which develop in system strong capillary forces, the bed remain fixed, though the drying agent velocity is that corresponding of theoretical fluidization velocity.
- Fluidized bed stage; the partial removing of the surface moisture allows the breakage of liquid bridges, determined by the capillary forces, producing the bed expansion and the normal fluidization.

In first stage of drying, we can introduce supplementary, for the liquid bridges breakage, a mechanical mixing energy. That mechanical energy can be removed when the fluidized state is achieved.

The present work pursues the energy consumption reducing at hip fruit extract drying, using the simple or modified fluidization (by inert add and mechanical mixing) as intensive technique

The hip fruit extract is a powdery biomaterial, of C class (according Geldart), highly hygroscopic, which at initial moisture can't be fluidized in normal conditions. Due to the reduced sizes of particle and its hygroscopic proprieties, the material bed is dominated by the strong van der Waals, cohesion and capillary forces. Due to those characteristics, it is recommended that drying process is developed only to the surface moisture removing, the internal diffusion stage being avoided due to the thermal degradation of the biomaterial.

The solutions proposed for the hip fruit drying as a purpose has the determination of the drying time in conditions of the simple fluidization and in conditions with inert ads and with mechanical mixing, and the comparison the obtained values for the identification of the optimal method from the energy consumption point of view.

The fluidization, an intensive procedure, which determines the growth the energy consumption for the dynamics fluidized state realize, due to the intensification of heat and mass transfer and the reducing of drying contact time and of contact temperature of the drying agent, it can be used as an economical procedure for the biomaterial drying process.

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Electrochemical Control and Waste Water Electrochemical Depollution

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Electrochemical processes can contribute considerably to environmental control and protection by means of wastewater purification processes and production integrated waste minimization. Almost all the chemical processes, which involve redox reaction, can be led by unconventional, electrochemical way in a manner that can be both ecologically and economically advantageous.

The possibilities and the limits of electro chemical pollutant degradation in aqueous solutions based on redox processes on the level of hydroxyl, nitro and azo groups are discussed.

Continuing our interest in the field of the electroanalytical methods applied to the control of pollutants concentration - inorganic (metal ions, nitrates) [1] and organic pollutants [2-4], this contribution presents the performances of different electrochemical and spectrophotometric methods applied for the control of phenols, nitrophenols and azodyes in waste water.

We studied the influence of pH, concentration and scan rate over the electrochemical behavior of phenol, nitro phenol and different azo-dyes in Britton-Robinson buffer on glassy carbon with the electrochemical computerized BAS 100 system and UV-VIS Unicam Helios β spectrophotometer.

In the azo dyes containing nitro group, the electrochemical reduction of $-NO_2$ takes place at more negative potentials especially in alkaline medium where the peak separation is about 300 mV. Depending on the pH, the peaks potentials of the systems is quite different. The electrochemical oxidation (or combustion) of azo dyes with simultaneous oxygen evolution has been investigated using different electrodes and conditions.

The cyclic voltamogrammes were recorded in order to establish the oxidation and/or reduction potentials of the phenols and nitrophenols. Depending on the pH and nature of the anode, the oxidation peaks are located in the potential range 300-700 mV / Ag, AgCl and the reduction of the nitro group in the negative potential range -(300-700) mV / Ag, AgCl.

A simplified mechanism for the electrochemical oxidation or combustion of organics is presented according to which selective oxidation occurs with oxide anodes (MOx) forming the so-called higher oxide and combustion occurs with electrodes at the surface of which, OH radicals are accumulated.

Using two different type of cell (Hg batch cell for the reduction of nitro and azo group and the "redox" cell, equipped with porous graphite felt electrodes, for both oxidation and reduction of mentioned compounds) the coulometric electrolyses have been realised, with *on line* control of the consumed starting compound.

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The Adsorption of Organophosphorous Insecticides on Cationic Surfactant Modified FAU and HEU Zeolites Studied by ³¹P NMR and UV/VIS Spectroscopy

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Zeolites are widely used in the the processes of catalytic decomposition and adsorption of inorganic or polar organic pollutants. The large non polar molecules can not be adsorbed into zeolite pores. The adsorption capacity of zeolite increases if zeolite external surface is modified by cationic surfactant (1). The zeolites modified by surfactants are promising adsorbents for organic pollutants like insecticides. Organophosphours insecticides are complex organic compounds that contain different functional groups. The adsorption and catalytic degradation (2) of insecticides are significant environmental problems.

The aim of this work is to investigate the adsorption of the insecticide O, O-dimethyl O-4-nitro-mtolyl phosphorothioate (fenitrothion) on surfactant modified zeolites (SMZ). The adsorption of cationic surfactant, stearyl-dimethyl-benzyl-amonium chloride, on FAU and HEU type of zeolites and subsequent adsorption of fenitrothion are studied by UV/VIS and ³¹P NMR spectroscopy.

The 0.2 % suspension SMZ in water with 0.160 mmol of fenitrothion were stirred for four hours at room temperature. UV/VIS spectra show that fenitrothion is totally adsorbed on both types of zeolites. The ³¹P NMR spectra of adsorbed fenitrothion were recorded in suspension. The fenitrothion adsorption depends on type zeolite used. ³¹P NMR spectra of fenitrothion in suspension show sharp peak for zeolite FAU and very broad peak in the case of zeolite HEU. The fenitrothion's degradation is evident on HELL zeolite. The new peak appears in the ³¹P NMR

The fenitrothion's degradation is evident on HEU zeolite. The new peak appears in the ³¹P NMR spectrum of filtrate after adsorption on zeolite HEU.

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The Possibilities of Producing Bottled Natural Drinking Water from the Spring "Mareza" in Podgorica

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Spring Mareza is located on northwest of Podgorica. The distance from this spring to the center of Podgorica is about 8 km. The area of this spring extends on region of about 30 individual wells, which rise in level of river Morača or under river.

Drinking water from this source, conform to regulations for drinking water, without special treatments, except processing with gas chlorine.

Podgorica, which has 180.000 population, is supplied by 62 % off total amount drinking water from source Mareza. Capacity of spring Mareza in minimum amounts to 1800 dm³/s, but in maximum amounts to 10-12 m³/s.

Taking into consideration that the aim of this paper is a research of quality of unprocessed water from the spring Mareza, from aspects of using this water for producing bottled natural drinking water, samples without chlorine were taken directly from old pump station.

Researches on the samples are done in situ, than in Laboratory for water on Faculty of Metallurgy and Technology and in the Institute for sanitary protection - Podgorica.

Based on theoretical knowledge, rules about sanitary property for drinking water [1] and experimental results, we concluded that this water of Mareza from physical, chemical, microbiological and radiology aspects conform to legal rules.

Researches should be continued for getting final conclusion about use of defined amounts of unprocessed water from spring Mareza for producing natural bottled drinking water.

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Alleviation of Cd Toxicity by Naphthenate Treatment

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In our previous studies we found that a mixture of naphthenic acids from Vojvodina crude oil "Velebit" exhibited physiological activity similar to that of plant hormones of auxin and gibberelin type (1). In view of the fact that mixtures of natural naphthenic acids obtained from middle and higher oil fractions of the "Velebit" oil exhibited physiological activity similar to plant hormones on the one hand and the known role of plant hormones in detoxification of heavy metals on the other, it was interesting to examine the effect of plant treatment with naphthenic acids in the presence of heavy metals. The aim of this study was to examine the effect of treatment with sodium naphthenate on content of Cd, its particular forms in the inetercellular space and inside cells, as well as on some physiological and biochemical parameters of young soybean plants grown in the presence of Cd.

To extract naphthenic acids, atmospheric gas oil fraction (distillation interval 168-290 $^{\circ}$ C) of Vojvodina crude oil "Velebit" was used and the isolation was carried out by the optimized procedure of alkaline extraction as described by Ćirin-Novta et al. (2). Young plants of soybean (genotype NS-L-320-251) were grown in Hoagland nutrient solution to complete formation of the first physiologically active pair of leaves. After that they were divided into four groups: control, in which plants were continued to grow in the same solution and three test groups in which plants were grown in the same medium with the addition of Cd²⁺ at a concentration of 1 mmol dm⁻³ in the form of CdCl₂, sodium naphthenate at a concentration of 10⁻⁷ mol dm⁻³, and both Cd (1 mmol dm⁻³ Cd²⁺) and sodium naphthenate (10⁻⁷ mol dm⁻³), respectively. After growing plants under the given conditions for two weeks, i.e. to the appearance of the third pair of leaves, samples of plant material were taken for analyses. Contents of particular forms of Cd in the intercellular space as well as in cells of root, stem and leaves were determined as described in previous work (3).

Presence of naphthenate reduced in average by 40 % content of total and intracellular Cd in root, stem and leaves. The results suggest the possibility that naphthenate acts on the level of plasma membrane of root cells, altering its permeability to Cd ions. Treatment with naphthenate alleviated also the harmful effect of Cd on some physiological and biochemical processes, e.g. activity of nitrate reductase and content of photosynthetic pigments.

Acknowledgement.

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Regeneration of Carbonyl Compounds from Phenylhydrazones Using Bi(III) Salts Under Microwave Irradiation

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Protection and subsequent deprotection of a functional group is almost inevitable in multistage organic synthesis ¹. Phenylhydrazones serve as important synthetic intermediate and they can be preferably used for isolation, purification and characterization of aldehydes and ketones². Developing of mild, efficient, eco-friendly and selective cleavage of phenylhydrazones continues to be a significant aspect of organic chemical transformation. There has been considerable attention in the creation and development of ever green and solventless method³ in organic methodology dictated by stringent environment protection laws⁴.

Most of Bismuth(III) salts are commercially available reagents and require no special handling. They are attractive candidates for use in green chemistry because bismuth is the less toxic of the heavy metals⁵.

In continuation of our work, utilizing Bismuth(III) nitrate pentahydrate ⁶,in this communication we wish to report that supported Bismuth(III) chloride can cleave various phenylhydrazones under microwave irradiation in solventless system.

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AIFe-Pillared Clay as an Environmental Catalyst

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Introduction

AlFe-pillared clays (AlFe-PILC) are very efficient solid catalysts for the oxidation of organic compounds with hydrogen peroxide in water solutions (1, 2). Their properties such as acidity, surface area, pore size distribution and hydrothermal stability depend on the method of synthesis, pH, temperature, OH/metal ratio, etc., as well as on the host clay. In this work the catalytic wet peroxide oxidation of phenol over AlFe-PILC, in dependence of OH/metal ratio, was studied.

Experimental

Two samples of AIFe-PILCs, with OH/metal ratio 2 and 4 (denoted as sample 1 and 2, respectively), were prepared by a procedure reported earlier (3). Their activity was tested as described elsewhere (2, 4).

Results

The sample 1 shows an excellent catalytic activity in phenol oxidation process, while the sample 2 swells intensively in phenol-water solution and has no measurable catalytic activity. Therefore, the catalytic activity of sample 2 was further investigated in N₂O reduction using NH₃, in conditions described elsewhere (4). In this conditions sample 2 has shown a significant activity for DeNO_x reaction. The different catalytic behavior of two samples can be explained with different coordination of Fe³⁺ ions. In the sample 1 Fe³⁺ ions are separated and uniformly distributed on the AlFe-pillars, while in the sample 2 Fe³⁺ ions appear not only on the pillars but also as a bulk Fe₂O₃-form. The results obtained by temperature programmed reduction and Mossbauer spectroscopy reveal the difference in iron ion distribution.

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Decomposition Pathways of Chloromethyl Hypochlorate

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Alkyl and haloalkyl hypohalites have been considered to be important atmospheric species ever since the first observations of the severe catalytic role played by halogenated species in the stratospheric ozone cycle.¹ The presence of an halogen atom in the alkyl group is known to lower the reactivity towards O₂, a fact which permits the haloalkyl radicals to build up to significant concentrations and undergo reactions with other important atmospheric radicals such as OH, HO₂ and CIO, BrO. The rich intermediates thus, formed may dissociate into various products^{2,3} and affect in turn the stratospheric ozone chemistry.

Chlorine hypochlorite, CICH₂OCI, is an interesting such species which may be dissociate according to the following scheme :

 $CICH_2OCI \rightarrow HCI + CHOCI$ $CICH_2OCI \rightarrow HCI + CICHO$ $CICH_2OCI \rightarrow CICH_2 + OCI$ $CICH_2OCI \rightarrow CICH_2O + CI$ $CICH_2OCI \rightarrow CH_2O + CI_2$

The isomerization channel to dichloromethanol is also significant :

CICH₂OCI -> CI₂CHOH

In the present work the decomposition pathways of chloromethyl hypochlorite are investigated using high level ab initio quantum mechanical methods. Among the various channels, $CH_2O+ Cl_2$ formation is found to be the most feasible energetically reaction pathway, while 1, 2 HCl elimination leads to the most stable thermodynamically products, HCl + ClCHO.

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Potassium iodide and iodine leaching solutions have been evaluated for use in a process for removing mercury from contaminated solid wastes. Most of the experimental work was completed using solid wastes in the area ex Chlor-alkali factory in Vlora region (Albania).

The mercury content of the wastes was measured and determined to be approximately 10.000 - 50.000 mg/kg.

A solution consisting of potassium iodide and iodine proved to be most effective leachant used in the experiment when applied for 2-4 h at ambient temperature.

lodine recovery and recycle of leaching agent also accomplished successfully.

The objective of experiments was to demonstrate the removal of mercury from the spent leaching solution and the recovery of iodine for use in subsequent treatment cycles, with the optimum leaching process established in the laboratory studies.

Methods and procedures

Two types of laboratory experiments were conducted: Full-cycle experiments, where the soils contaminated with mercury were leached with potassium iodide and iodine solution and the spent leaching solution was processed to remove mercury and recover iodine, and multiple-cycle experiments, where up successive batches of mercury contaminated solids were treated with recycled leaching solution.

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Heavy Metals in the Ground Soil and Road Dust of Tourist Areas

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In nature, heavy metals could be found in all types of ground. Industrial era is the era of the increase of heavy metal concentration in each part of eco-system including ourselves. For instance, the content of lead in the organism of a contemporary man is approximately 500 times greater than that in the organism of a pre-industrial man. Numerous researches¹ have confirmed the traffic is denoted as source of heavy metal mass pollution, particularly Pb, Cd, Cu, Ni, Co, Cr, and Zn. A man has been familiar with the toxic effect of lead (tetraethyl lead is ant detonator) practically from the very start of its use in the petrol motors in 1921. Zinc and cadmium are released by wearing motorcar tires. Lubricating oil often contains cadmium, copper, and zinc. Nickel, cobalt and chromium are found in car plating, in welded plates and in tires. Recent researches² confirms numerous established relations of a type: frequency of automobile trafficconcentration of heavy metals; distance from traffic artery-concentration of heavy metals; time of exposure to the impact of exhaust gases-the contents of heavy metals in body liquids of humans, etc. Most of the researches were carried out in the cities adjoining the traffic arteries that have the extremely high or extremely low frequency of the traffic. The impact of transit-traffic was examined closely within the researches that were examining the influence of railroads and roads with high frequency of the traffic. No written data are found about the examination of automobile traffic (tourist traffic) influence on the contents of heavy metals in the ground soils neither of tourist centers neither on the seaside, nor of the tourist centers in general.

The goals of the work were manifold. The main goal was specifying the concentration of the contents of heavy metal in the soils and road dust of the main tourist centre on the south–Adriatic coast–Budva, which has a specific circular system of traffic built up all around the city during the last five years. The next goal was defining the relation between the concentrations of heavy metals in these of two types of sample. Next, it was necessary to define impact of traffic frequency on the contents of heavy metals in the soils and road dust too. Finally, where possible, it was needed to establish the relations between the usual concentrations of a certain type of ground (Terra Rosa) and the specific concentrations.

The total number of collected samples was 25 (12 samples of the soil and 13 of road dust). They were picked in the places located along the traffic arteries with the high frequency of the car passing and in the outskirts of the city where the number of vehicles are much lower. The sapless were taken from the surface layer of the ground (to 15 cm). The road dust was collected from around the curbstone. After the drying at the 110 °C and sieving, the samples were prepared with a wet acid digestion procedure. The concentration was determined with atomic absorption spectrometer PerkinElmer 6500

The results of this analysis show that there is a concentration of heavy metals and the type of sample. The considerable difference is evident in the relation Pb/Zn. The relation: frequency of the traffic of motor vehicles– concentration of heavy metals in the soils and in road dust was proved. Non-existence of the referential parameters and low regulations concerning the soils in this region prevented the fulfillment of the last goal, which had been set. However, in comparison with the other data from the literature³ there is an obvious increase of the contents of heavy metals, especially Pb – even to 3 times more concerning maximum allowable limits.

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Enhancement of the Aerobic Bioremediation of Methyl Tertiary Butyl Ethers and Other Gasoline Compounds Using Solar Radiation

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Methyl tertiary butyl ethers (MTBE-s) are synthetic chemicals which are added to gasoline in order to enhance its oxidation. However, these compounds show their damaging effects and they can be found in groundwater, surface watercourses and soils in Serbia. MTBE remediation is slowed down because of xylenes (BTEX-s) presence and other conventional fuel components. Since various conventional methods of remediation are not effective enough, as they are long-lasting, require large space and complex system for purification and remediation, it is necessary to find an alternative method, which is more efficient and economical methods of remediation.

On such method is an aerobic bioremediation of water polluted by MTBE and BTEX samples. This very method is extended by the direct exposure to solar radiation photons and usage of oxygen release compound (ORC) which is directly injected into soil. Sodium-peroxide is used as ORC and it's the catalyst in the reaction. The process on oxygen release lasts between six months to one year, so that in ambient conditions, with the ORC addition, can assure constant flow of oxygen. Without sufficient amount of oxygen the degradation of contaminated components would either stop or it would proceed with much slower anaerobic process, since oxygen are the limited factor for micro-organisms capable of biodegradation contaminants, and the depth of oxygen penetration into soil is limited.

With this experiment we have investigated the influence of ORC and aerobic bacteria on MTBE degradation, as well as the influence of other hydrocarbons-for examples BTEX. Aerobic bacteria flourish with long-lasting oxygen affect, which brings it to accelerated natural attenuated contamination such as: BTEX, MTBE, gasoline and diesel range organics, nitro aromatics, chloroaromatics, vinyl chloride and dichloromethane. The rate of MTBE degradation follows Michealis-Menten kinetics form taking into respect dissolved oxygen. When BTEX was in the sample next to MTBE, there was a deceleration of MTBE degradation namely, MTBE degradation appeared after BTEX concentration decrease. However, when MTBE's concentration was higher in the samples, MTBE represented the inhibiting factor for the biodegradation of other hydrocarbons. This characteristic can be used for remediation of other hydrocarbons were taken as a surplus.

Results show that the best results are achieved when using microbiological-culture, sodiumperoxide and concentrate solar radiation. As a result, the time of monitoring is shorten.

Study of the Growth Regulating Effect of 2-Hydroxyethyldimetylammonium – 3,5-Diaminobenzoate (XIIa) on Monocotyledonous and Dicotyledonous Plants

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Plant growth regulators are defined as organic compounds, other then nutrients, which affect the physiological processes of growth and development of plants when they are applied in low concentrations. The term "plant growth regulator" includes either natural hormones (phytohormones) or synthetic compounds.

The paper presents the results concerning the biological activity of an untested synthetic product, obtained in our laboratories, containing a benzoic structure: 2-hydroxyethyldimethylammonium -3-5- diaminobenzoate, namely XIIa compound.

For the determination of the biological activity of XIIa compound, as stimulator of the plant growth, laboratory tests were carried out on monocotyledonous - wheat caryopses (Alex variety) and on dicotyledonous - cucumber seeds (Cornichon variety) using the general Tsibulskaya – Vassilev biotest method comparatively with water control. The concentrations used were: 10 ppm, 50 ppm, 100 ppm for monocotyledonous and 1 ppm, 5 ppm, 10 ppm for dicotyledonous. The seeds were held in Petri dishes on agar medium at 22-25°C, during six days. After that, the biometric measurements of the average length of the plants, the number of the roots, the length of the roots and the dry substance were carried out. The obtained data were calculated in percentage and compared to the water control.

