Eighth National Conference on Chemistry

Chemistry for Sustainable Development

Book of Abstracts

26–27 June 2014, Sofia, Bulgaria

Union of Chemists in Bulgaria

СХБ
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Eighth National Conference on Chemistry
Chemistry for Sustainable Development
26–27 June 2014, Sofia, Bulgaria
Venue: University of Chemical Technology and Metallurgy

ORGANISATION

Institutions

Union of Chemists in Bulgaria
Union of Scientists in Bulgaria
Bulgarian Academy of Sciences
University of Chemical Technology and Metallurgy, Sofia
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Symposia

Title	*Chair*
Physical chemistry and electrochemistry:	M. Bojinov, Tz. Tzvetkoff
Organic chemistry and technology:	V. Dimitrov
Inorganic chemistry and technology:	E. Zhecheva
Analytical chemistry:	D. Tsalev
Catalysis:	G. Kadinov
Chemical engineering and environmental protection:	V. Beschkov
Polymer chemistry and biomaterials:	N. Dishovsky, S. Nenkova

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Sofia 2014

Compilation by V. Beschkov, Ch. Bonev, I. Havezov
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Schedule

Thursday, 26th June 2014

Room 210

08:30–18:00	**Registration and information:** CIM Company

Asen Zlatarov Hall

09:30–09:45	**Opening session:** Organising Committee (V. Beschkov)
09:45–10:30	PL1-Plenary lecture: L. Petrov
10:30–11.00	Presentation by Alfa Laval Company
11.00–11.30	**Coffee break**
11:30–12:15	PL2-Plenary lecture: Ch. Tsvetanov
12:15–13:00	PL3-Plenary lecture: Tz. Tzvetkoff
13:00–14:00	**Lunch**

Hall 424
Session 1 Symposium 7: Polymer chemistry and biomaterials

14:00–15:15	Oral presentations (7-O1-O5)
15:15–15:45	Poster presentations (7-P1-P21)
15:45–16:15	**Coffee break**
16:15–17:30	Poster presentations (7-P1-P21, continued)

Hall 431
Session 2 Symposium 6: Chemical engineering and environmental protection

14:00–15:00	Oral presentations (6-O1-O4)
15:00–15:45	Poster presentations (6-P1-P17)
15:45–16:15	**Coffee break**
16:15–17:30	Poster presentations (6-P1-P17, continued)

Hall 439
Session 3 Symposia 3 and 5: Inorganic chemistry and technology. Catalysis

14:00–14:30	5-K1. Keynote lecture**:** S. Todorova, I. Yordanova, A. Naydenov, G. Kadinov
14:30–15:45	Oral presentations (3-O1-O2, 5-O1-O2, 3-O3)
15:45–16:15	**Coffee break**
16:15–17:30	Poster presentations (3-P1-P19, 5-P1-P5)

18:00–21:00	**Welcome reception at University of Chemical Technology and Metallurgy**

Friday, 27th June 2014

Room 210

08:30–18:00	**Registration and information:** CIM Company

Asen Zlatarov Hall

09:30–10:15	PL4-Plenary lecture: Ch. Boyadjiev
10:15–10:35	Presentation by AQUACHIM Company (K. Arishtirova)
10:35–11.00	**Coffee break**
11.00–11:45	PL5-Plenary lecture: S. D. Kolev
11:45–12:30	PL6-Plenary lecture: I. Rashkov, N. Manolova
12:30–13:30	**Lunch**

Hall 424
Session 4 Symposium 1: Physical chemistry and electrochemistry

13:30–15:30	Oral presentations (1-O1-O8)
15:30–16:00	**Coffee break**

Hall 431
Session 5 Symposium 4: Analytical chemistry

13:30–14:30	Oral presentations (4-O1-O4)
14:30–15:30	Poster presentations (4-P1-P11)
15:30–16:00	**Coffee break**

Hall 439
Session 6 Symposium 2: Organic chemistry and technology

13:30–14:30	Oral presentations (2-O1-O4)
14:30–15:30	Poster presentations (2-P1-P9)
15:30–16:00	**Coffee break**

Asen Zlatarov Hall

16:00–17:30	**Discussion: Chemical science and energy sources of the 21st century:** V. Beschkov
17:30–17:45	**Closing session:** Organising Committee (V. Beschkov)

Programme

(as of 12th June 2014)

Thursday, 26th June 2014

Room 210

8:30	18:00	**Registration and information**	CIM Company Conference Organiser

Asen Zlatarov Hall

9:30	9:45	**Opening session**	V. Beschkov Organising Committee
9:45	10:30	PL1-Plenary lecture: Preparation of clean hydrogen by ammonia decomposition	L. Petrov Kingdom of Saudi Arabia
10:30	11.00	Alfa Laval in the chemical industry: Products, basic concepts and applications	
11.00	11.30	**Coffee break**	
11:30	12:15	PL2-Plenary lecture: Temperature-responsive polymer mesoglobules as templates for fabrication of nanocapsule carriers	Ch. Tsvetanov Bulgaria
12:15	13:00	PL3-Plenary lecture: 40 years ionic melt electrochemistry in Bulgaria	Tz. Tzvetkoff Bulgaria
13:00	14:00	**Lunch**	

Hall 424

Session 1 Symposium 7: Polymer chemistry and biomaterials

14:00	14:15	7-O1. Utilisation of waste single-based propellants to compositions of liquid fertilisers	Tz. Tzvetkoff, I. Glavchev Bulgaria
14:15	14:30	7-O2. Processing and performance characteristics of elastomeric composites with addition of epoxy resin as a filler	D. Zaimova, E. Bayraktar, N. Dishovsky, D. Katundi Bulgaria, France
14:30	14:45	7-O3. Comparative analyses of keratin biocomposites with composites based on collagen	D. Zheleva Bulgaria
14:45	15:00	7-O4. Lignocellulosic biomass as a source for bioethanol production in Bulgaria	V. Blyahovski, S. Petrin, I. Valchev, S. Nenkova Bulgaria
15:00	15:15	7-O5. Improvement of the physical-mechanical properties of printing production with biodegradable printing varnishes	Ya. Nedelchev, T. Bozhkova, I. Spiridonov, R. Boeva, A. Ganchev Bulgaria
15:15	15:45	**Poster presentations (7-P1-P21)**	

15:45	16:15	**Coffee break**	
16:15	17:30	**Poster presentations (7-P1-P21, continued)**	

Hall 431

Session 2 Symposium 6: Chemical engineering and environmental protection

14:00	14:15	6-O1. Indicators describing pressures on environment from industry	L. Ilchev, N. Davcheva-Ilcheva Bulgaria
14:15	14:30	6-O2. Catalytic conversion of sulphides into energy in sulphide-driven fuel cell	V. Beschkov, E. Razkazova-Velkova, M. Martinov Bulgaria
14:30	14:45	6-O3. Denitrification of wastewater with immobilized cells of Pseodomonas denitrificans	T. Ivanov, I. Lalov, L. Jotova Bulgaria
14:45	15:00	6-O4. CFD simulation of the hydrodynamics of external loop airlift reactor. Effect of gas sparger construction and location	R. A. Stoykova, D. K. Moutafchieva, D. S. Popova, S. N. Tchaoushev, V. D. Iliev Bulgaria
15:00	15:45	**Poster presentations (6-P1-P17)**	
15:45