On the monocotyledonous plants (wheat), the average length of the plant increases for 11-15% at the concentration 50 -100 ppm, and the average number of the roots increases for 29% at 50 ppm and for 16% at 100 ppm concentration. The dry substance increases for 18%.

With respect to the dicotyledonous plant (cucumber), the average length of the plants increases for 20% at 1 ppm concentration, 31% at 5 ppm and 21% at 10 ppm. The average length of the principal roots increase for 163% at 1 ppm, 80% at 5 ppm and for 30% at 10 ppm concentration. From the point of view of the average number of the secundary roots, was reported an increase of 81% at 5 ppm and 99% at 10 ppm concentration.

The dry substance increases for 8% at 1 ppm concentration in comparison with control.

So we can say that the product XIIa has a significant biological activity upon monocotyledonous and dicotyledonous plants.

Application of AI-Pillared Clays in the Food Industry

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Introduction

Pillared clays belong to the most frequently studied microporous new materials, because of their specific textural characteristics. Pillared clays as adsorbents can offer improvements in purification of raw materials and final products in different branches of food industry (1,2). In this paper we investigated the applicability of Al-pillared montmorillonite clays in vegetable oil industry.

Experimental

Natural and purified montmorillonite clays were acid activated and then used for synthesis of Alpillared activated clays with OH/AI molar ratio 2, as described elsewhere (3). The textural properties of the prepared samples with low temperature nitrogen adsorption method (ASAP 2000, Micromeritix) were measured. Investigated raw sunflower oil was darker and contained higher quantity of oxidation products.

This oil was stirred with 2% clays at room temperature for 20 minutes and filtered afterwards. The quality of obtained oil samples was investigated with spectrophotometrical (Hewlett Packard 8452) and other JUS ISO standard methods.

Results

The results of texture measurement showed remarkable increase in surface area, followed by increase of micropore area, especially in purified activated ($342.0 \text{ m}^2/\text{g}$, $28.5 \text{ m}^2/\text{g}$) and purified Alpillared activated clays ($411.80 \text{ m}^2/\text{g}$, $91.2 \text{ m}^2/\text{g}$) comparing to natural clay ($93.9 \text{ m}^2/\text{g}$, $24.0 \text{ m}^2/\text{g}$). The best effect in decolorisation was revealed after treatment with purified activated and purified Al-pillared activated clays, which was confirmed with tree and two times higher transparency at 455 nm than in untreated oil, respectively.

The decrease of specific absorbance at 232 and 270 nm exhibits a positive effect that applied clay samples have in elimination of secondary oxidation products.

Besides that, during treatment with Al-pillared activated clays the peroxide values were practically unchanged as well as the acidity. This implies that clays have not decreased oil oxidation stability.

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Environmental Benefits of Waste Mineral Oil Recycling Considering Soil and Water Pollution

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Environment and resource protection as a global problem favors the application of waste material recycling in all fields of industry. In petroleum industry, solvent extraction processes are wide spread in petroleum refining. The US Environmental Protection Agency (EPA) has listed a number of PAH compounds to be considered as priority pollutants that should be monitored in the environment. CONCAWE report refers to certain oil refining procedures that are environmentally favored, concerning the PAH content in refined products. Polycyclic aromatic compounds with three to seven benzene rings are considered to be the substances in mineral oils that have the carcinogenic potential. The relative carcinogenic potency of specific PAH is determined as a ratio to benzo(a)pyrene stated to be a compound with high carcinogenic potential, which has carcinogenic potency referred as 1. Recycling of used mineral insulating oil by N-methyl-2pyrrolidone (NMP) extraction was performed in order to investigate the possibilities of its application as an procedure favored from environmental point of view and to determine whether it satisfies environmental regulations. The main parameter concerned, the polycyclic aromatic hydrocarbon content (PAH) was measured in waste mineral oil before recycling procedure and afterwards in six recycled oil samples and corresponding extracts. Silica solid phase extraction (SPE) was used for the sample preparation. Content of 15 different PAH in each sample was determined using high performance liquid chromatography (HPLC) with fluorescence detector. NMP solvent power and it's selectivity for PAH was determined by varying the extraction process parameters, based on yield of recycled oils and PAH distribution between the recycled oils and corresponding extracts.

Soil and water contamination degree was considered taking into account the concentrations of PAH in water and soil samples measured at the location of one oil spill in industry area. Oil samples were prepared using C-18 SPE and analyzed by GCMS technique. In comparison with the degree of soil and water pollution, waste mineral oil recycling process shows the benefits of it's application, taking into consideration the conserving of resources.

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Several studies on bacterial and animal cells have shown that electric and magnetic fields influence a large variety of cellular functions [1-3]. Less studies of this kind have been conducted on plants but the effects on static magnetic field on the metabolism and growth of different plants had already been reported. Moreover, the feasibility of magnetic field perturbations as a tool for controlling enzyme-regulated biochemical reactions has gained interest and could develop particular attention for alteration of growth and development [4-6].

The purpose of this work is to improve the general knowledge of the response mechanism of living systems to low magnetic field in the presence of other physical stimuli such as screened geoelectric field, negative thermal shock and ferrofluid presence.

We exposed *Nigella damascena* seeds to an extremely low magnetic field for short periods and to a combination action of the mentioned stimuli. Since *Nigella* sp. has a small number of long and morphologically different chromosomes which present synchronised mitotic divisions in the root meristem constitutes a proper subject for cytogenetics studies and evaluation of the effect of environmental factors.

Since peroxidases are known to behave like an excitable system capable of displaying complex responses towards perturbations with time-varying external stimuli and since they are involved in common response to abiotic and oxidative stress, we evaluated the pattern and activity of isoperoxidases in *Nigella damascena* plantlets grown up from as above mentioned treated seeds. Germination grade, viability and morphometric parameters of the seedlings were compared with control seedlings. The effects on cellular mitosis and the induction of chromosome aberration were evaluated too.

The electrophoretic separation of isoperoxidases showed three cationic isoforms with different activities and an anionic one. Both peroxidase components are specifically influenced by the investigated stimuli and effects were manifested at qualitative and quantitative level. Negative thermal shock induced a significant qualitative and quantitative variation of the cationic component and a quantitative variation of the anionic isoforms and the effect was maximum for the shortest exposures. The combined action of low magnetic field and negative thermal shock revealed the screening effect of low magnetic field against the response induced by negative thermal shock. Constitutive cationic isoforms are also sensitive to low magnetic field whereas the anionic isoforms not. The combined action of screened geoelectric field and negative thermal shock was clear at the qualitative level of the spectrum. The general effect is the inhibition of cationic and anionic isoforms that resulted in a dramatic change of the proportion between cationic and anionic activity. In this case cationic and anionic activity tended to become equal.

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The Relationship between Some Meteorological Parameters and High Ozone Concentration Occurrences

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Ozone is a highly reactive gas, a secondary pollutant produced in the troposphere from natural and anthropogenic precursors involved in photochemical reactions in the presence of sunlight and high temperature. The emissions of precursors of O_3 are still sufficient to promote photochemical episodes over most of Europe. High concentration of ground level ozone is known to have harmful effects on human health and vegetation.

Ozone concentrations were measured at four locations in the urban area of Belgrade during the period between June and December 2002. Strong correlations have been found to exist between ozone level and various meteorological conditions. The most extreme ozone events occur in multiday high ozone episodes lasting up to 5-10 days. Strong seasonal variation of ozone was observed. The daily maximum one-hour ozone concentrations ranged from 19 ppbv (December 23) to 118 ppbv (June 23). Ozone concentrations of 90 ppbv (\sim 180µg/m³) or higher, continuing for 1 hour or more, were registered at three measuring locations (according to Directive 92/72/EEC EU Member States have to inform the public when hourly average ozone concentrations exceed the information threshold of 180 μ g/m³). Concentrations equal to or higher than 100 ppby, which represent a potential danger for vegetation (EU Directive 92/72) were registered in 28 instances between June 23 and September 3, 2002. High daily ozone values were mostly registered at high air temperature, low relative humidity, low wind speed mainly from the north i.e. from mostly agricultural zones, which indicated that measured ozone was locally produced. The diurnal ozone concentration at the various sites mostly show the typical pattern of photosmog formation, i.e. a steep rise of ozone in early morning, a maximum in the afternoon and a decrease after sunset. Nocturnal ozone concentration is at most sites on the order of 10 to 20 ppbv, but sporadically, the ground level ozone concentrations may significantly increase during the night. These variations of the ozone concentrations are found to be largely affected by local transport of air masses. It was clearly noted that the mean ozone concentration tends to increase with increasing distance from the city center. The results obtained suggest that measurements made at a single location cannot be view as representative of the entire city.

The results presented in this paper show that there are conditions favourable for occurrence of moderate to high ozone concentrations in Belgrade urban area, during summer season from June to September, of sufficiently long duration to represent a risk for human health and vegetation.

Surface Ozone Phenomenology and the Relation Between Ozone and Water Vapor

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Across Europe increasing ozone concentrations are observed from Scandinavia to the Mediterranean basin but there are fewer (if any) systematic measurements for the Balkan region (Greece is an exemption), where the experimental evidence of oxidants is very limited. Meteorological conditions favourable for the build up of ozone are frequent, from early spring to early autumn, in Belgrade and surrounding area. Some photochemical smog events that occurred in Belgrade and were recorded in our measurements were characterized by high ozone concentration values. Although, these measurements were carried out for more than a decade published information is scant and difficult to find. In spite of the fact that elevated level of O_3 has been considered as an environmental problem for more than 30 years, interest for ground level ozone is still increasing because of the clear chemical coupling between ozone and tropospheric aerosols. By publishing these data, we intend to increase coverage of the current state of knowledge with respect to ozone seasonal cycles in the troposphere over the Balkan region.

The concentrations of NOx and O_3 and accompanying continuous measurements of major meteorological parameters (temperature, relative humidity, wind speed and direction, precipitation and insolation) were carried out at two different locations within the urban area of Belgrade and the period from 1993 to 1999 is included in the present consideration. Ozone production in photochemical smog events depends on several variables but mostly on the concentration ratio of precursors and meteorological conditions. High surface ozone levels are mainly observed during periods with warm and sunny weather in combination with stagnant air masses and build-up of precursor pollutants. During this period photochemical smog events often show different features and are not always in accordance with sunshine and daily temperature.

Data analysis has shown two main different patterns of photochemical smog events in Belgrade area. During strong ozone events O_3 concentration reached 80 to 110 ppbv. The daily ozone peak occurred between 14 h and 16 h local time and the ozone concentration dropped below the background level overnight (10 to 20 ppbv) as deposition processes remove ozone. In addition, a night peak often occurred between 23 h and 04 h, sometimes reaching unexpectedly 80 ppbv, when a rapid and reversible interaction of ozone and water vapor can be clearly noted. In the presence of high humidity the nocturnal gas phase ozone loss was rapid and significant. The analysis of this phenomenon is rather complex, preliminary and is not yet completed.

Potential Risk Manifestation of Alkali-Silica Reactions (ASR) in Concretes Prepared by Aggregates from Different Riverbeds in Albania

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The deterioration or failure of concrete besides of many reasons may be caused even by the use of unsuitable raw materials, such as high-alkali cement and alkali-active aggregate. The aggregate of a concrete mixture is not only filler or inert material. The nature of the aggregate and its chemical and physical characteristics are of a great importance for the future behavior of the concrete.

In this regard, it has been studied the behavior of aggregates taken from some main riverbeds of Albania on various cement-aggregate combinations. The experiments are carried out according to the method of continuity of tests: petrographic examinations of aggregates and the rapid tests. The results are taken through measuring the expansion of mortar bars, stored for 14 days in NaOH solution (1N), in 80°C. The different behavior of samples in this alkaline environment is graphically shown and statistically tested and commented.

The results taken from the tests show that among the examined aggregates some are suspected to show alkali-aggregate reactions (22% of the samples resulted to be potentially alkali-active.) One of the aggregates is taken from one of the main rivers of Albania, which is very much exploited for inert material. This is a supplementary reason to immediately stop the overexploitation of these rivers for aggregates.

These manifestations make obligatory the assessment of alkali-active potentials of aggregates used in Albania before using them in concrete. Apart from that it is suggested to make even their mineralogical examination which will finally decide if it can be used in the production of the concrete. These measures will avoid the use of alkali-active aggregates and prevent the possible future failure of the concrete caused by alkali-silica reactions.

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Industrial Wastewater Treatment Containing Heavy Metals Experimental and Mathematical Model Study

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The treatment of industrial wastewater containing heavy metals is a major concern because of their high toxicity. Although standard technologies are being employed for the treatment of such effluents, the researches have been focused on the development of cleaner-removal technologies allowing the reuse of these compounds.

The application of activated composite membrane for the recovery of Cd (II) and Zn (II) from aqueous solutions using di (2-ethylhexyl) phosphoric acid (D2EPHA) diluted with hexane as carrier was considered in this study. The membrane should be stable from the chemical point of view, have a good hydrofobicity and good complexing and decomplexing properties for an efficient transport¹. The influence of phase composition and support type on the membrane transport properties was also studied².

The effect of various factors on the extraction process were investigated for determining the optimal extraction conditions. Using an extraction tube the overall rate of transfer per unit area, the overall mass transfer coefficient for liquid phase and the membrane resistance were determined. The effect on the overall mass transfer rate of carrier concentration, of pH of feed and stripping solutions and of metal concentrations in feed solution was studied.

The maximum flux and permeability of $1,12 \times 10^{-5}$ mole/(m² s¹) and $6,23 \times 10^{-11}$ m²/s, at carrier concentration of 0,05 M were obtained. The distribution coefficient of Cd (II) and Zn (II) ions into organic phase were increased with increasing the carrier concentration. The pH solutions of feed and stripping were between 2.21 and 4.65.

A model describing the transport mechanism and indicating the different rate-controlling steps was presented. The validity of the model was evaluated with experimental data. A good agreement between the results of model and experiment was obtained.

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The Influence of Banoset and Banoset K on Flower Cuttings

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Banoset and Banoset K represent auxinic compounds having naphthalenic nucleus, obtained by synthesis.

Natural and synthetic auxins are contributing to the initiation and acceleration of the secondary roots. After the growth of principal roots is stopped, the auxins are migrating from the top of these roots to the specific points of growing of the secondary roots. The use of auxins has found large utility in garden practice because they strongly manifested in generation of the roots from flowers species witch usually a difficult to realize rooting by cuttings.

This paper illustrates the effect of Banoset and Banoset K on the rooting of the gerbera, chrysanthemum and carnation. Rooting experiments were carried out with apical green cuttings in the august month, using perlit as the substrate. Three methods of treatment were used, consisting in: the immersing for an hour long, the immersing four six hours long and by powdering the cuttings. The number of the cuttings treated per variant was 100. Concentrations of 100 ppm were used for solution and of 1000 ppm for powder.

The obtained data were calculated in percentage and compared with the untreated control. The statistical processing of the data was carried out by Statgraphics program. The best method of treatment was that consisting in the powdering of the cuttings.

At carnation (Samantha cultivar) the best results were obtained at cuttings treated with Banoset 93.3% followed by Banoset K 91.2% and control was 70.4%. Concerning the quality of the root system the best results were obtained at variants treated with Banoset, the average number of roots has grown up to 21.4 (124%) comparatively with control (17.3) and the average length of the roots increased at 9.5 cm (211%) at variants treated with Banoset comparatively with control (4.5 cm).

At chrysanthemum (Indianopolis cultivar) the variants treated with Banoset K gave a rooting percentage better (92.5%) than Banoset (91.9%) and control (82.2%). The average number of roots has grown with 41.7 (111%) comparatively with control (37.5) the average length of the roots increased with 7.3 (133%) at variants treated with Banoset comparatively with control 5.5. The variants treated with Banoset K, registered a increase of the average length of the roots with 6.5 (118%)

At gerbera (Clementine cultivar) the use of Banoset stimulated the rooting of the cuttings with 91.5% comparatively with Banoset K (84.8%) and control (61.5%).

The treatments with these products gave high positive results both regarding the increase in the rooting percentage of the cuttings and the quality of root system. The results obtained were statistically assured.

Bioproduct Quality Assurance during the Spray Drying Process

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Drying of biomaterial is a technological process very complex, which can change different parameter of the dried material, such as biochemical (cell atrophying), enzymatic (activity waste), chemical (decreasing of nutritive value and activity) and physical (solubility, rehydration, contraction, aroma waste). This changes can appear separate or simultaneous.

Biomaterials are delicate in nature and therefore require extreme care during production, processing and handling. Thermal processing of biomaterials, when the heat impact has a major influence on the biomaterials properties and determines the product quality, involve the principles and methods used in process engineering and biological science.

The advantage of spray drying is that both mass and energy are transferred in a very short time using an relative large exchange surface and keeping the product temperature at a required value. The present paper proposed mathematical model of biomaterial in a spray drying process, with the purpose to determinate the correlation between spray dryer dimension and droplet size distribution for spray drying process.

This model considers that the initial droplets are no uniform size in spray drying. For this we using the mathematical model of Topar, at which we bring some changes in modeling conditions, obtaining droplet size distribution; the results will compared with the experimental research data. In the case of using the Sauter average diameter of droplets instead of the real size distribution it was found to cause great error in the results and in determination of the main sizes of the equipment as well.

The mathematical model applied gives a good possibility to determine the optimal operating parameters of the dryer.

The Content of Ni, Cd, Pb, Cr and As in Some Species of the Genus *Micromeria*

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Presence of toxic pollutants such as inorganic contaminants in soil, air, surface and underground water may cause contamination of flora, fauna and humans. Heavy metals, including nickel, cadmium, chromium, lead and arsenic, may accumulate naturally in the soil or may originate from industrial and mining processes¹. This may affect growth and result in altered composition of secondary metabolites of plant species used in medicine². Regarding the facts, plant genus *Micromeria* are known for their pharmacological activity³, we have examined the heavy metal content (plus As), to eliminate possible negative consequences of their application.

The plant material was collected on July 2002 (*Micromeria parviflora* - Canion of river Moraca, Montenegro; *Micromeria kosaninii* - Galicica Mountain, Macedonia; *Micromeria juliana* - Canion of river Cijevne, Montenegro).

The heavy metal distribution was investigated separately in three plant species, *M. parviflora*, *M. kosaninii* and *M. juliana*. The samples were prepared for AAS analysis by two different ways of ashing, wet and dry according to the previously published procedure⁴. Selected elements were determinate from the sample solutions (five each) of ashed plants by the flame (Pb, Cd, Cr, Ni) and hydride method (As) AAS technique using Perkin Elmer Analyst 2000.

The highest concentration of the metals was in the species *M. juliana* (9.82 μ g/kg Cd, 0.738 mg/kg Cr, 0.68 mg/kg As, 3.52 mg/kg Ni, 4.74 mg/kg Pb, in dry ashing). Among all of the examined contaminates of *Micromeria* Ni and Pb contents have the highest values in all plant species (3.60 mg/kg, 2.38 mg/kg, 3.52 mg/kg, dry ashing, in *M. parviflora, M. kosaninii* and *M. juliana* respective for Ni, and 2.55 mg/kg, 2.29 mg/kg, 4,74mg/kg dry ashing, in *M. parviflora, M. kosaninii* and *M. juliana* respective for Pb) whereas Cd presented a minor contaminant (47 μ g/kg, 3.15 μ g/kg, 9.82 μ g/kg, in *M. parviflora, M. kosaninii* and *M. juliana* respective). The minimum concentration of the metals was in the species *M. kosaninii* (3.15 μ g/kg Cd, 0.43 mg/kg Cr, 0.13 mg/kg As, 2.29 mg/kg Pb, 2.24 mg/kg Ni in dry ashing).

The results obtained by dry ashing are in good accordance with those yield by wet digestion. Level of examined metals content is tolerable, comparing to metal content of pharmacologically interesting plants.

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Textural Effects of the Resin Matrix on Proton/Cadmium(II) Ion Exchange Kinetics

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The presence of cadmium ions in both ground and wastewaters is of particular concern because these heavy cationic species cause detrimental effects on human health and the environment. Ion exchange is considered an attractive method for cadmium removal and recovery from wastewaters arising mainly from metal plating operations, lead and zinc extraction, pigments and semiconductors industries. The objective of the present work is to investigate the effect of the texture of the resin matrix on the proton/cadmium(II) ion exchange kinetics. The selected resins were Purolite C100 and C150, sulfonated styrene-divinylbenzene copolymers, with gel and macroporous skeleton, respectively. The macroporous resins are frequently used in industrial water treatment having a higher resistance to osmotic shock and oxidative reaction than gel-like resins. The macroporous resins are characterized by a bidisperse pore structure. A particle of such resin is an agglomerate of microspherical gel particles with a high degree of cross linking, which contains micropores, separated by a continuous non-gel porous structure forming the macropore system. The functional groups are grafted on macro and micropore walls. The diffusion of the entering ions in micropores slow down the overall ion exchange rate, if the process occurs with particle diffusion controlled mechanism. Interdiffusion of ions in macroporous resins is a more complex process than in gel-like resins. The proton/cadmium(II) ion exchange rates were monitored using a potentiometric method. The experiments were done in concentrated external solutions in order to favor a particle diffusion controlled mechanism. The influence of different sizefractions of the resin beads, and of different stirring speeds, on the ion exchange rates at 303 K were used to assess the mechanism. The results are in agreement with a particle diffusion rate controlling step ion exchange kinetics. Five guasi-homogeneous resin phase kinetic models (1) and the Ruckenstein et al. bidisperse pore model (2) were used to obtain the proton/cadmium(II) integral interdiffusion coefficients (3, 4) in the gel and macroporous resin, respectively, and their variation with the fractional attainment of equilibrium. The ratio of the ion exchange capacity due to the functional groups grafted in micro and macropores of the macroporous resin was evaluated using a procedure previously proposed, based on a limiting case of the Ruckenstein model (4, 5), supposing that the ion exchange process occurs in two stages, with the macropore diffusion being much faster than the micropore diffusion. The proton/cadmium(II) ion exchange rates on the macroporous Purolite C150 resin are smaller but close to those on the gel-like resin Purolite C100 (~8% divinylbenzene). The macroporous Purolite C150 resin ensures fast ion exchange kinetics, because of the small retardation effect due to the micropore diffusion.

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Photocatalytic Oxidation of Dichlorvos in Aqueous TiO₂ Suspensions

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Dichlorvos (DDVP) is an organophosphorous pesticide, a very toxic pollutant which contaminates the surface and ground water. The aim of this paper is to elaborate an experimental method to destroy it up to mineralization.

Dichlorvos in aqueous solutions (1.7 x 10^{-4} M) containing TiO₂ powder keept as suspension by stirring was photodegradated using UV light (under 380 nm) and bubbling continnously O₂ in a quartz cell of 13 ml. Using TiO₂ concentrations in the range 3.03 x 10^{-5} –1.212 x 10^{-4} g/ml we selected 6.06 x 10^{-5} g/ml as optimal. The experiments were carried out at pH 4 to prevent from DDVP hydrolysis. The kinetic was followed by monitoring Cl⁻, H⁺, PO₄⁻³ ion concentration as well as the consumption of DDVP. They obeyed a first order kinetic, namely:

$$k_{Cl^{-}} = 3.95 \times 10^{-4} s^{-1}$$
, $k_{H^{+}} = 3.87 \times 10^{-4} s^{-1}$, $k_{POl^{-3}} = 9.5 \times 10^{-5} s^{-1}$, $k_{DDVP} = 2.18 \times 10^{-4} s^{-1}$

One observes that k_{Cl^-} and k_{H^+} are similar and four times higher than $k_{PO_4^{3-}}$. The same

experiments carried out at pH 2.76 gave similar results but the monitoring of pH variation was not possible. We was able to evidence by spectrophotometric measurements the appearence of formaldehide as intermediate. The same experiments carried out without bubbling O_2 lead to values two times smaller.

We studied also this photodegradation at pH 9.1 when obtained:

$$k_{Cl^{-}} = 2.68 \times 10^{-4} s^{-1}$$
, $k_{H^{+}} = 2.49 \times 10^{-4} s^{-1}$, $k_{PO_{T}^{-3}} = 1.96 \times 10^{-4} s^{-1}$, $k_{DDVP} = 1.23 \times 10^{-4} s^{-1}$

The rate constants k_{Cl^-} and k_{H^+} have again similar values approximately to times smaller than at pH 4. This behavior suggests that DDVP hydrolysis operates parallel with the photodegradation catalyzed reaction.

Our results permitted to advance a photo-oxidation mechanism which takes into account the presence of radicals and intermediates generated by [•]OH during irradiation of TiO₂ semiconductor suspensions in DDVP aqueous solutions.

Bismuth (III) Nitrate Pentahydrate, a User Friendly Catalyst for a Variety of Organic Reactions Under Microwave Irradiation in Solventless Systems

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Functional group manipulations are of great importance in organic synthesis. In spite of wave reports in literature, introduction of new methodologies, for such conversions are still in much demands. The preparation of fine chemicals following environmentally benign strategies represents a great challenge in organic synthesis today [1-3].

Microwave heating and its application in organic chemistry for reaction is currently begin developed successfully and in recent years and there has been a tremendous interest in this area [4-6]. Remarkable decrease in reaction times and in some cases cleaner reactions and better yields have been reported with microwave irradiation.

Reaction under dry conditions was originally developed in the late 1980's. Synthesis without solvents under microwave irradiation offers several advantages. The absence of solvents reduces the risk of hazardous explosion when the reaction takes place in a closed vessel in an oven. Moreover, aprotic dipolar solvents with high boiling points are expensive and are difficult to remove from reaction mixture. The low boiling point solvents are also flammable and toxic. During microwave induction of reactions under dry conditions, the reactants adsorbed on the surface of a solid-support, absorb the microwave where as the support does not nor does it restrict their transmission. Consequently, such supported reagents efficiently induce reactions under safe and simple conditions with domestic microwave ovens instead of specialized commercial microwave systems that require sealed teflon bombs. Due to environmental concerns, there is an increasing need and interest in developing processes that minimize production of toxic waste; therefore there is emphasis on the use and design of environmentally friendly solid acid-base catalysis. Within the framework of Green Chemistry a noticeable improvement is provided by the association of solvent-free techniques and microwave activation. Bismuth compounds are attractive candidates for use in green chemistry because bismuth is the less toxic of the heavy metals. The biochemistry, toxicology and environmental effect of bismuth compounds have been well documented.

Bismuth (III) nitrate recently has been used a versatile reagent for functional group manipulation under classical heating.

Here, we wish to report that $Bi(NO_3)_3.5H_2O$ supported onto different solid and such as silica gel, montmorillonite K-10, zeolite HZSM is an efficient reagent for selective oxidation of alcohols to aldehydes and ketones, direct oxidative deprotection of silyl and THP ethers, regeneration of carbonyl compounds from oximes and semicarbazones and Hanztsch pyridine synthesis under microwave irradiation. In conclusion, this work demonstrates the use of bismuth (III) nitrate pentahydrate in various functional group manipulations. Bismuth (III) nitrate is relatively nontoxic, it is easy to handle, insensitive to air and inexpensive.

These features coupled with dry and mild condition and use of microwave irradiation in order to reduce the reaction time make the methods even more attractive. Minimization o side products and high yields are the other advantages of these methodologies.

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Boron Sorption on Metal Oxides

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Boron in aqueous solution is normally present as boric acid and borate ions. Boric acid is a very weak (K= 5.8 10^{-10} at 25 °C) and monobasic acid, which behaves in solution not as a proton donor (Broensted acid) but as a Lewis acid: B(OH)₃ + H₂O \leftrightarrow B(OH)₄⁻ + H⁺

However, boron levels above 0.3 mg L⁻¹ in irrigation waters are considered to be toxic for sensitive crops (e.g. citrus trees). Since boron has been treated as a potential toxicant, several technologies of boron removal from waters and wastewaters have been proposed and applied. Removal of boron by sorption on solids such as activated carbon, alumina, clays, soils, and other minerals has been also proposed and studied by many investigators working in the field of geochemistry and soil science.

The present paper deals with the adsorption of boron on metal oxides at various conditions (e.g. initial boron concentration, amount, pH and contact time) and discusses the effect of these parameters on boron adsorption and the corresponding mechanism. The results obtained from this study lead to the following conclusions:

- The optimum pH for boron removal by sorption on metal oxides is given at pH near to PZC value of the solids
- The sorption of boron on metal oxides follows the Freundlich isotherm, indicating variation in the heat of adsorption as a function of the surface coverage. The sorption process can be an endothermic or an exothermic reaction depending on the oxide and the pH.
- The sorption mechanism is based whether on surface complexation by formation of 1:1 complexes or on electrostatic attraction between the positive charged surface and the negative charged borate anions by formation of 1:1 ionic couples. Formation of out-sphere complexes is also possible particularly at increased ionic strength



inner-sphere complexation

ionic couple formation

out-sphere complexation

The maximum removal efficiency is given for some oxides at relatively increased boron concentrations ([B] > 5ppm) and other oxides at low boron concentrations ([B] < 1 ppm), depending on the sorption mechanism.

Solidification/Stabilization and Vitrification Technology for PBC-Contamined Waste

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Solidification/stabilization and vitrification is one of the seven non-incineration remedial technologies (bioremediation, dechlorination, soil washing, solvent extraction, thermal desorption and landfilling) for the treatment and disposal of polychlorinated biphenyls-contaminated media (soil, sediment, municipal solid waste, sludge, oil, wastewater) [1].

Solidification / stabilization

Solidification/stabilization is the process which hazardous waste is converted to less soluble and mobile state. Solidification is the process that involves encapsulating waste into a solid material of high structural integrity. It does not necessarily form a chemical bond between solidification additive and contaminant. Stabilization is the process that chemically converts contaminants to less mobile, soluble and toxic form [1]. Cement, lime and binders are examples of materials used as solidification/stabilization additives. This technology first has been used to treat metals and other inorganic compounds. Now it is used to treat contaminants before their acceptance into landfill or for placement back on site (these results in 25 - 30 % volume increase).

Pretreatment processes include segregating incompatible waste types and conditioning or removal of waste material with high concentrations of oil and grease. The treatment is suitable for liquids, sludge, soils and sediments, but not for contaminants in municipal landfills. Mixing during stabilization could promote the release of volatile air emissions. Therefore, it may be necessary to cover the mixers and to filter the exhaust through activated carbon. It is not possible to stabilize organic waste with only inorganic materials such as cement, lime and fly ash. The organic compounds retard the cement polymerization process, so that waste product is unable to pass TCPL (Toxicity Characteristic Leaching Procedure - EPA) testing [2]. Stabilization of organic wastes is not viable option if organic content of waste is greater than 3%. For *ex situ* stabilization treated waste material must be deposited on site for long-term storage or transported off site for ultimate disposal (increasing costs). The long-term viability of *in situ* stabilization is unknown. The risk of contaminant leaching at very low rates into environment still exists.

Vitrification

Vitrification is the process of converting materials into glass or glassy substance [3]. Organic compounds treated by this process are primarily destroyed thermally, so their potential fates are destruction by pyrolysis or combustion, removal in off gas system and migration to surrounding soil. This technology decreases volume of soil by 20 - 40%. There are two methods – electric and thermal heating using fossil fuels. This treatment can be either *in situ* (ISV) or *ex situ* (ESV). ISV involves placing electrodes into soil, generating electric current between them which produces temperatures high enough to volatilize or pyrolize PCBs and to melt soil (1600 - 2000 °C). When the soil cools, it integrates contaminants into glass complex. The treatment limitations are: cost (high energy consumption), potential for some organic and inorganic contaminants to volatilize and become airborne, potential for explosions and for ISV, there is concern that some contaminants may remain or migrate to surrounding soil. The main advantages are: high efficiency in PCB removal, and product is physically and chemically durable, flexibility of glass to incorporate wide variety of contaminants, process can treat both organic and inorganic contaminants (even radioactive) and volume of waste material is reduced [1].

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Valorization of Sugar Beet Pulp by Slurry State Fermentation

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Sugar beet pulp is produced in large quantities as an agricultural by-product. The annual world production of sugar beet pulp is $30 \ 10^6$ mt, it is produced mainly for utilization for ruminant nutrition. However, its composition suggests some alternative utilization with a higher added – value. Sugar beet pulp consists of (25-30 %), hemicelluloses (25%), and cellulose (20 %). The pulp also contains a certain amount of protein, minerals and lignin. In recent years there has been renewed interest in valorization of sugar beet pulp by different fermentation processes for the production of bioactive compounds. Sugar beet pulp has a satisfactory composition, and is a suitable carbon source for microbial utilization as substrate for solid state and submerged fermentation. The object of the proposed research is to investigate the most promising development in slurry state fermentation using sugar beet pulp as substrate. Valorization of sugar beet pulp by slurry state fermentation has rarely been studied. Slurries are commonly processed by anaerobic fermentation producing biogas, a process with low control problems, while very little information can be found in the literature about direct utilization of agro-industrial slurries by aerobic fermentation.

Production of Biodiesel Fuel Using Immobilized Lipase from Mucor miehei

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Alkyl esters of fatty acids produced by alcoholysis of vegetable oils are widely used as substitutes for diesel fuel. The biodiesel fuel prepared in such a way has important environmental advantages over existing one from petroleum. It is biodegradable, non-toxic and renewable source of energy with lower emission of particulate matters and greenhouse gasses than conventional diesel fuels (1). At present, biodiesel has been produced chemically in Europe and USA. However, requirement of removal of catalyst and excessive energy requirements are the major drawbacks in alkali or acid catalyzed process.

One possible way to overcome these negative aspects of biodiesel production is usage of biocatalysts. Lipase from various microbial sources is extensively investigated because it can catalyze transesterification of triacylglycerols in very mild conditions (2). However, the production of biodiesel fuel by enzymatic method has not been adopted industrially, because of the high cost of enzyme catalyst. This problem can be solved by application of immobilized enzymes, which are appropriate for multiple usage.

In this paper, transesterification of sunflower oil triacylglycerols by methanol using lipase from *Mucor miechei* immobilized on macroporous carrier was investigated. The content of obtained fatty acid methyl-esters (FAME) was determined by GC method. The influences of reaction temperature and concentration of catalyst on yield of FAME were investigated by performing reaction at different temperatures (30°, 35°, 40° and 45°C) and with different concentrations of immobilized enzyme (0.3%, 0.6%, 0.9%, 1.2%, and 1.5%). Since methanol was reported to be inactivator of lipase, entire stechiometric amount of methanol was not added at the beginning of reaction. Two kinds of stepwise processes (two-step and three-step addition of methanol) were compared in order to clarify optimum conditions of transesterification. Enzyme was easily separated from reaction mixture and showed activity in repeated reactions. Obtained results indicate that immobilized lipase from *Mucor miechei* successfully can catalyze formation of FAME, especially in case of three-step transesterification.

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The Influence of Different Genotypes on Phytochemicals in Soybeans

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Soybeans present a good source of high quality protein and other nutrients. For a long time, many phytochemicals in soybeans have been considered as antinutrients and irrelevant to nutrition, since they yield neither energy nor function as vitamins. Recently, there have been many important discoveries, which have demonstrated that various physiologically active phytochemicals may play critical roles in prevention of diseases such as heart diseases and cancers (1). It has been suggested that trypsin inhibitors: Kunitz and Bowman-Birk inhibitors, suppress both initiation and promotion stages of carcinogenesis.

So far, the influence of different treatments on biologically active components, especially trypsin inhibitors, was investigated (2,3). But the influence of different genotypes on phytochemicals in soybeans is insufficiently understood. This investigation was undertaken in order to correlate genetic influence on inhibitor composition and corresponding activity. Twelve soybean genotypes grown in 2001 with maturate groups from 00-II were selected and tested for trypsin inhibitors content and trypsin inhibitor activity. Polyacrilamide gel electrophoreses and scanning densitometry of the obtained gels was used to estimate the trypsin inhibitors content. Trypsin inhibitor activity was estimated according to method of Liu and Markakis. The results were analyzed by statistical softver Statistica ver. 5.0

The investigated soybean genotypes express significant differences in both, trypsin inhibitors content and trypsin inhibitor activity. Trypsin inhibitors content range from 2.32-13.16% of soluble protein and correlated activity range from 60.36 ± 1.72 TIU/mg to 100.95 ± 2.62 TUI/mg. The differences in trypsin inhibitors content were mostly provoked by variation in Bowman-Birk inhibitor content. Naimly, Bowman-Birk inhibitor content varied among genotypes from 0.33% to 6.32% of soluble protein, while Kunitz trypsin inhibitor content was mostly around 4.5%. Positive correlation was found between trypsin inhibitors content, Kunitz and Bowman-Birk inhibitors content and corresponding activity.

The lines with high percent of trypsin inhibitors, especially Bowman-Birk inhibitor, could have significant role from nutritional and nutraceutical standpoint of view. Namely, Bowman-Birk inhibitor is rich in sulfur containing amino acids, which are deficient in plant proteins. These lines could have possible use for production of Bowman-Birk inhibitor concentrate, which might be used in cancer prevention and therapy.

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Possibilities of the CO₂-Laser Photoacoustic Detection of Typical Pesticides

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Detecting pesticides and measuring their concentration is a regular concern and objective of analytical chemistry. The usual way would be to take a solid sample (of ground, plant, fruit, etc.) and analyse it by any suitable conventional method - gas/liquid chromatography, or similar. However, a fast and real-time checkup would be if it could be assessed nondestructively, while still in the field, for example. One idea would be atmospheric measurements. On the other hand, these two typical pesticides do not have significant vapour pressures at ordinary temperatures. But, they are never alone in a commercial mixture used for the purpose... And the other components do have measurable vapour pressures.

We investigated the possibilities of detecting Malathion and Fenitrothion by a CO_2 -laser, using a photoacoustic technique developed in our laboratory. The experiments include recording of laser/vapour spectral coincidences in the usual range of CO_2 -laser wavelengths, the vapour being: commercial mixture of the pesticide found on the market, pure pesticide (at commercial purity of the raw component), additives (emulsifiers and solvents), all with and without air added to a mid-pressure and to 1 bar.

Below is a typical coincidence spectrum of Malathion with air added to 91.6 mbar total pressure.



Biotechnological Characteristics of Sugar Beet Sorts on Soil Infected with Rhizomania

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In 2003, in Srem production area, i. e. in Sremska Mitrovica, a sort micro-essay of sugar beet was realized with sorts tolerant of rhizomania. The soil was with maximum level of rhizomania infection, which is confirmed by the results of the control (intolerant of rhizomania). There were 20 sorts and hybrids examined, including the control.

Average sugar beet root crop at the site was high and amounted 59.69 t/ha. The control had only 8.20 t/ha.

Average sugar amount in beet was of average value and was 14.35%, and the control was with the lowest value of 12.47%. As for the control, the remaining indicators of technological quality of sugar beet were at low level, too.

Granulated sugar crop for the examined sorts was on the average high and amounted 7.308 t/ha. On the other hand, the control sort, intolerant of rhizomania, had only 0.850 t/ha.

Difference established between the first-graded sort (Leila, 8.970 t/ha) and the last (the control, 0.850 t/ha) was 8.120 t/ha or 10.55 times.

Biosorption of Fe (II) from Aqueous Solutions by Polyporus Squamosus

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Many industries such as coatings, car, aeronautic and steel industries generate large quantities of wastewater containing various concentrations of iron. These concentrations are usually too low to be treated by standard methods. The search for alternate and innovative treatment techniques has focused attention on the metal uptake capacities of various microorganisms. The active mode of metal accumulation by living cells is designated as bioaccumulation. A major advantage of biosorption is that the need for cell growth and biomass propagation is separate from the metal-sorbing function.

The purpose of the present study was to investigate the use of P. squamosus in Fe (II) removal. Thus, the present study is directed towards the determining the possibility of using P. squamosus biomass originating from an industrial wastewater treatment facility that employs the fungus. Metabolically active cells of P. squamosus were used to determine their effectiveness in sorbing Fe (II). The effect of various operational parameters such as pH, biomass and metal concentrations, and addition of glucose or NaCl to the metal-containing solution on the biosorption was studied.

Fe (II) biosorption isotherms determined based on the Freundlich and Langmuir models adequately described the biosorption of Fe (II). The increases of the initial Fe (II) concentrations and pH of the solutions resulted in an increase Fe (II) uptake. Preincubation of the biomass with glucose or NaCl enhanced the metal adsorption.

The Removal of Beryllium and Arsenic with *Aureobasidium pullulans* and Poly(GMA-co-EGMA)-en from Aqueous Solutions

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To-date results show that *Aureobasidium pullulans* CH-1 and macroporous poly(GMA-co-EGMA)en can be successfully applied for biosorption and polymer sorption of metals from waste waters. These metals (beryllium and arsenic) were chosen for the sorption experiments due to their extreme toxicity.

Both processes have advantages. During the biosorption with this microorganism the metals accumulate in the biomass, while poly(GMA-co-EGMA)-en can be regenerated and reused (1). Macroporous cross linked poly(GMA-co-EGMA)-en [poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate)] with attached ethylene diamine as a ligand has high capacity and good selectivity for the heavy metal ions, combined with chemical and mechanical stability.

The batch experiments for biosorption and polymer sorption were conducted separately under batch conditions in Erlenmeyer flasks containing 100 cm³ of on a rotary shaker at 200 rpm at 26 °C and initial pH 6, during 72 h. The amounts of metal ions in filtrate solution on start of the experiments and after desired treatments periods were determined by atomic absorption spectrophotometry. For biosorption, in aqueous solution were added in (%): $(NH_4)_2SO_4$; KH_2PO_4 ; MgSO₄ x 7H₂O 0.2; NaNO₃ 5.0 and yeast extract 0.05. After the experiment for biosorption was finished, the fermentation broth was centrifuged at 8000 min⁻¹. For correlation both of them processes amounts of metals in biosorption were calculated per 1g of biomass. For polymer sorption on poly(GMA-co-EGDMA)-en, metal-uptake capacities for Be and As under competitive conditions were determined in back experiments (0.5; 1; 24; 48 and 72h), by contacting 1.0 g of modified copolymer in aqueous phase.

The obtained results show that both processes may be successfully used for metal removal and/or recovery from aqueous phase.

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Analysis of Coffee Quality by Different Methods

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Samples of roasted and ground coffee bought in stores were taken for the analysis of the quality of the coffees that could be found on our market: Sample 1: coffee from a small private roaster's shop, Zemun; Sample 2: "Don" coffee ("Minas" mixture), produced by GOLEX PRODUCT D.O.O., Belgrade; Sample 3: "Grand" coffee, produced by GRAND PROM D.O.O., Belgrade.

In coffee samples it was done: organoleptic analysis by boiling and first estimating of coffee without the addition of sugar; determination of moisture content by the method of drying in the vacuum dryer; determination of ash by the method of direct burning and determination of matter

soluble in water; the analysis of the presence of mycotoxine aflatoxine in coffee was done by the chromatography method on a thin stratum of silica gel. The caffeine content in samples of roast and ground coffee was determined by reverse-phased liquid chromatography of high pressure.¹

Heavy metals (lead and arsenic, according to regulations were determined by the process of acid digestion during determination of complete and resoluble metals by atomic absorption spectrophotometry (AAS) in flame technique and generation of the hydride technique. Determination of arsenic in the coffee was done by the generation of the hydride method, method with boron hydride.



All analyses were done by *Atomic absorption spectrophotometer* Varian Spectra AA 200. The results obtained by the analysis of the samples of coffee mostly consumed on our market showed that the coffee quality corresponds to the values as given in the Law of Health Food.

It was not found that any of the parametres which determine food quality exceeded permitted values.

Content of heavy metals and aflatoxines is below permitted values.²

The least content of caffeine was determined in a coffee sample roasted in the private roaster's shop, and only in it the presence of coffee surrogates/substitutes was not proved.

The obtained results of the coffee analysis showed that the coffees of most popular producers are very equal, and results of caffeine analysis are even more equal. This indicates the most probable fact that coffee is of the same origin, and that later on, during production, a different mixture was made, which affects the final product and gives aroma and taste to the liquid.

Acknowledgements

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Trace Metal Concentration in PM₁₀ Urban Particles

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As the strong negative health effect of inhalable particulate matter PM_{10} exposure in the urban environment has been confirmed, the study of the mass concentrations, physico-chemical characteristics, sources, as well as spatial and temporal variation of atmospheric aerosol particles becomes very significant. As pollution-derived elements (such as heavy metals) are often concentrated on fine particles, they could remain in the air with relatively long residence time and could efficiently penetrate human lungs.

Sampling of particulate matter with aerodynamic diameter D<10 μ m, PM₁₀ and D<2.5 μ m, PM_{2.5} was conducted at three sites in the very urban area of Belgrade during the period of June 2002-June 2003.

Suspended particles were collected on Pure Teflon filters, using the low volume air sampler Mini-Vol Airmetrics Co., Inc., (5 I min⁻¹ flow rate). Particle mass was gravimetrically determined after 48 hours conditioning in a desiccator, in clean room Class 100 at the temperature $T=20^{\circ}$ C and constant relative humidity RH around 50%. After weighting, samples were digested in 0.1 N HNO₃ on ultrasonic bath and metals were analyzed with DPASV and AAS.

Extraction with dilute acid has been used for the evaluation of elements which can become labile depending on the acidity of the environment. This procedure gives the valid information on the extractability of elements, because the soluble components in aerosol are normally dissolved by the contact with water or acidic solution without us in the actual environment (T. Kyotani and M. Iwatsuki, 2002). Significantly higher labile fraction of Cd, Ni, Mn, and Zn were found at urban areas (90%, 82%, 71% and 93%, respectively) suggesting the dominance of easily available metal forms in urban atmospheric particles (D. Voutsa and C. Samara, 2002).

The Pb concentration of PM_{10} measured in Belgrade varied between 35 and 1460 ng m⁻³. The average value was around 260 ng m⁻³.

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Adsorption Behavior of Cu(II)HZSM-5 and Cu(II)HMOR Zeolites

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Introduction

Among other nitrogen oxides, nitrous oxide is known to be a pollutant which contributes to both global warming and ozone destruction. The permanent increase in atmospheric N₂O concentration is a reason for growing scientific interest on its removal from the atmosphere. Several catalytic systems have been tested for decomposing N₂O, among them, transition-metal ion-exchanged zeolites exhibited high activities [1-4].

In our previous work [5], we investigated the adsorption of N₂O on copper ion-exchanged NaZSM5 zeolites; its adsorption on Cu^+ ions is recognized. In this work, the adsorptions of N₂O, CO and NH₃ on Cu(II)HZSM-5 and Cu(II)HMOR zeolites were investigated.

Experimental and results

The parent NaZSM-5 zeolite (Si/AI = 50) was home synthesized and its cristalinity was confirmed by XRD technique. NaMOR zeolite was supplied by Norton. NH_4^+ forms of these zeolites were obtained by ion-exchange procedure in aqueous solutions of NH_4CI performed at 100°C. Subsequently, aqueous Cu(II) acetate solutions (0.01M, pH = 5.5 – 5.6) were stirred the obtained H- forms at room temperature. The samples with both under-exchanged and over-exchanged levels of Cu(II) were prepared. The samples were denoted as CuHZSM-x, and CuHMOR-x, where x represents the % of ion-exchange. The heats of adsorption were measured following the overnight pre-treatment at 400°C in vacuum (10⁻³ Pa), using a differential heat flow calorimeter (C80, Setaram) equipped with a standard adsorption-desorption device. N₂O and CO were adsorbed at 30°C, while the adsorption of NH₃ was performed at 150°C. Successive known doses of any gas were sent on the investigated sample until a final equilibrium pressure of 66 Pa was obtained. The equilibrium pressure corresponding to each adsorbed amount was measured using a differential pressure gauge from Datametrics. In that way, differential heats of adsorption (Q_{dif}) versus the amounts of adsorbed gases were determined.

The exposure of N₂O, CO and NH₃ to the active sites in two different zeolitic structures gave information concerning theirs strength and the amount. The influence of the type of the structure is noticed. The obtained differential heats of all adsorbed gases demonstrate the dependence on the copper content. However, it is important to notice that the amounts of N₂O, CO and NH₃ adsorbed on both Cu(II)HZSM-5 and Cu(II)HMOR structures are lower in comparison with Cu(II)NaZSM-5 and Cu(II)NaMOR, previously investigated [5]. This result indicates the influence of Na⁺ cation in the processes of adsorption.

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Energy Dispersive X-Ray Fluorescence Spectrometry as a Powerful Tool in Phytopharmacy

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Objectives

Herbs are used in many ways. However, the ultimate objective of their use is their direct interaction with our body chemistry. Inorganic components, especially major and trace elements (Fe, Cu, Zn, Mn, Ca, K, ...), play an important role and might be partly responsible for normal grow of plants and the completition of their life cycle. On the other side there are toxic elements, such as Cd and Pb with no physiological function yet reported but should be considered as a high risk factor to public health in general.

Determination of major and trace elements in 10 various medicinal herbs samples, widely used in the treatment of ailments, was performed by energy dispersive x-ray fluorescence spectrometry (EDXRF). EDXRF is a highly attractive nondestructive technique, which allows simultaneous identification and quantification of elements at least at ppm level in different matrices [1].

Experimental

Ashed samples were obtained by heating on a hot plate first $(100 - 110^{\circ}C)$, followed by ashing at $500^{\circ}C$ for 2 hours, in a furnace. All the samples were grounded in a stainless steel mill, homogenized and pressed to make pellets.

Elemental analysis of the samples was carried out with a Canbera EDXRF spectrometer. Excitation was performed by radioactive ¹⁰⁹Cd source. The characteristic x-rays were detected by a semiconductive Si(Li) detector with Be window, coupled to a multichannel analyzer. The used detection system had a FWHM (full width of half-maximum) energy resolution of 156 eV at 5.9 keV. Integration time was 2000s.

Results

Because the concentration of the most elements in crude samples was too low to be directly determined by radioisotope EDXRF, there was no possibility to detect any of trace elements. Ashing was carried out in order to decrease detection limits and homogenize the samples as well. The enhancement effect and/or absorption of characteristic x-rays emitted by the sample constituents in very complex matrix make quantification of the detected elements difficult. But, analytical method was based on the principle that when a sample powder is shaped into a very thin pellet, the excitation effect on the matrix is neglible as well as the attenuation of characteristics x-rays. In the most analyzed samples similar elements were detected but in the different extent.

For validation of the proposed method certified reference material NIST 1633b fly ash was used and an external calibration method was applied as well. Ten medicinal herbs were analyzed by means of EDXRF. With no time-consuming sample preparation, no solvent usage, this nondestructive technique was successfully applied to direct elemental analysis in these multi element plant samples.

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Correlation of the Values of Plant-Available Pb in the Soil and Amounts in the Plant Parts of Wheat

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The plant-available amount of Pb in the soil determined by using extraction solutions^{1,2}: **1**) 0.5 M Na₂EDTA, pH=5.2; **2**) 1 M KCl, pH=7; **3**) 0.1 M KCl, 0.05 M Na₂EDTA, pH=6.2; **4**) 2 % CH₃COOH, pH=2.5; and **5**) 1 M CH₃COONH₄, pH=4.8. In the experiments chernozem from the Middle Banat are used. The plant material was decstructed with HNO₃ and HClO₄³ and the Pb and Cd concentrations in sollutions was determined by atomic absorption spectrophotometry.

The sampling took place on the parcel of the village of Farkaždin in the Midlle Banat in the period between 20 December 2000 and 5 July 2001 (the sampling took place four times). The sampling of the plant and soil material took place simultaneosly. In each period 4-5 samples took places. Each samples has been analysed 3 times.

The obtained correlation factors of linear depedence of Pb amount in plant parts on plant-available amount of Pb in the soil are given in the Table I.

	Pb (1)	Pb (2)	Pb (3)	Pb (4)	Pb (5)
Pb (in root)	-0.95	-0.87	-0.89	-0.92	-0.87
Pb (in stalks)	-0.94	-0.98	-1.00	-0.99	-0.99
Pb (in leaf)	-0.55	-0.45	-0.64	-0.57	-0.56

 Table I: Correlation factors of linear depedence of Pb amount of plant parts on plant-available amount of Pb in the soil

On the basis of the obtained data it is concluded that the existence of the linear dependence of Pb amount in root and stalks on plant-available amount of Pb in the soil for ever extragens. It is also concluded that Pb amounts in a leaf is not exist linear correlation with Pb amounts in the soil.

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The Protection of Some Fruits by Plant Extracts

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On fruits, being sour microbe layer, mold is easily developed. By their hydrolasis they act upon pectine polyuronide which results in change of fruit consistence and its softening. Fruit epidermis is a mechanical barrier for microorganism penetration and activity. Various chemical compounds make an ingredient part of the epidermis, such like flavonoides or anthocyanins and they influence the range of reactions at fungi,

It is well known that fruit impregnation by lignine widens their resistance to infections because mechanical barrier of fruit to fungi is bigger. As well application of caoline in the form of spray has the same effect of protection from microorganism penetration. Besides mechanical protection, the usage of pesticide, herbicide, fungicide or feromone slows fruit infection down by its influence on vital metbolic reaction of fungi.

Having in mind the data stated, our work has the conception aiming at giving an answer about to what degree the application of water plant extrats *G. macrorrhizum (Geraniacae)* and *H. perforatum (Gittiferae)* influences development of fungi *Phialophora fastigata (Lagneb)* and *Penicillium conescens (Sopp)* which are isolated from infected lemons and oranges during june 2003. Both plants contain terpenoids and different fenolic compound such as tannins and flavonoids. The kind of plants *H. perforatum* containd anthraquinones and red pigment hypericin which, besides its redox reaction, have significant effect of inhibition on fungal enzyme activity.

The influence of the chemical compounds mentioned is in making the resistance of fruit peel stronger by producing a polymere film of phenol compounds and inviolable redox surrounding for inoculation and fungal development.

In that sense, our work embraces three experimental wholes - examining antifungal activity of *G.macrorrhizum* i *H. perforatum* plant extracts (50 mg) on fungi *P. conescens i Ph. fastigata*. The other part is examining metabolic reaction of fungi developed at nutrient medium with addition of 100 mg/ml of an water plant extracts. In the third part of the work we have impregnated fruit (apple, lemon, orange) by water plant extracts and infected it by fungi

P. conescens i *Ph. fastigata*. The fruit was kept at 20[°]C and the moisture of the place of 30%.

The obtained results indicate that plant extracts of *G. macrorrhizum* and *H. perforatum* show maximum antifungal acitivty of about 25%, byt in the mixture, the activity is up to 60%.

The impregnated fruit infected by fungi during 21 days has not given signs of sporulation and the peel damage of apples, lemons and oranges.

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The Quality of Waste Streams at Uncontrolled Waste Dump Sites – Case Study

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Dumping on land has been common way for solid waste disposal for a long time in Serbia. This nonsanitary way of municipal solid waste treatment cases a lot of problems. One of main is environment pollution by waste streams, which are result of solid waste decomposition, so rehabilitation of these sights is necessary. Waste streams as leachate and landfill gas are pollutants that endanger underground water, surface water, air etc.

In procedure of solid waste dump rehabilitation for G.Milanovac town, arrangement of mud as a result of solid waste degradation was defined as main problem. During work accomplishment permanent inflow of mud had been stated from deposited solid waste (dump is about 15 years old).

As the sight was designed for municipal solid waste dumping, problem of transportation and deposition of this mud has highly arised. Also technical problem of evacuation and treatment of the mud was urgent and irremissibly, due to works in preparation of dump sight for future deposition, that had to be finished in a very short time.

Quantity of mud deposition had also to be calculated in aim to define volume of container for mud acceptance, as well as type and frequency of mud transportation. Estimation of mud quantity shown that there is about 1370 m³. plus cca 700 m³, of mud deposition that has already been moved away, and some of it is in the pockets on the sides of rocks. Total amount of the mud is cca 2470 m³.

Physic-chemical analyses of the mud shown that presence of elements, which qualify this waste stream as hazardous waste. Appearance of the mud was result of solid waste degradation, but quality was due to uncontrolled throwing of different kind of rubbish at the sight. Analysis had shown that the mud is hazardous because:

- It is origin according to Directive on hazardous waste (91/689/EEC) and Commission Decision of 16 January 2001 amending Decision 2000/532/EC as regards the list of wastes (2001/118/EC);
- Expanded content of cadmium, so according to Waste Classification Regulation U.S. EPA 1998, waste shows hazardous characteristic H11;
- Expanded content of TOC in EP extract, so according to Federal Law Gazette for the Republic of Austria Landfill Ordinance 1996 shows hazardous characteristic H13.

In this paper possible way of problem solution is presented.

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- 3. Chemical analysis's of leachate at dump site in G.Milanovac, Belgrade, (2003)

The Growth of Maize Seedlings Influenced by the Controlled Input of N Fertilizers

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In high production of maize seeds, the first, previous step of our investigation of nitrogen fertilizer application was to define optimal quantity and it was 120-150 kg ha⁻¹ N, while the plants had smaller habitus^{1,2}. Near the yield, this amount of N-fertilizer influenced mainly uniform seed mass. The next, second step is planed to find the N-form and time of incorporation.

The N-form (NH₄, KAN and UREA) was applied as N in soil + N in fertilizer = 120 kg ha⁻¹ N (Nmin) and for the time search as full quantity of 120 kg, was applied: half in autumn and half in spring, before sowing (1/2). The two inbred lines of different nitrate reductase (NIR) activity (L1 and L2-five fold smaller) were growth in such conditions and produced seeds were used to determine quality of seedlings in the next generation.

The seed mass (S_m) and total plant mass (FM), as well as, coefficient of seed utilization (C_{util}) was the highest at KAN application (Table I). The L1 FM was higher in ½ of all fertilizer combinations, what was the case with seed utilization, also. The L1, inbred with higher NIR activity had 44% higher plant FM and according to this 40% higher C_{util} than L2.

N-	Application	S _m (mg)		FM (mg)		C _{util}	
form	Application	L1	L2	L1	L2	L1	L2
	Ø	340	285	850	368	0,149	0,033
NH_4	1/2	333	306	1022	515	0,266	0,090
	Nmin	331	334	973	438	0,218	0,129
KAN	1/2	343	351	1062	593	0,393	0,266
	Nmin	347	329	841	758	0,167	0,178
UREA	1/2	328	289	888	297	0,369	0,237
	Nmin	338	322	866	655	0,241	0,146

Table I. The influence of N-form and time of fertilizer application on the seed mass (S_m) ,fresh mass of plant (FM) and coefficient of seed utilization (C_{util})

Since the one of the main compounds responsible for conservation of germination ability for a long time is glutathione system, our further investigations will be to determine N-form that influenced glutathione amassing in seed as important economical and environmental factor.

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Modelling of the European/Chinese Mechanism of the Remedy for Silicosis: Aluminum Lactate or Tetrandrine

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Generalities

Occurrence of Si in Earth crust corresponds nearly to 28% and the quartz is one of the most abundant minerals [1]. Quartz exposure is possible in some occupational domains as: mining, building industries and treatment of building materials. Silicosis is the most known lung disease, due to prolonged inhalation of significant concentration (~ 0.5 mg/ m^3) of SiO₂ crystalline particles.

Aluminum lactate - an European remedy

In Europe the recommended remedy for the silicosis is administration of aluminum lactate and for this reason there exist many studies concerning its action. We evidenced the interaction between SiO_2 and $Al(lactate)_3$ experimentally, based on IR spectral method, and theoretically by molecular modeling [2]. In both approaches results that aluminum lactate is bonded at surface of reactive quartz by physical forces *e.g.* electrostatic and van der Waals.

Tetrandrine – a Chinese remedy

The traditional Chinese medicine uses for treatment of silicosis tetrandrine, a bis-benzyl isoquinoline alkaloid extracted from the roots of *Stephania tetrandrae* S. Moore. We evidenced by the same experimental method a strong interaction between tetrandrine and α -quartz, which may be assigned to a chemical force of interaction [3]. In literature exists also experimental evidence on antioxidant activity of tetrandrine *vs.* radical species as •OH, O₂, resulted from silica-cell interaction [4]. Modelling study can explain the pH dependent antioxidant activity of tetrandrine.

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Strategies to Achieve Euro 2005 Diesel Fuel Specifications by Romanian Refineries

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To meet the future stringent Diesel fuel specifications, refiners are faced with two general processing options: severe hydrotreating of gas-oils from primary distillation or hydrocracking heavy gas-oils with maximum of Diesel fuel yield. The both alternatives are very expensive and for Romanian refineries it is very difficult to achieve this target, because our technologies are quite old and the hydrogen sources are very limited.

In spite of these limitations the Romanian refineries must change their strategies of petroleum processing in order to exist and to produce the new fuels asked by European market.

Analyzing the published data of the most important Romanian refiner S.N.P. Petrom which assure almost 90% of Diesel fuels for Romanian market, an increasing of Diesel fuel production with 12,5 % in 2005 comparative with 2003 is reported, without a greater processing capacity.

Meeting the new low sulfur fuel specifications presents a significant challenge in the strategically management of the refinery, because it is not easy to choose the better way when total investments founds assured by S.N.P. Petrom, for the period 2001-2005, in order to increase the fuels quality (gasoline, Diesel and heating oil) are only 180 millions USD.

The new strategy must be based on the available crude oil sources and first of all, the refiners can choose to alter their crude oil slate by purchasing crude oils that have lower sulfur levels. The objective would be to lower the Diesel pool sulfur level enough, so that the existing hydrotreater capacity is sufficient to meet any new lower sulfur specifications.

Anyway, if a major change in sulfur level is required, simply changing crude slate is not sufficient and we suggest to keep this idea as a first possibility to reduce the sulfur level without major investments, but direct hydrodesulfurization is the most efficient method of controlling the sulfur level. The Romanian refiners have already installed distillate hydrotreating capacity to meet the 350 wppm sulfur specifications. Increasing the performances of existing hydrotreaters is the most valuable solution in order to obtain high quality of the products. There are many possibilities to achieve better performances like: using a more active catalyst, increasing the purity of the makeup hydrogen, installing gas scrubbing equipment to remove hydrogen sulfide from the recycle gas, increasing recycle gas compressor capacity, or adding additional reactor volume.

The limits of this process are the difficulties to convert the most refractory compounds as dibenzotiophenes (DBT), because this operation needs very active catalysts and high hydrogen pressure with higher operational costs. Because revamped units cannot operate at pressure high enough and because refinery hydrogen consumption is usually limited, we suggest to choose an innovative way for outrunning this deadlock.

The newest technology for deep desulfurization of middle distillates is the biodesulfurization process (BDS), which is a highly selective biological process for oxidation and removal of heterocyclic sulfur compounds. This process can complement conventional hydrodesulfurization and since the BDS process is oxidative, installation of additional hydrogen generation capacity is not required.

Another way to reduce dibenzotiophenes is the extraction process with furfural which extracts the aromatic compounds, including all species of DBT. This process will be applied to the hydrotreated gasoil and it will assure a decreasing of aromatics and sulfur compounds, both asked by new environmental specifications. The problem is the higher cost of extraction and the wantonness of the extract with a very high aromatic and sulfur content.

The third way could be a blending process between Diesel fuel and biodiesel, a novel fuel obtained from vegetable oils. The sulfur content in biodiesel is zero and this one could be mixed with Diesel fuel in any proportion, but the most useful is 80% of Diesel fuel to 20% biodiesel.

EU Soil Policy - The Thematic Strategy on Soil Protection and Soil Contamination

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In response to concerns about the degradation of soils in the European Union, the European Commission has outlined the first steps in a strategy to protect soils. As a first step in the development of an encompassing EU policy to protect soils against erosion and pollution, the Commission has published a Communication "Towards a Thematic Strategy for Soil Protection". The next step is to draft a Directive on soil monitoring and a Communication on erosion, organic matter and contamination in soil.

We should follow and be included in this EU policy area which will be focused on the methodology for pollution prevention, the inventory, clasification and prioritization of major hazards of contaminated land and their control.

To be included in this policy area, the major actions have to be done:

- national inventories of soil quality
- quality standards
- national inventories of contaminated sites,
- site ranking priorities for decontamination actions
- regulatori enforcment
- information exchange
- control of the transfer of contaminated lands

This actions have to be done until 2012.

Effect of Gallic Acid and *Thymus vulgaris* on the Aroma Constituents of Tofu

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Thymus vulgaris L. (family Lamiaceae) is famous medicinal plant also traditionally used as aromatic perennial herb, particularly for seasoning of meat and meat products. Our previous investigations of domestic plant species have shown that *Thymi herba* among other constituents (i.e., flavonoids, terpenoids) contains significant amount of gallic acid which has not hitherto been isolated from this plant species¹.

In spite of soy nutritional value and increasing reports of health benefits from consuming soy protein products, the demand for soybeans in human food has not been large. Mostly, this is due to the undesirable flavor and odor associated with soy products. Recently it was reported that the addition of gallic acid removes from soyfood unfavorable aroma constituents belonging to the series of specific aldehydes, alkyltrisilfides and a furan derivate².

In this work we report the influence of the *Thymi herba* and gallic acid addition on the properties of soy protein curds and tofu, respectively. Tofu was prepared from two different varieties of soybean. An experimental line L91-4042 lacking Kunitz type of trypsin inhibitor (KTI) was selection of the Maize Research Institute Zemun Polje. Soybean cultivar Balkan was selected for high protein content in seed at the Institute of Field and Vegetable Crops in Novi Sad. The experiments were done on a pilot-plant scale using commercial rennet for coagulation of soymilk³. 100 ppm of gallic acid was added to soymilk. 0.1% (w/v) of *Thymi herba* (calculated on the basses of the starting soymilk volume) was mixed with filtered protein curd prior to the treatment in water expelling press.

Similar tofu yield was obtained from soybeans of both varieties. The addition of gallic acid and *Thymi herba* during tofu preparation resulted with significantly higher yield for both investigated soybean varieties. Two-fold higher effect on yield of tofu made from Balkan soybeans compared with L91-4042 tofu yield was recorded. One could suppose that the same way of the effect, but to a different extent might be caused by the differences in protein patterns⁴ of two investigated soybean varieties. Also, the results of tofu solids analysis suggest that the aroma modifiers have greater effect on solubility properties of soybean proteins than on its' water holding capacity.

The results of sensory analysis showed that tofu flavor and odor intensity was highly influenced by the genotype of soybeans used. The variety lacking KTI showed itself more desirable sensory characteristics than high-protein variety of soybeans. It was obvious that the gallic acid and *Thymi herba* addition reduced the overall odor intensity and improved flavor of curd and tofu from both investigated varieties. The nature of this influence remains to be examined further.

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The Soybean Isolate Polypeptide Composition Influenced by the Hydrothermal Modification of Biologically Active Compounds

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Soybeans become the most important vegetable source of proteins. Major storage proteins of soybean are globulins. There are four protein fractions that are classified according to their sedimentation properties. They are 2S, 7S, 11S and 15S fractions [1]. The utilization of soybean based protein products is limited due to the presence of certain biologically active componds. Among these are protease inhibitors, hemagglutinins, phytic acid, saponins and isoflavones. Biologically active components may have beneficial but also adverse effect in diets. Thus, their content and their activity must be balanced in soy based products [2]. The application of soybean and its protein products requires the use of thermal treatment for the purpose of inactivation of components with antinutritive activity. Thermal treatment causes the change of physico-chemical properties of soybean proteins; consequently their possible use [3]. The possible nutritive use of heat treated soybean flour is influenced by the degree of residual trypsin inhibitor activity and changes of the major soybean protein fractions [4].

In this paper, the influence of cracked soybeans thermal treatment on inactivation of biologically active components and characteristics of soybean protein were investigated. Hydrothermal treatment was performed under 0.5 bars above the atmospheric pressure during 5, 10 and 15 minutes. Lipid from soybean flour (80% of flour passed through 80-mesh screen) was extracted according to immersion procedure with n-hexane. Soy protein isolates were prepared from treated samples, according to the modified typical procedure [5]. Treated samples were analyzed in triplicate. In this paper, the influence of treatment duration and steam pressure on inactivation of biologically active components has been presented. Live steaming of cracked soybeans inactivated trypsin inhibitors, efficiently. Rezidual activity of Kunitz inhibitor was detected (21.70-6.55%), only. Bowman-Birk inhibitor, as well as lypoxigenase was not registered in protein isolate extracts. Soybean isolate proteins composition was determined by densitometric analysis of SDS-PAGE gel. Treated samples had higher glycinin (69.36-53.14%) than β-conglycinin (11.57-14.97%) content. High content of acidic (47.83 -32.84%) and basic (23.06-20.30%) polypeptides of glycinin was registered. The literature data indicate that glycinin fraction formed stronger gels due to its higher water holding capacity. Also, glycinin formed more stable emulsions due to its higher content of hydrophilic groups; thus, treated samples culd be useful as gelling and emulsifying ingredients.

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Formation of Atmospheric Sulfates (SO₄²⁻) Monitoring of Some Parameters that Affect It

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There are many studies reported in the literature, which indicate the important environmental parameters (physical and chemical) on which SO_4 formation depends. These include: concentrations of SO_2 , PM, NH₃, OH*, pH, WC and other metal catalysts. Sulfates present in the atmosphere are mainly formed through the conversion of SO_2 . Due to many side effects caused by the presence of sulfates in the environment, we would like to emphasize the need for the control and reduction of this substance in the environment. Reduction of sulfates in the environment requres control and reduction of the SO_2 concentration but also control of additional parameters which affect conversion of SO_2 to sulfate, e.g concentration of particles in the atmosphere, presence of heavy metals, ammonia, etc.

The goal of this research was to explaine formation of sulphate in function of sulfur dioxide (SO₂) concentration as well as the concentrations of other elements present in the atmosphere, using an experimental approach. Concentration of SO₂ and main parameters of conversion were monitored and compared at three different locations - one in urban area – near the highway, and two in rural area. Investigation was carried out on four sampling sites at each locality. Presented data are average values of measured concentration at these four sites. Obtained data includes mean concentrations of SO₂, the amount of total suspended particles-TSP, the amount of sulfates from soluble part of total suspended particles, the amount of Fe and Mn from non-soluble part of total suspended particles. Each of these parameters is measured on mentioned locations during the period of ten months (from april 2003 until february 2004). During this period, significantly higher levels of sulfates were observed on location in urban area compared to both locations in rural area. We speculate that this is due to higher concentrations of SO₂, TSP, Mn, and Fe in the urban area compared to the natural environment.

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Effects of the Long-Term Application of Phosphorus Fertilizers on the Uranium Content of Some Serbian Soils

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Main anthropogenic source of uranium in the environment is processing of phosphates and application of phosphorus fertilizers. It is estimated that around 21000 tons of uranium are introduced into the environment annually and this estimate is based on annual processing of phosphorus ores in the world (around 135 million tons). This represents 73% of total uranium input. Around 1500 t of mineral fertilizers based on phosphorus are applied per annum in Serbia. It is estimated that around 210 kg of uranium (30 g/ha) are introduced in this way into the environment. Due to this fact there is a risk of exposing local population to ionizing radiation. The purpose of this paper was to determine whether long-term application of phosphorus fertilizers causes increase of uranium content in arable soils. Apart from this, the effect of soil depth on concentration of uranium was investigated. These investigations were made possible thanks to a number of field experiments that were set up on three types of soil (chernozem, smonitza and pseudogley) more than 30 years ago. Same variants of mineral nutrition were used in these experiments which all had parcels without application of fertilizers (controls). Soil samples were taken from two soil layers (0-30 and 30-60 cm) continuously for a period of five years. Uranium content was determined by fluorometric method after extraction with a synergistic mixture of tri-noctyl phosphine oxide in ethyl acetate. Total uranium was determined after digestion of the samples with concentrated HF and HNO_3 . Available uranium was determined after extraction with a mixture of ammonium acetate and acetic acid.

Statistical analysis of the results obtained indicates that significant differences (at p<0.05) exist between the control and application of phosphorus fertilizers in the layer from 0-30 cm, whilst no such differences were found for the layer from 30-60 cm. Statistically significant differences were not found between the investigated soil layers.

There are significant differences in average uranium content between pseudogley on one side and other two soil types (chernozem and smonitza) on the other side. Highest value for uranium content was in chernozem and the lowest in pseudogley. Physicochemical soil properties have effect on process of uranium migration and mobilization, and for this reason fixation of uranium by investigated soil types decreases in the following order: chernozem > smonitza >> pseudogley.

Results of the content of available uranium in chernozem soils indicate that there were no statistically significant differences between the control and the variant with the application of phosphorus fertilizer. It can be concluded that phosphorus fertilizers did not contribute to the increase of available forms of uranium. This fact is of great value from the aspect of environmental protection and prevention of uranium (of anthropogenic origin) to be incorporated in food chain.

Natural content of uranium in Serbian soils is in the interval from 0.08 to 5.9 ppm, so it can be concluded that the results obtained in this investigation are within natural limits. Namely, the values obtained for total uranium content in the investigated experimental variants were in the range from 0.65 to 1.94 ppm.

Adsorption of Copper(II) from Water Using Agricultural Waste Lignocellulosic Materials

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In this paper agricultural waste lignocellulosic materials (wheat straw, cornstalks, corn cob) were used as low-cost, locally available adsorbents which were studied to determine their efficiency in removing copper(II) ions from simulated contaminated water samples. These materials were grinded, sieved from sieves, and fraction with particle size 0.5-1 mm was used in batch adsorption experiments. Working conditions were: adsorbent concentration 5 g/l, contact time 2 hours and pH4. The results showed that the adsorbents had certain adsorption capacity but it was observed leaching some organic materials from them in water during adsorption. Because of that, two methods of modification of adsorbent were used. It was applied method of modification with formaldehyde and sulphuric acid, and method of modification with sodium hydroxide solution. After modification, the adsorbents was dried and wastewaters from modification were analysed. After modification of adsorbents with formaldehyde it was decreased leaching from wheat straw and cornstalks in water during adsorption, but for corn cob leaching is larger then was natural corn cob applied as adsorbent. Adsorption capacity of adsorbents modified with formaldehyde were slightly lower then applied natural adsorbents. Modification with 5% NaOH caused significantly destruction of lignocellulosic complex of corn wastes. During this modification of about half of weight of these materials were losed. Leaching of organic materials during adsorption was increased many times, and adsorption capacities were almost the same as adsorption capacities of natural cornstalks and corn cob. Modification of wheat straw with 5% NaOH decreased leaching of organic materials in water. But, loss of weight during modification was also great and adsorption capacity was unchange, too.

Although modification of wheat and corn wastes give some amendment, in some cases, from the present results it can be concluded that the modification of these materials were not recommendable. Confirmation for that conclusion were results of analyses of wastewaters from modification, which were highly loaded. Agricultural lignocellulosic waste materials, without modification, are good adsorbents for copper(II) ions from wastewaters, when some increasing of organic matters in water is not cause a problem for further treatment.

Metal Speciation (Ni, Cu, Zn, Pb, Cd) in a Recent Accumulation Sediment

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Modify sequential extraction (Polic, Pfendt) was used to study the operationally determined chemical forms of five heavy metals (Ni, Cu, Pb, Zn and Cd) and their spatial distribution in the sediments of early formed accumulation designed for water supply (Barje, Leskovac, Serbia).

Results of the sequential chemical extraction have showed that exchangeable fractions of heavy metals for samples taken in March exhibit several time higher concentrations than the exchangeable fractions for the other samples. It could be due to well known phenomenon of pH decreasing during the snow melting in the springtime.

Fraction dominated the Zn distribution in sediments, accounting for over 51 % of the total Zn concentration. Among the nonresidual fractions, the Fe-oxides fraction was much more important than other fractions in all sediments, which accounted for 18 % of total Zn and the second in order was fractions with Mn-oxides and carbonates which accounted for 9 % of total Zn. The adsorption onto Fe-Mn oxides has higher stability constants than onto carbonates, but calcium carbonate is a strong absorbent to form complexes with Zn as double salts ($CaCO_3 \cdot ZnCO_3$) in the sediments. Zn coprecipitation with carbonates may become an important chemical form, especially when hydrous iron oxide and organic matter are less abundant in the sediment. In the "Barje" lake sediments, the percentage of Zn bound to organic and sulphides fraction was very low (<2.2% of total Zn) in those sediments.

The percentage of Cu associated with different fractions in the sediments from all sites was in the order of: Fe-oxides (49.9 %)> residual (41.9 %)> Mn-oxides (5.9 %)> exchangeable (2.1 %)> organic (not detectable). In spite of high formation constants of organic-Cu compounds the association of Cu with organic matters appeared to be less pronounced due to low content of organic matters in these sediments.

Nickel was mostly concentrated in the residual fraction, although it was present in small amount in other fractions. The Ni inclusions are protected against natural decomposition as well as reagent alteration, and only the dissolution of the silicates would ensure their extraction. Our results were with above agreement. Percentage of the extracted Ni was in the following order: residual (65.9%)> Fe-oxides (11.8%)> Mn-oxides (10.5%)> organic (7.34%)> exchangeable (4.7%).

Cd and Pb are more leachable from sediments than other examined heavy metals.

All cadmium content was extracted in second fraction, so we can expect carbonates and Mn-oxyhydroxide as substrates of Cd.

Significant amounts of Pb were extracted in fractions bound to Fe-oxides (51.6 %) and Mn-oxides (36.1 %). Exchangeable Pb was abundant only in samples taken in spring time (12.3 %) and in the other samples were barely 0.6 %. Organic and residual fractions of Pb were not detectable. This suggests that anthropogenic Pb were immobilized in sediments by fixing reactions involving mostly Fe-Mn oxides which may be the major carriers of Pb in sediments. This conclusion is in the agreement into literature data.

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Inhibition of Tin Dissolution in Fruit Preserve Cans

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The influence of potential inhibitors (additive) on white tin corrosion was analysed by the usage of polarization techniques, using as the electrolytic solution pieces of peach in syrup with or without adding nitrates while a filled can was simultaneously used as electrolytic cell and as working electrode. Cans (ϕ 99) or white tin of 0.23 mm thickness T-3 with the 1.2/5.6 g/cm³ tin coating were analysed. Saturated Calomel Electrode (SCE) as the reference electrode was used and the accessory electrode was platinum wire. Content of the can was prepared according to standard industrial praxis and storaged with adding of the corrosion inhibitor (additive). Potential inhibitors that were used was sodium benzoate (0.1-0.3 wt.%), potassium sorbate (0.1-0.3 wt.%), sodiumlauric-sulphate (0.005-0.01 wt.%) and p-aniline acid (0.005 wt.%). If these substances are added in canned pieces of peaches in syrup, certain reduction of tin resolution is noticed. After filling, the can was closed and treated for 11 minutes at 83°C in sterilizatore and then cooled to 40°C. Cans were storaged on temperature of 20-23°C. During the one-year period of storage the content of tin, iron and lead in the product were periodically controlled by the atomic absorption spectroscopy. Anodic and cathodic polarisation curves in examined samples with and without addition of 50 ppm nitrate were recorded by polarisation technique. Polarisation curves were received by the appliance of 300 mV potential in the period of 10 min and its progressive reduction of speed of 25 mV/min, in order to receive cathodic curve. When the corrosion potential was reached, and anodic curve was recorded. As it was expected the positive deviation was noticed at the ends of the curves near corrosion potential, which was attributed to the presence of reductible substances in the solution. The reproductivity of cathodic spots, although low, is considered to be adequate for comparative purposes. The systems corrosion rate (icorr) could be calculated from the middle of extrapolated Tafel anodic and cathodic lines. The corrosion rate of the system, calculated in this way, could be used for quantification of the inhibition effects of the added substances in the solution in relation to original solution without inhibitors – additives.^{1,2}

The results without adding of 50 ppm nitrates indicate that all analysed inhibitors (additives) show inhibiting effects on white plate corrosion in pieces of peaches in syrup with acceptable efficiency of protection. Especially the 0.3 wt.% solution of potassium sorbate causes 67 % of the corrosion speed reduction. Addition of 50 ppm nitrate caused high acceleration of corrosion. The content of the tin was 4 times higher after one-year storage. Tested inhibitors effected on the decrease of high corrosion rate. The best results showed p-aniline acid, which efficiency of protection was 32 % and which was added in concentration of 0.005 wt.%.

According to the form of anodic and cathodic polarisation curves, for all tested substances could be stated that inhibiting produce by interaction with cathodic semireaction. The formation of the fine film absorbed on the metal surface could be attributed to the nature of tested substances and their anion character.

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Ultrafiltration Method for the Removal of Heavy Metal Ions from Industrial Wastewaters

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Introduction

Toxic heavy metals in air, soil and water are global problems that are growing threat to the environment. Therefore, the removal and separation of toxic and environmentally relevant heavy metal ions are a technological challenge with respect to industrial and environmental application. Number of methods have been employed for the heavy metal removal. Among them, polymer-assisted ultrafiltration (UF) processes (also known as complexation-UF or binding-UF) have been shown to be promising for the removal of trace metallic species from aqueous streams. The basic idea is that the metallic species can be retained after binding with water-soluble polymers, whereas the unbound species pass through the membrane. This process has been applied to various purposes such as the treatment of waste effluents, groundwater, and seawater, as well as the separation of radionuclides.

Experiment

The rejection of divalent heavy metal ions including Zn(II), Pb(II) and Cd(II) from water by complexation-ultrafiltration was investigated. Polyethylene glycol (PEG 5000), diethylaminoethyl cellulose (DEAE23) and dextrin were selected as complexing agents. Experiments were performed at three trans-membrane pressures (2, 3 and 4 bar), by using three diferent membranes, to make a comparison of polymers and membrane performances as flux and rejection. Experiments were also performed as a function of solution pH. The UF experiments were carried out in stirred dead-end cell. The concentration of heavy metal ions after ultrafiltration in aqueous solution was determined using atomic absorption spectroscopy (AAS).

Conclusion

It was shown that the efficiency of studied process depends on pH, removal of metal ions was more efficient at alkaline condition than at neutral or acidic conditions. Within an operating pressure range of 2 to 4 bar, the maximum retention coefficient of Zn(II) Pb(II) and Cd (II) ions by the Versapor 0,2 μ m membrane has been shown to be 98.1 %, 98.8 % and 96.9 % respectively, when the diethylaminoethyl cellulose made use of as a chelating agent.

In general, the complexation-ultrafiltration process was efficient for metal removal from wastewater, leading to a better effluent quality when compared to ultrafiltration without any ligands addition.

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Food Safety in Today's Society

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International agreements and regional cooperation specify the tasks of free movement of goods and the elimination of technical barriers to trade, mutual recognition and technical harmonization; to this end, the needs of the market are increased. The concept of Quality is being broadened to include additional aspects, tools and procedures. Some specific needs refer to fields of particular importance; food quality including all relevant issues represents a main priority, interrelated to the protection of the environment and the quality of life. In a series of policy papers and legislative documents, the European Commission underlines the need for specific measures to be taken in the food sector to ensure quality and safety, therefore to protect human health from risks originating from various stages in the food chain. This presentation is focused on the discussion of main issues dominating Food Safety.

The official control of foodstuffs provides for foodstuffs, food additives, vitamins, mineral salts, trace elements and other additives intended to be sold as such as well as materials and articles intended to come into contact with foodstuffs. Main issues are sampling, chemical analysis, microbiological examination, sensory analysis and reporting. In order to ensure reliability of measurements, the laboratories for the official control of foodstuffs should comply with the accreditation criteria. Furthermore, adequate information and education are required.

Barriers faced by small countries relate to their geographical isolation and difficulties in the cooperation with other countries, especially in the case of island states, the characteristics of their economy and the high cost to establish the necessary infrastructure. When trying to meet the set tasks, policies on Food Safety issues should inevitably take into consideration all these factors.

Further to other measures to be taken, we need good practices in all steps in the food production, distribution and consumption chain: Good manufacturing practice and good laboratory practice as well as good farming practice and good consumers behaviour!

Diffusion of Emitted Pollutants into the Surroundings of Coal-Fired Power Plants

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Permanent control of contamination gives possibility for the judgment of the quality of air in the observed space.

Analyses of spatial and time distribution of contaminating materials are possible by applying diffusion model of their distributions. This model putting is based on the emission of relevant pollution, diffusion parameters and values of turbulence obtained from microprobes measurements of meteorological parameters.

In the industrials zone of one of lignite processing installations, concentrations of pollutants (solid particles, sulphordioxide, nitrogen oxides) were determined for controlled emitters.

Distribution of the stations for measuring of concentrations of the pollutants was determined on the basis of: type of contamination source, density of population, topographic terrain and meteorological conditions.

During 24 hours over 4000 measurements of emission of relevant pollutants have been done in four stations during one year period.

The obtained results show that the concentrations of the pollutants can be 10^3 to 10^4 times lower in comparison with the values of the source, depending on the distance and atmospheric conditions, However, concentrations of some suspended and deposited materials and higher than the limited values of some unknown emitters.

Phenol Adsorption on Activated Carbon Cloth: The Influence of Sorbent Surface Acidity and pH

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There has been an increasing interest in the study of adsorption of organic molecules on activated carbon materials. This is due to the importance of the removal of organic pollutants from water streams and the atmosphere [1,2]. The adsorption process depends on several factors, which include the nature of the adsorbent, adsorbate and adsorption conditions. Adsorbent characteristics include the surface area, pore size distribution, ash content, hydrophobicity as well as the density and type of functional groups present at the surface. On the other hand, the nature of the adsorbate depends on its polarity, its hydrophobicity, the size of the molecule, and its acidity or basicity. The last is determined by the nature of the functional group present. Adsorption conditions include the temperature, the polarity of the solvent, pH of solution and the presence of other species competing for the adsorption sites.

The adsorption of phenol and substituted phenols from aqueous solution on activated carbons has been intensively investigated for decades, because the phenol molecule, which is relatively simple and well characterized, is frequently used as a model for the adsorption of more complicated organic compounds [3]. However, this subject remains highly controversial as described in a recent review by Radović et al. [2].

In this work the effect of the surface acidity of activated carbon cloth (ACC) and pH of solution on the phenols adsorption has been studied. The aim was to get deeper insight to the mechanisam of phenols adsorption on carbon materials. In the previous papers surface acidity of ACC samples was determined in the terms of their surface functional groups composition [4], pKa values and point of zero charges (PZCs) [5]. For this investigation three ACC samples, having acidic, neutral and basic surface has been chosen. Two phenols widely different in the terms of their pKa values (phenol and 2,4-dinitrophenol) have been the object of the study.

It has been shown that phenol adsorption was favorised by low pH values of solution and high PZC values of ACCs. Increased amount of carboxyl groups at the surface of ACC samples lead to decreased capacity for phenol adsorption. The adsorption of 2,4-dinitrophenol was promoted at low pH values of solution as well, but it was less influenced by ACC surface acidity. The results obtained support hypothesis that phenols are adsorbed on the carbon materials mainly trough disperzion forces between π electrones in phenol aromatic ring and π electrones from the basal carbon planes. The ester bond formation between phenols and surface carboxyl groups, suggested by some authors [1], is less likely to be an effective adsorption mechanism for phenols on ACC.

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Determination of the Fluoro - Derivative 8-Hydroxy Guanosine in Human Material by GC/ECD Analysis

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Presence of free 8-hidroxy guanosine, which is a basic constituent of DNA, in urine and blood is a preliminary bioindicator of damages of genetic material of human tissue of persons who were exposed to various toxic substances. During DNA oxidation several products were obtained and 8-hidroxyguanosine is the most abundant (8-OHdG)¹. Damages of DNA are the main cause of occurrence of malign neoplasma and presence of oxidation nucleosides in human blood and urine is the first signal for malign changes.

8-OHdG was isolated from urine sample by SPE-method which separates partially purified residuum containing 8-OHdG from salt and other nonvolatile components. The next steps are extraction of 8-OHdG, derivatization by pentafluorobenzylbromide and purification of obtained mixture. Residue concentrations of fluoro-derivates of 8-hidroxyguanosine and its structural isomers were determined by gas-chromatographic analysis (GC/ECD).



Determination of fluoro derivates of 8-hidroxyguanosine in blood and urine is important in preliminary diagnostics and in an early prevention of malign diseases in people and children, especially in professionally exposed people (oncologists, radiologists, etc.).

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Acid-Modified Bentonites as Heavy Metal Sorbents

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Heavy metals are released into the environment from a wide range of natural and anthropogenic sources. Pollution by heavy metals is one of the most severe pollutions. Keeping in mind that in worldwide scale the volume of waste water reaches about 440 km³/year, the significance of heavy metal removal gain in importance. In past 50 years a numerous methods for heavy metal removal have been proposed such as sedimentation, flocculation, co-precipitation, cation and anion exchange, precipitation, oxidation, reduction, microbiological activity even plant uptake. However, the well-established toxicity of heavy metals requires stable, accessible method for purification of waste water. Furthermore, method should not cause secondary water pollution. From economical point of view, the waste water treatment should be cheap, simple and easy to handle. Perspective method that provides answer to all these requests is adsorption. Some naturally occurring clay minerals may play a role of low cost sorbents suitable for heavy metals removal. Since the natural bentonite clays usually do not exhibit sufficient sorption capacity compared to synthetic sorbets, these materials should be modified in order to enhance sorption properties. Among various types of modifications (treatment with inorganic and organic compounds, bases and acids), the acidic treatment is chosen as the most accessible¹. Acid activation leads to significant removal of calcium, magnesium, and alkali metal oxides and partially diminishes the iron and aluminum oxide content of clay minerals. Komarov² has proposed an advanced method for clay treatment. After acidic treatment clay suspension should be neutralized by ammonium or sodium hydroxide, thereby most of dissolved components should form a reprecipitate AI and Fe in the first place.

The primary aim of this work was to investigate the removal of heavy metals from aqueous solution using bentonite and acidic-modified bentonites as sorbents. The complete chemical, physical and textural characterization of starting and modifying materials was performed³. The starting material was bentonite from coal mine "Bogovina", East Serbia. Bentonite fraction <0.074 mm was acid activated by solutions of HCl of nominal concentrations: 1.5, 3.0, 4.5, 6.0 and 8.0 mol/dm³ at 90°C for 2 h. The samples were dried to constant mass at 110 °C and used for further investigations.

For each investigated sample the same amount of sorbent (1g) was stirred in 100 ml of heavy metal solution of defined concentrations (1g/dm³ -10mg/dm³). Heavy metal solutions were prepared by dissolving appropriate nitrate salts. The investigations were performed in interval of pH values of 2-10, while pH values of solutions were adjusted by addition of 0.1mol/dm³ HCl or 0.1mol/dm³ NaOH. Both initial concentration and concentration after performed sorption was measured using polarograph 757 VA Computrace – Metrohm. The same amounts of solutions were periodically taken for analysis. Polarographic technique was chosen since it enables simultaneous determination of concentration of all investigated metals. After filtration and drying of sorbent samples desorption of previously sorbed heavy metals was tested after treatment with water with defined pH (4.5-5). The obtained results show that capacity of bentonites to adsorb heavy metals depends on modification conditions. Capability of heavy metal removal varies within investigated samples, and depends of metal species. The optimal pH value for each adsorbed metal was estimated.

Acknowledgements

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Nutrient Removal Efficiency of Pilot-Scale Vertical-Flow Constructed Wetlands Treating Simulated Wastewaters

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Vertical-flow constructed wetlands can be used for urban, domestic and/or industrial wastewater treatment, although only limited performance data are available. Vertical-flow wetlands are intermittently flooded and drained, allowing air to refill the substrate pores within the bed. The study evaluated the performance of duplicated pilot-scale vertical-flow constructed wetlands, planted with *Pragmites australies* for nutrients removal.

Four polyethylene containers were used as microcosms, with dimensions 0.9 m height and 0.55 m internal diameter. The microcosms were located outdoors at the Department of Chemistry (Aristotle University, Thessaloniki). All microcosms were filled with a 17 cm layer of washed river gravel with diameter 8 –16 mm and had a subsequent layer (45 cm) of sand (diameter 0-4 mm). Another layer (3 cm) of gravel 4-8 mm was located on the top. All microcosms were planted with P. australis using clumps of reeds. For health and safety reasons, the microcosms were fed with dilute synthetic sewage simulating medium strength municipal sewage. Sampling of the effluent was taken place weekly. The samples were analyzed for, PO₄-P, TN, NO₂-N, and NO₃-N. During the first three months of application it was found that the main removal mechanism for orthophosphate was the chemical adsorption in the unsaturated substrate, that resulted in 50% removal of phosphate, while nitrogen was transformed though the process of nitrification, first to nitrite and then to nitrate, denitrification did not occur due to the lack of anoxic conditions

Importance of Water Quality Control in Economical and Environmentally-Friendly Paper Production

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Paper and board mills commonly use large volumes of water. In paper processing, water is considered as the second raw material, just after the fibrous material (wood, cellulose or recycled paper). Beside quantity, the huge importance in paper production also has the water quality, included all kinds of appearing water - from the fresh water intake, via process water, recycling water and waste water at the place of discharge.

Relatively high values of specific water consumption and increased content of pollutants in waste water in some paper mills, indicates necessity for conduction of detailed measure of water flows and monitoring of water quality in all segments of paper production. Such examination of water quality was conducted in one paperboard mill in Serbia & Montenegro. The main control parameters of water were temperature, pH value, total suspended solids (TSS), conductivity, total hardness, content of O_2 , content of $SO_4^{2^\circ}$ and Cl⁻ ions and KMnO₄ consumption. Water quality parameters were measured or determinated at several points in the process, which is shown in the following figure.



Technological scheme of production in a board mill with marked measuring points

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Symposium C

Teaching and Understanding Chemistry: New Concepts and Strategies for Changing Times

INVITED LECTURES





Alchemical symols for weights

One pound
Equial quantity
One ounce
One dram
One scruple
One pinch
One pint

Education Today and Science/Chemistry Teaching: What, How, Why?

Ivan Ivić

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Education today

Education for all, quality and quality assurance, efficiency.

Science/chemistry teaching : for all ? How to achieve quality and efficiency?

Notion of general culture : humanities + science + ...? Specific contribution of science/chemistry teaching to general culture.

Science/chemistry teaching/learning : what and why

What to teach : theoretical-technological knowledge, abstract-concrete, pure-applied, conceptual-experimental.

Nature of scientific knowledge, scientific methods and scientific mode of thinking and their roles in education.

Why scientific/chemistry teaching in Serbia as small, undevelopped country, country at the periphery in era of the globalization : participation in international scientific competition, capacity building for technological use of knowledge, human resource building, capacity building for international communication ?

Science/chemistry teacing/learning : how

Science/chemistry in life of young generation today: problem of motivation for science/chemistry teaching/learning.

Chemist and chemistry teacher : one or two professions? Roles of chemistry teachers today and here.

Textbooks for science/chemistry teaching today: what this means today, textbooks for what and for whom, quality standards.

Teaching/learning methods: transmission of knowlwdge to students,

construction of knowledge by students and students intellectual autonomy, interplay of what, why and how in science/chemistry teaching/learning.

Active learning project in chemistry teaching/learning in Serbia : an interdisciplinary enterprise.

University Level Chemical Education in Serbia

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The aim of this contribution is to inform the participants of Symposium C on how university level chemical education is organized in Serbia, to describe and comment on some of the more important issues which are (unfortunately) specific to Serbian education system in its present state. The talk will cover the following points:

Structure and organization of universities in Serbia

We give a brief overview of how university education is organized in Serbia. In particular we look into the high level of autonomy of individual faculties within a given university, how this effects the efficiency of teaching/learning and research processes and increases these institutions inertia to change.

How and where one can study/learn chemistry in the country

As a professional calling, university level chemistry studies are indepedently organized at a large number of institutions even within a single university. At the University of Belgrade such studies exist at the Faculty of Chemistry, Faculty of Physical Chemistry and Faculty of Technology and Metallurgy. In other Serbian universities chemistry is taught at various departments or institutes within corresponding Faculties of Science and Mathematics.

The subject is also taught in many related applied fields, as chemistry for "non-chemists". Such instruction is organized at corresponding Faculties of Agriculture, Medical Faculties, Pharmaceutical Faculties as well as at a host of different technical faculties.

Advantages and weaknesses of the present concept and organization of university level teaching/learning of chemistry in Serbia

We discuss the concept of teaching/learning in chemistry in general, the aims of teaching/learning chemistry for both of the above types of instruction (chemistry for chemists or applied chemistry) focusing primarily on the advantages and disadvantages of faculty organized teaching of chemistry as opposed to the teaching of the same subject in a central university organized setting. To do this we will address the following key questions: How can the teaching of chemistry be made more efficient on certain faculties, do certain professional profiles share a nucleus of common knowledge?

How to improve university level teaching of chemistry in Serbia

We end by looking into possiblilities for improvements in curriculum and content, in timing and organization of courses, in employed teachin/learning methods and in other conditions that effect the quality of both chemistry teaching and research. We address the following questions: What could be changed (easily), how should these changes be brought about and by whom?

Aspects Regarding Environmental Education In Romania in High Education and Research Institutes and Other Training Firms

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The environmental education in Romania is necessary to by structured so that it has the components and institutions necessary for a permanent education.

The permanent education system is defined as the total of the learning experiences offered by the society during the entire life of the individual.

In function of the learning activities engaged by the system, the permanent education includes three components:

- "formal education" carried out in specialized institutions (kindergartens, schools, universities, research institutes, specialized consultancy and/or training companies) according to official programs, and finalized with certificates and diplomas.
- *"informal education"* is complementary and can be used to support for formal education; it is an extracurricular education, for instance scholarships, study, visits, conferences, a.s.o.);
- *"incidental learning*" spontaneous, occasional, without formal connection with the institutionalized educational activities.

In universities and research institutes, the environmental education deals especially with the characterization of various ecosystems, pollution control methods and technique, processes and equipments for pollution prevention and is addressed to students and young graduate (master, doctorate, a.s.o.).

Within the specialized training companies, the thematic are: environmental legislation, environmental management systems, training of managers, auditors and environmental assessors and are oriented for the completion of the training of specialists working in the environmental protection field.

The paper presents some aspects of the formal and informal education in Romania, in universities and in the institutes with environmental protection preoccupations.

In the formal education are presented:

- new directions in the technical high school learning for preparing chemical engineers: biochemical engineering and environmental protection engineering;
- post universitary studies in environmental protection field, addressed to the high school graduates indifferently of their initial specialization.
- In the *informal education* the examples of the activities organized are:
- the intensive programs under the auspices of EU Socrates initiative, including partners as Universities and Institute of Technology from Romania, France, UK, Ireland;
- the activities organized by professional societies and main companies with main topics as:
- methodology for environmental aspects identification and assessment;
- methods and technique for the environmental pollution control;
- assuring environmental legal compliance within environmental management system framework;
- environmental management system the simplest way to comply with environmental legal requirements.

Problems Associated with the Instruction of Chemistry at the High School Level

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Science teaching and particularly chemistry teaching is described as a non-popular and difficult discipline, so students do not choose it in high-level classes in secondary schools. At present, chemical education does not contribute in a sufficient way to the development of non-cognitive skills, such as social, communication, cooperative or high-order thinking skills. Science and chemistry education have to serve the interests and the needs of all students as future citizens.

Chemistry is characterized by three main components-levels (Johnstone). The macroscopic level (learning about solids, liquids, metals, non-metals, acids, bases, fuels, etc.), the particulate level of molecules, atoms, electrons and the symbolic level that deals with symbols, formulae and chemical equations. The first level is concrete, tangible and accessible to the students. The other two are not, they are remote, abstract and complicated. Teaching and learning about atoms, molecules, formulae and chemical equations is a difficult task for both teachers and pupils. Students frequently do not relate these three levels and hence have difficulties in making sense of laboratory experiments and they do not integrate the threefold representation of matter in their long-term memory. Providing links between the various representations can be enhanced using the social constructivist model of learning. When students are presented with conflict situations and interact with each other and their instructor, they reflect on their knowledge and construct meaning. New programs that are based on making chemistry relevant through problem solving and collaborative learning are promising for reforming chemistry education. Related to the above, some areas of students' alternative conceptions are the following: states of matter, particle theory, changes of state, compounds and mixtures, chemical changes, acids-bases-neutralization, stoichiometry, chemical bonding, thermodynamics, chemical equilibrium.

The curricula are often content-loaded, too constrained and inflexible, oriented bureaucratic demand, especially those concerning assessment. The teacher teaches students to pass the exams, "teaching to the test" and not for enjoyment. There is not enough time for laboratory activities and practical work and "no time for the good bits". The Chemistry lesson should accompanied by interesting, not stereotyped experiments, performed by the students themselves. The curricula should be revised and improved, taking into consideration teachers' own experiences, suggestions and judgments and should include subjects related to every-day life, environment, pollution, food, drugs etc. The Chemistry lesson must be simple and easy to understand for the great majority of students. The Chemistry textbooks also should be well written and easy to understand.

Continuing professional development of teachers in-service must be guaranteed. They must be trained following constructivistic principles and equipped not only to identify their student's alternative conceptions, but also to design and implement teaching interventions that are studentand knowledge-centered. Learning chemistry has to start from students' knowledge and experience.

emical education research seldom makes contact with practice to discuss the problems and transfer the research findings into the classroom. "Researchers are funded to research and teachers are paid to teach". The accumulated evidence from empirical research on teaching and learning do not inform the curriculum development process or the chemistry textbook writing.

The Cycles of a Former Chemist: Completing the Circle to Improve the Educational Experience

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Life is a series of cycles, from the daily cycle determined by the sun rising and setting, to the annual cycle of winter preceding the start of the growing season. Since completing my PhD degree in organic chemistry in 1970 I left the subject to work on plant physiology. However, over the years, I have drifted back into the subject. But not as part of my professional activities, rather than to pass on my skills to others through various educational activities.

In the UK, as in many other European countries, over the years interest in the sciences as a profession for schoolchildren completing their secondary education has waned. This is just as true in Serbia, where applications to the Chemistry and Physical Chemistry Faculties of Belgrade University fall far short of the places available to freshers. For example, in 2002 the number of places offered to applicants and actual applicants in the first (main) round of entrance exams in these two faculties were 300 and 126, respectively, for Chemistry and 180 and 24, respectively, for Physical Chemistry.

In an attempt to counter this trend in the UK, an initiative was established in the 1990s in the Norwich region of East Anglia, called the Teacher-Scientist Network (TSN - www.tsn.org.uk). This was a voluntary scheme whereby scientists working in the area could offer their services to local schools to develop whatever relationship was possible between the scientist and the school: school visits to give a lecture on a specific topic, visits of schoolchildren to the scientist to see science in action, and so on. Other organisations focusing on building educational links between schoolchildren and practising scientists have since developed, such as the Biotechnology and Biological Sciences Research Council (BBSRC) initiative on scientist-school liaison: Making that Link (www.bbsrc.ac.uk).

When I joined the TSN I was appointed to a first school in Norwich (age range 5-8 years) and for many years visited the school every two weeks to teach (or more precisely, to demonstrate) some simple aspects of science to youngsters still learning to read and write, but whose curiosity knew no bounds. This was a particularly rewarding experience.

So, one cycle of a former chemist has been to impart to others still at school the interest in science that I developed many years ago. Another cycle has developed since moving to Belgrade. Research in much of Western Europe is based on hypothesis testing - you develop a hypothesis, design experiments to test it, collect the results and interpret them to see whether they fit your hypothesis or not. This concept of hypothesis-testing seems to be alien to many researchers in Eastern Europe.

As part of Serbia's first training course for university academics on improving pedagogic and research skills organised by the Education Forum (www.obrazovanje.eu.org/univ/index-eng.htm), a module including a description of the research cycle for hypothesis testing proved particularly popular with post-diploma students.

So, although chemistry has not been the subject area of my career, the skills that I learnt during my training as a chemist have been valuable in helping me to pass on to others an interest in the subject, by 'completing the circle to improve the educational experience'.

High School Chemistry Education in Serbia in the Past 150 Years

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Chemistry was early integrated into the high school education, first within physics in 1853, and from 1874 as independent subject, with obligatory experiments. By the end of 1881 the modern school plan and program was brought, as well as standards for the chemistry cabinets equipping. During 1888 number of chemistry classes was decreased from five to three hours per week, and from 1893 the chemistry lost the autonomy and was lectured together with mineralogy. Chemistry was also early introduced in vocational schools; it was represented mostly in "Realka".

Between two wars, the chemistry schooling did not develop. Although programs were made following the European models, and the School Law enacted in 1929-30 was made by the existing pedagogic theories and principals, because of inadequate school conditions, lack of cabinets, big number of pupils within one classroom, teachers' lack of expertise, lecture couldn't develop, especially within the experimental part.

Since the Second World War until nowadays, educational system has been changed through a number of reforms, with the aim to synchronize education with political development of society. During this period, reforms were different from the previous ones because they were initiated by political institutions and implemented through political resolutions and programs of the parties.

Chemistry teaching was developing in continuity, independently from reforms and political events. School plans were changed, as well as goals and tasks, and a program has been enlarged and enriched with new contents every few years, following the chemistry development at the University. The most important reforms regarding the chemistry teaching were from 1958, 1960, 1965 and 1969.

High school development was interrupted in 1977, with the Common basis of Vocational orientated education made for the whole pupils' population. By the 1987 Reform, that is the 1990 one, the Gimnasia was brought back into the education system, but because of the difficult political and economic situation in the country, the chemistry teaching did not develop. Modern, but extensive programs, could be realized only within well equipped cabinets and well organized experimental work, with proficiently and well pedagogically prepared teachers and good text books.

ORAL PRESENTATIONS





← Previous page: Sulfuric acid production in the 16th century

Chemistry Teachers' Approach to Primary School Education

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Chemistry teachers' questionnaire was conducted during school year 2002/03 and 2003/04. The questions were referring to the initial teachers' education, programs, textbooks, schools' equipment, teaching/learning methods, chemistry teaching goals, pupils' achievements and teachers' training. The questionnaire included 94 teachers from around Serbia.

The primary schools chemistry is mostly realized by women (87% of interviewed were women, and 13% men). The average number of teachers' working years in education is 19, while the average number of years since the basic studies is 21. Larger number of primary school teachers graduated at faculty (55%), while the rest has graduated the High Pedagogy School (45%). Around 29% of teachers, out of those with the faculty degree, have finished the teaching study group. Only one interviewed had the specialization, that is the post graduation degree. More than 50% of teachers with high school and faculty education didn't have any complain on their initial (basic) education. The others emphasized that more practical work is needed during elementary (basic) studies (23%), that the teaching material is too extensive and discordant with the knowledge requested for work in elementary school (7%), they don't have the sufficient computer knowledge (5%), and that basic studies need more pedagogy and chemistry didactic contents (2%).

The percentage of teachers considering themes within seventh grade school program necessary, is between 95% (*The structure of substance*) and 37% (*The review of the most important nonmetals*). For the necessity of the already existing themes within the eight grade program replied 78% (*Hydrocarbons*) to 46% teachers (*The review of the most important metals*). Most teachers consider the reviews of the most important nonmetals and 21% for metals). Also, most teachers believe these themes have too many information (34% for nonmetals and 28% for metals). On the other hand, themes *The structure of substance* and *Hydrocarbons* were valuated as those with huge number of new concepts. More than one quarter of teachers emphasized that themes *Hydrocarbons* (24%), *Organic compounds with oxygen* (37%), *Inorganic compounds* (46%) and *The structure of substance* (55%) are difficult to learn. As easiest, teachers quoted themes like *Chemistry and its importance* (71%) and *The basic chemistry concepts* (61%).

The percentage of teachers considering themes within textbooks are treated in a comprehensive way is between 31% and 58%. Average evaluation of textbooks is the same for seventh and eight grade - 3,8 (on a scale from 1 to 5).

More than 50 % of teachers did not answer the question on missing themes within school programs, which are necessary for studying. Those who answered emphasized most of all ecology, (13%), oxidation-reduction reactions (7%), history of chemistry, implementation of chemistry in agriculture (5%), new discoveries (4%), contemporary materials (3%), industrial production (3%), vitamins (2%) and metallurgy (2%). Also, more than half of teachers did not answer the question on themes which don't exist in the program, and which pupils would like to have. Others emphasized ecology, history of chemistry, nuclear and chemical weapon, everyday life substances, drug, computer chemistry.

Around two third of teachers wrote that they have cabinets in schools, equipped regularly in 14 % of the case. The average restoration period for the cabinet equipment is seven years.

The other data will be available at the Symposium.

Chemistry Test as a Predictor of Success in Complex Entrance Exams

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The choice of future study group is a significant moment for every student of secondary school, and often a moment of final choice of profession. Nowadays it is evident a very different interest for some university schools and study groups, which is most often not in accordance with the society needs. In order to harmonize students' wishes with studying demands and needs for certain profiles, faculties must make an optimal selection among students. For a long time, the most popular school of the University of Novi Sad has been the Medical School, with departments for General Medicine, Dentistry and Pharmacy, all of which have been attracting a large number of candidates – up to three candidates for 1one available place. Thus, the selection of future students of the Medical School is a special problem, public and experts being specially interested in it. Criteria for candidates selection consist of their achievements in secondary school, and also their achievements on tests of chemistry and biology, or chemistry and mathematics. The success that candidates achieve on these tests is not often in accordance with their secondary school grades, which poses a dilemma: Are the entrance exams in the present form a good tool for selection of candidates, or do they make impossible the optimal choice of future students of the Medical School?

In this paper the predictory function of chemistry tests was investigated in the process of classification of candidates during the complex entrance exam for the Medical School. At the Medical School, entrance exams consist of chemistry test in combination with biology test (departments of General Medicine and Dentistry), or tests of chemistry and mathematics (department of Pharmacy). Chemistry test participates in the complex entrance exam with maximally 30%, as well as biology and mathematics, while the secondary school achievement participates with 40%. The purpose of this investigation is the assessment of the significance of chemistry test in the candidate's total score at the entrance exam, according to the defined aims: characterization of investigated variables (components of the complex entrance exam), and evaluation of the predictory function of the chemistry test as a part of the entrance exam. Statistical analysis took into account the basic statistical parameters of investigated variables and correlation analysis. Investigation was performed on the sample of 494 candidates who applied for the entrance exam at the School of Medicine in Novi Sad in 2001/2002. Basic statistical parameters of analyzed variables indicate a negative asymmetry up to the j-distribution for secondary school achievements, while there is a normal distribution for chemistry and biology tests. Correlation matrix of the Pearson's correlation factor for all analyzed variables indicates the lowest correlation between scores at the chemistry/biology test and chemistry/biology grade in the secondary school. Moderate correlation exists between scores at the chemistry and biology tests. Score at the chemistry test and total candidate's score have very high correlation, which indicates the predictory significance of the chemistry test in the complex entrance exam at the School of Medicine.

Using Educational Software to Learn Chemistry

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As informatics tend to take up more and more aspects of our lives, education is bound to adopt the new methods in order to evolve. The development of software now comes to the help of students, revealing processes and principles that until now could be presented only theoretically.

The use of software in educational purposes has a lot of advantages. The first of these is that we can now present different phenomena taking place at microscopic level (such as dissolving, ionization etc) on computer-designed models. The processes can be shown in all their stages that explain its nature.

The second argument in favor of using software in teaching is more pragmatic – the facilities available in the laboratories. There are many cases in which the laboratories do not have the necessary equipment in order to do the required experiences. This is a situation in which a detailed computer-presentation can be of great help in understanding the experience in question.

Another great advantage of the software teaching method is that students can use them outside the classroom or a fixed schedule. They can come back anytime and watch the presentation again, or even learn more on the subject in their free time, if they are really interested. The material is there 24 hours a day, which gives the student a more flexible learning schedule. E-learning is becoming the best solution to many problems of education today (lack of facilities, trained teachers, special equipment etc).

However, this method can help the teacher, as well as the student. At the end of every module, we offer the student a set of problems, arranged in an increasing order of difficulty. These items are ment to give the student the opportunity of self-evaluation and self-improvement. This is also the way in which teachers can design their evaluation tests. These can be structured as multiple-choice tests, with normal or radio-buttons, depending on the number of choices possible. Also, each question can have its own answering time, at the end of which the software automatically displays the next one. However, this feature can be programmed to have a global answering time, the student dividing it, as they need. The questions can be displayed in a certain order (increasing difficulty, or on modules or lessons etc) or can be randomly shown. The teacher has complete control all the time, being able to stop the test for any given student if they so consider.

We intend to further develop this kind of software, especially for organic reactions(breaking of bonds and forming of new ones, different mechanisms etc) and design the lessons as an interactive text-book, that can give the student both the theoretical knowledge as well as more detailed practical aspects of the phenomena. Also, at the end of each module self-evaluation tests will be available.

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Major Educational Trends Towards a New Age in Nanosciences and Nanotechnologies

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At present it is worldwide recognized that nanosciences and nanotechnologies represent a new multidisciplinary approach to materials science and engineering, as well as for design of new devices and processes. Research at the nano-scale frontier is unified by the need to develop knowledge, techniques and expertise on atomic and molecular interactions.

The strong challenge provided by the most advanced groups acting in this field in U.S. and Japan determined a new strategy for European Research & Development focused towards a strong position in nanosciences that needs to be translated into a real competitive advantage for the European industry.

The perception of the EU on this subject is revealed in Framework Program 6, where one of the priorities – thematic area 3 - is dedicated to "Nanotechnologies and nanosciences, knowledge-based multifunctional materials and new production processes and devices". Other thematic areas, like "Life sciences, genomics, and biotechnology for health" and "Food quality and safety" are closely related to fabrication and special applications of nanostructured novel materials.

Several initiatives are taking shape in various parts of the world, in response to the development of research activities on nanotechnology, but only a few major international centers have the potential to succeed in what is in fact the new industrial revolution.

In Europe the most integrated platform is the European Reference Pole for Micro and nanotechnologies – MINATEC – the new infrastructure built in the Grenoble area, having important facilities grouped mainly in three components: research platform, industrial development complex and training infrastructure.

The training in this field reveals the multi-disciplinarity approch including:

- nanosciences physics (nanomagnetism, lasers, biophotonics, nanooptics, quantic effects and devices), chemistry (nanochemistry, nanomaterials, molecular electrochemistry, biomaterials, molecular engines);
- biology genomics/proteomics, structural biology; nanobiotechnologies; bioinformatics;
- intelligent systems integrated smart materials/informatics, smart devices, content and uses.

During training activities the emphasis will be on new concepts, like nanofabrication, the synthesis of nanodevices as nanometer-sized assemblies of atoms and molecules that can be used in technological applications. In making electronic nanodevices it is also possible to use quantum mechanical effects which speed electron conduction in digital nanoprocessors.

The study of nanodevices can also advance our basic understanding of chemical reactions. Nanometer-sized chemical reactors can serve as laboratories for study of chemical reactions in constrained environments. Some of these reactions could become the foundation for construction of nanometer-sized chemical sensors, with potential applications in medicine. For example, nanodevices with carefully designed properties could replace viruses and bacteria as the active species in vaccines. On the other hand, construction of new biochips based on DNA hybridization will have enormous applications in genomics and proteomics such as quality control, active components screening, toxicology, pathogen panel detection, gene expression profiling for pharmaceutical, agro-food, cosmetic, and diagnostic industry.

It is obviously now that nanotechnologies could improve the protection of human health and environment, but research and training should be also developed on a novel strategic direction of ecological impact of nanostructured materials as possible environmental hazards.

Demonstration Fuel Cell for Educational Purposes

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Fuel cells are energy converters, which generate electricity and heat as a result of electrochemical oxidation of fuel introduced in the system. They demonstrate the highest efficiency compared with the other analogous devices known. Among all fuels used, hydrogen is the most attractive as regard to high-energy density and zero emission burning. As a result of an intensive research during past fifty years, several types of fuel cells, using hydrogen as a fuel, have been established and developed – *alkaline fuel cells* (AFC), *proton-exchange membrane fuel cells* (PEMFC), *phosphoric acid fuel cells* (PAFC), *molten carbonate fuel cells* (MCFC) and *solid oxide fuel cells* (SOFC). Special devices, which reform the traditional fuels into a hydrogen-rich gas, have been also invented. Efforts have been made to use some fuels directly in the fuel cells (DMFC). One of the perspective types is the *regenerative fuel cell* (RFC), which combines the technology of water electrolysis for hydrogen production and that of hydrogen fuel cells.

It is predicted that during next 5 to 10 years fuel cells will be commercialized and take a big share on the market. This will lead to significant changes in the future economy, called *hydrogen economy* by the specialists.

Recently, we tested several hydrogen storage alloys and compounds for potential application in fuel cells. On this base we developed a fuel cell system without using of precious metals as catalysts. The system works on the principles of regenerative fuel cells and can generate power output of about 50 mW. It is used for education of students in our university.







Mediaeval Indian sublimation apparatus. The upper dish is filled with cold water.

 \leftarrow Previous page: **Distilling apparatus**, from John French, The art of distillation, London 1651.
Virtual Representation of Chemical Information Using UML-an Object Oriented Approach, to Improve Chemistry Learning

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We report on the development of an object oriented approach (OOA) in order to describe accurately and in detail the chemical information for better understanding and improving the learning of chemistry. To achieve this assay, Unified Modeling Language (UML) is used to provide multiple dimensional access to the inherent information concerning a biochemical process, which is essential for reforming chemistry education.

In this paper an OOA is used to visualize and describe, through diagrams of UML, an enzyme catalyzed system¹. The enzyme used for modeling, is acid Phosphatase (AP). Acid Phosphatases (APs) are a family of enzymes that are widespread in nature and can be found in many animal and plant species. We use wheat germ acid phosphatase (E.C.3.1.3.2) as a reference enzyme and phosphate ester of p-nitrophenol as substrate, since the product formed after ester hydrolysis, p-nitrophenol, can be easily photometrically measured. We have to mention that such kind of laboratory experiments are fundamental in the learning of chemistry-biochemistry and constitute useful exercises in the University teaching program.

Utilizing the Rational Unified Process framework of Rational Suite Development Studio, a detailed representation of the enzyme catalyzed system is given through structural and behavioral diagrams of UML.



Students frequently have difficulty in making sense of laboratory experiments and in understanding sophisticated concepts. In addition, chemistry instruction that uses unfamiliar materials, by using language that is defined differently in science than in everyday situations, makes learning difficult.

By providing various representational diagrams in order to describe in simplicity the static as well as the dynamic behaviour of a chemical system, we propose an alternative efficient way for improving Chemistry learning which

would allow an important collaboration-inter-action between different disciplines as well as a promising tool for reforming chemistry education. This article provides and reveals links between different disciplines which could lead to an improved way of communication between scientists, better understanding and in a more efficient collaboration between them.

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Considerations on Teaching Physical Chemistry Applied to the Study of Occupational Risk

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In a precedent work /1/ we have argumented the orientation adopted in the teaching of certain physical-chemical disciplines at the section of Environmental Chemistry, which is accredited in the Faculty of Chemistry from the University of Bucharest.

Now, we are presenting another recent experiment connected with the conceiving and organization of a course corresponding to post graduate level entitiled: *The Control and Protection of Occupational Environment*, which we developed intensively between 21 – 31 October 2003 at the Department of Physical chemistry, Faculty of Chemistry as a self financing type of activity.

The problems connected with pollution control of occupational environment are of strigent actuality /2/ and as a consequence this form of study for the perfectioning of people, working in this domain, is a necessary alternative.

In the period of the curricula conceiving of this post graduate course we have been consulting some specialists from our country and from USA (Professor Roy Buchan from University of Colorado, Boulder). We finally adopted a ten day programme which contained 60 hours of course, 14 h assigned to applications and 4h for initial and final evaluations.

The included disciplines are: *Health of Occupational Environment* (5h), *Industrial Hygiene* (45h), *Ergonomy* (5 h), *Romanian and European Laws of work security* (5 h). Lectures are sustained by specialists from the Department of Physical Chemistry and from the Bucharest Institute of Public Health. We used the time allocated to applications organising practical demostrations on specific instruments for noxes control, presented by the Sepadin SRL (in co-operation with SKC England) and Real Westech SRL (in co-operation with DIONEX) firms.

These firms also offered a support in the documentation and learning process of enrolled post graduate students by partially sponsorizing the printing of our book edited by the Romanian Academy /3/.

Indirectly, we have also supported from the same funds some of the costs for the book printing destinated to second year master of *Chimie Physique Organique*, entitled *Interactions moleculaires*, which is part of our post university specialisations, supported by university budget.

Finally, we conclude that the activity connected with the course *Control and protection of Ocupational Environment* was very interesting for 40 postgraduate students, which were evaluated..The majority of them work in the regional branches of the National Institute of Public Health or in laboratories for Environmental quality control, considering this stage as a necessary period for improving their career.

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Methodological Aspects Regarding the Use of the Computer for Chemistry Learning - Applications

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The paper presents the main advantages provided by the computers in teaching chemistry. To support the topics presented in this paper we realized an educational software for the **alkene** chapter.

In the Romanian high schools we use the software named EAS (Educational Assistant for Schools) but it does no cover completely the scholar curriculum. We intended that our software be complementary with EAS.

The novelty consists in the advanced features of the software conceived by the chemistry teachers in close relation to the computer science teachers.

We tested the program extensively on four different groups of students and it proved to be very useful due to its attractive presentations. The involvement of the students was very intense during all the lessons and their results were clearly improved.

Results Achieved by Active Learning of the Basic Concepts of Chemistry

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Contemporary school demands great activity on the part of pupils in all segments of the process of learning. The paper presents achievements in combined methods of teaching/learning where a pupil was a thinker, a problem solver, an organizer, a self-assessor and an active participant of communication. The classes comprised the concepts of physical and chemical changes of substances, a pure substance, and a mixture. For the purpose of learning new teaching contents pupils brought along substances, considered and studied their properties, and performed changes on them. Through guided experimental work, they analyzed similarities and dissimilarities of substances' properties as well as similarities and dissimilarities of changes. They grouped substances and changes and drew conclusions on types of substances and types of changes. To systematize teaching content, pupils prepared drawings where physical and chemical changes were presented. They analyzed each other's drawings, listed and explained the presented changes. To assess the achievements in applied methods, a test was administered. The 98 pupils, having acquired knowledge by the described method, were tested (Group 1) as well as 104 pupils having acquired those concepts by the monologue-dialogue method along with performing of demonstration experiments (Group 2).

All tasks required the application of the concepts of types of substances (pure substance, homogeneous and heterogeneous mixture) and changes of substances (physical and chemical). Task A combined multiple choice and supplementation. In a schematic representation of the hydrological cycle pupils were to define the types and name of the presented changes in water (evaporation and condensing). Also, they were to define the type of designated substances and provide explanation for responses. In other tasks pupils were to list a physical change on a piece of coal (B); two chemical changes (C); and to complete the drawing of a scene from the yard by one physical and one chemical change (D).

Took			4			р	6	
Task	evaporation	condensing	water	cloud	drop of rain	Б	C	D
Group 1	67%	71%	74%	76%	87%	83%	88%	84%
Group 2	51%	35%	36%	60%	68%	67%	78%	54%

Tab. 1.Results of solving test task	s
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The results (Tab. 1) show that pupils from Group 1 were more successful in solving all tasks. Tasks demanding explanation should be pointed out because they can provide insight into knowledge comprehension and application (Task A). All responses containing explanation were accepted as correct for the type of substance (a cloud and a drop of rain). For example: rain is a pure substance because it is condensed steam; rain is heterogeneous mixture because it contains particles of dust; rain is homogeneous mixture because it contains dissolved substances, and the like. We think that at the very beginning of learning those concepts, and due to the nature of substances themselves, the choice of the type of substances cannot be incorrect if there is the choice of arguments.

Pupils of both groups perceived very well that for a physical change on a piece of coal they could perform breaking into pieces (crumbling and smashing). In listing the examples of chemical changes (task C) and in completing drawings with changes (task D), a greater diversity in responses of pupils from Group 1 was noticed. The number of correct responses for the three tasks was higher in Group 1.

Concerning pupils' achievements (level of concepts acquisition, creativity expression, technical solutions), the applied approach is considered to have achieved its anticipated goals.

Teaching Aids for Knowledge Checks about Concepts of Chemistry - Pupils' Drawings

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The teaching of *Physical and chemical properties of substances* involved pupils' task to perform as many changes on substances they had brought along as possible. All changes carried out were arranged into two groups based on the discussion and conclusions on properties of substances prior to and after the changes. Pupils were given the task to prepare, for the next class, drawings where three physical and three chemical changes, at the most, from everyday life would be presented. Pupils were very willing to do the task. The result were creative drawings which evidenced that pupils understood the concepts of physical and chemical changes and they knew how to apply them. Also, all pupils did their best to make good and interesting drawings from the artistic aspect.

Each pupil's homework, "a drawing-a report", was used as a teaching aid for knowledge check during the next class. Pupils' joint discussion confirmed the accuracy of their drawings and they took part in assessing their friends' works. The class was organized in such a way that each pupil was presenting his/her drawing, while the other one was listing physical and chemical changes he was observing in that drawing. After that, the pupil analyzing the previous work was to present his/her work and the next pupil was to analyze it. If the pupil analyzing the drawing made a mistake or missed some of the presented changes, the rest of pupils corrected his/her response. Thus, each pupil presented his/her work and analyzed other pupil's work, whereby there was achieved active participation of each pupil in the process of knowledge acquisition and knowledge check of the concepts taught.

The most frequently presented physical changes found in drawings were natural phenomena. Changes in water states were presented by 66% of pupils (rain falling – 29%, hydrological cycle – 18%, water evaporation – 15%, snow melting – 4%). Pupils also presented sunlight distribution (26%), rainbow phenomenon (25%), thunderbolt (13%). Apart from those changes, pupils presented hair dyeing and cutting, grinding of various materials and their dissolving. The 78% of pupils presented chemical changes by burning of various materials (paper 26%, wood 19%, matches 14%, candles 12%, cigarettes 7%). Changes in nature through changes of seasons were presented by 21% of pupils. Also, food digestion, fermentation, corrosion were used to present chemical changes.

The approach to the concepts of physical and chemical changes of substances allows for high activity of all pupils in both the teaching of new contents and knowledge check and systematization. Pupils' activity in knowledge check and systematization comprised:

- contemplating of the subject of drawing(teaching aid)
- making of a drawing
- quick analysis of other pupil's drawing
- presenting of perceived, relevant
- active listening to other pupils' presentations
- correction of errors in a reasoned discussion
- decision-making about a drawing considered to be the most successful.

We find that such approach, apart from knowledge acquisition, contributes to a greater independence and development of critical thinking in pupils. Of the infinite number of changes that is possible to present, pupils themselves made a selection of those they were to present. By applying the knowledge acquired, pupils determined the type of change and the style and mode of presentation. The achievements of such a method of work were visible during the next class when pupils applied their knowledge about physical and chemical changes to new situations, analyzing other pupils' drawings.

The Analysis of Student Replies Regarding Education in the Field of Natural Sciences and Mathematics According to the Achieved Success in the Mentioned Subjects

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This paper shows the results of the survey done among 1305 students of the eight grade ¹. The results are based on marks that these students got in mathematics, biology, geography and physics at the end of the first semester. The analysis of replies according to the marks in chemistry, is presented in a separate paper ².

At the end of the first semester in the last 2002-03 school year eight-grade students showed insufficient knowledge (marks E and F): 36% of all students in mathematics, 21% of all students in biology, 25% of all students in geography and 32% of all students in physics. Most of these students have not attended remedial instruction classes: in mathematics 72% of students who got F and 62% of those who got E, in biology 98% of students with F and 94% of those with E, in geography 93% of students with F and 93% of those with E and in physics 92% of students with F and 90% of those with E. In mathematics, among the students who got F 17% dedicated significant time to learning this subject; the same thing happened with 47% of students with F in biology, with 43% of students with F in geography and with 16% of students who got F in physics. Mark F (in case of mathematics and physics) is mostly connected with the fact that these were the least liked subjects. However, situation with biology and geography is opposite: 26% of students with F in biology and 25% of students with F in geography said these subjects were still their favourite ones. Generally speaking, majority of students said that, regardless of the mark in biology, this was their favourite subject; 44% of students with A in biology said this was their favourite subject. Physics, on the other hand, was the least favourite subject: 28% of students with A and 33% of students with B said that this was their least favourite subject, despite good marks at the end of the semester.

It is interesting that the main reasons for a subject being most or least favourite were identical in the case of all mentioned subjects, regardless of students' marks or differences among subjects. As the students said the main reasons for a popularity of a subject was interesting and clear teaching material; possibility to apply the knowledge in various situations was the second reason. 17% of students with A in mathematics, 18% of students with A in biology, 18% of students with A in geography and 16% of students with A in physics emphasised their teacher's positive influence as the reason for their liking the subject. Incomprehensible and difficult teaching material was the main reason for a subject to be least favourite; students also said that uninteresing classes were the second reason.

Supplementary lessons were attended by 39% of students with A and 29% of students with B in mathematics, by 20% of students with A and 11% of students with B in biology, by 17% of students with A and 7% of students with B in geography, by 12% of students with A and 8% of students with B in physics. Among the students who got A in mathematics, 41% of them dedicated significant time to learning that subject; the same was with 46% of students who got A in biology, 44% of students with A in geography and 30 % of students with A in physics.

The questionnaire indicate that students with better marks did not attend the supplementary classes as much as they ought to and that students with poorer marks did not attend the remedial instruction classes enough.

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What do the "Best Chemists" Among Primary School Students Think of Education in the Field of Natural Sciences?

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In the second semester of the 2002/03 school year views of 1305 primary school students' on important educational issues in the field of natural sciences and mathematics were analyzed. As many as 67 classes of the final eight-grade in 23 primary schools in different towns in Serbia were polled 1,2,3 .

Views of 79 primary school students' (6% of the whole sample) who got A in chemistry and who said that chemistry was their the most favourite subject, are presented in this paper. Among these students 58.2% were girls and 39.2% were boys; 2.5% of students did not mark their sex. Most of these students said that chemistry was their the most favourite subject due to interesting and clear teaching material (68%), possibility of applying their knowledge in various situations was the second reason (54%) and 48% of students said that interesting classes was the third reason. Also, 14% emphasized teacher's positive influence as on of the points for their liking chemistry. Beside chemistry, these students were most successful in biology (81% had A) and least successful in mathematics (53% had A). The majority of students said they liked physics and geography least or very little, (57%) and (44%) respectively. Main reasons for this were uninteresting classes (60%) and unclear of the curriculum (27%). Although the students had A in chemistry, they said they did not dedicate same amount of time to learning this subject: 35% of students said they spent most time and 17% least time in learning chemistry. Regarding various activities, 35% students wrote paper, 37% gave lecture to their friends, 14% made poster, 3% wrote seminar paper and a large number of students (41%) did nothing. Almost all students, 92% of them, watched or conducted experiments during regular chemistry classes. More than half of them (61%) did not attend supplementary classes. Chemistry is equally interesting subject in the seventh and eighth grade for most students (58%). About 65% of them said that the textbook helped them much or quite enough in learning, 33% said the book helped them little or very little, while 3% of students thought that the textbook did not help them at all. Most students (66%) evaluated their knowledge with A, although the number of those who evaluated themselves with B was not insignificant (30%).

About two third of students (71%) thought that doing a poll regarding school was useful and 70% explained this briefly.

The questionnaire results show that the indicated group of students was not involved enough during both regular and supplementary chemistry classes. It is evident that changes in the curriculum and in methodology are necessary with students who were top of their class in chemistry. Class activities that the students were involved in do not differ in any way from those all other students were occupied with. In order to improve the teaching methods, new class activities that would include more students regarding their foreknowledge, interests and abilities should be introduced. This would secure adequate students' development.

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The Problematisation: Active-Participating Method for the Learning Unit on Carbonyl Compounds

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Teaching-learning-assessment represent the three main activities which are equally performed within the process of education. The process of learning supposes actions which imply planning and projection, orientation and conducting, communication and stimulation, control and assessment, research and innovation. The problematic process, the heuristic learning, the laboratory experiment, the exercises and the problems are active-participative methods of learning Chemistry in school.

The problematic process represents a complex process in which the student has to find an answer, a theoretical or practical solution, starting from the knowledge acquired before, has to transfer his old knowledge to a new context [1-3].

In a sequence of problematized training, the teacher and his students will follow several stages:



We can exemplify by using the following program-scheme:

A mono-carbonyl compound contains 27.58 % oxygen.

One requests: - the molecular formula of the compound;

- the corresponding isomers for the found formula;
- the isomer, marked A, participates to the reactions:

A+ $[Ag(NH_3)_2]OH \longrightarrow B$

$$2A \frac{H^+}{-H_2O} > C \frac{H_2}{Ni} > D$$

Identify the isomer A and write the reactions corresponding to the scheme and transform the compound A into its carbonyl isomer.

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Model of Permanent Eco-Chemist Education of the Workers in the Employees in the Fertilizer Industry

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Fertilizer Industry is one of the most important branches in Serbia and Montenegro industry and it represents the potential source of chemist contamination of the environment. When the institutional education is over most of the employees in the different branches of chemical industry do not continue their further education. They have no interest in new scientific and technological solutions in a field of protection and improvement of financial conditions caused by chemist contamination. It is necessary to extend existing and find new information about eco-chemistry and use of it as well. Contents should be divided into general and special, depending on the professional and educational capability of the employees. These contents will have following topics:

- 1. Sources and prevention of the chemical contamination, especially in the industry of mineral soil. It is necessary to point to some changing during the production of mineral soil in order to reduce or completely remove the pollution.
- 2. Consequences of the chemist contamination on life forms and objects, especially consequences made by chemist contaminates which become by producing or using mineral soil.
- 3. The ways of protection and improvement of financial conditions of the damage caused by chemical contamination especially in the industry of mineral soil.
- 4. The international and state acts about the protection of the life environment.

This subject will present a model of the eco-chemist education of employees in the industry of mineral soil. For realization it is necessary to select appropriate methods and instruments in order to motivate the employees to extend their knowledge about eco-chemistry. That would make the foundation for permanent individual and organized education of the employees in the industry of mineral soil.

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Late Arrival

Determination of Polycylic Aromatic Hydrocarbons in Sugar and Sugar Beet Fibers

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Polycyclic aromatic hydrocarbons (PAHs) are fused-ring aromatic compounds, very important group of persistent organic pollutants that could be found in all environmental matrices, i.e. air, water, soil, sediments, animals and plants tissues. PAHs can be formed by thermal decomposition of any organic material containing carbon and hydrogen, mainly through the incomplete combustion. Most of them are very mutagenic and carcinogenic due to the ability of its metabolites to react with DNA inside the cell. Until the beginning of 20th century there existed a natural balance between the production and natural degradation of PAHs which kept the background concentration low and fixed. However, with the increasing development throughout the world, the natural balance has been disturbed and the production and accumulation rates of PAHs are constantly rising.

It is well documented that foods are an important source of human exposure to PAHs, more pronounced than the inhalation route. The presence of PAHs in food originates predominantly from environmental pollution, as well as food packaging and food processing. Processing procedures, such as smoking and drying of raw materials and products are accepted as a major source of food contamination by PAHs. The presence of PAHs in food is a matter for concern and requires continuous monitoring.

The aim of this work was to examine the presence of PAHs and some other persistent organic pollutants in by- and final products of two sugar factories from Vojvodina. Sugar-beet fibers, often used as animal feed, are dried in drier with gases formed during combustion of fossil fuel (residual oil). Due to the fact that carcinogenic PAHs are mainly associated with submicron particulates, it can be supposed that part of the ones passes the filter enhancing the PAHs level in dried sugar beet fibers. Wide spread industrial and domestic consumption of sugar imposes the necessity to know the PAHs level in this food item. Representatives samples of sugar crystal and sugar beet fibers from two industrial plants were examined in duplicate. Samples were prepared according to the modified Larsson's method which allows isolation of fractions with organochlorine pollutants (polychlorinated biphenyls-PCBs and organochlorine pesticides-OCPs) and with PAHs. Method contains of the saponification step, L-L extraction with dimethylformamide and cyclohexane, and purification step with adsorption chromatography on silica gel column. The analysis of organochlorine pollutants, 6 PCBs and 16 OCPs were carried out by gas chromatography with electron capture detector, while PAHs (16 compounds) were determined by gas chromatography with flame ionization detector and thin layer chromatography.

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The Presence of Heavy Metals in Some Plant Species of Genus Acinos Miller

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In the genus *Acinos* Miller (Lamiaceae) there are 10 species, which mainly inhabit alkaline soils, dry and sunny areas in Europe, the Mediterranean, Central Asia, N. Africa and N. America. The genus *Acinos* is represented by five species in the flora of Serbia and Montenegro.(1) Some of them are used for medicinal purposes like antiseptic, stimulant, tonic and antispasmotic.(2) Also, they are applicable internally in melancholy, for shortness of breath and improving digestion.

The aim of this paper was investigation of heavy metals content (Pb, Cd and Cr) in some *Acinos* species :*Acinos alpinus* (L.) Moench., *Acinos hungaricus* (Simonkai) Silic and *Acinos arvensis* (Lam.) Dandy. The plant material was collected on the following localities: *A. arvensis* (Rtanj), *A. hungaricus* (Seličevica) and *A. alpinus* (Šara). After preparation, the samples of plant materials were analysed using AAS PerkinElmer apparatus.

The examinated heavy metals were presented in plants in following amounts (mg/kg dry matter):

- A. arvensis-Cr 0,4;Cd 0,06 and Pb 0,84;
- A. hungaricus-Cr 1,05;Cd 0,43 and Pb 8,16;
- *A. alpinus*-Cr 1,10;Cd 0,28 and Pb 7,83.

The amount of the Pb is higher than amounts of the Cd and Cr in all investigated species. *A. arvensis* had undermost amount of investigated heavy metals than the others examined species, while higher amount of investigated heavy metals were contained in *A. hungaricus*. Quantity of investigated heavy metals was low in *A. arvensis,* herb picked up within rural area, while the quantity of metals was high in *A. hungaricus*, herb picked up by the highway. The high content of heavy metals in *A. alpinus* is probably its natural content. (3)

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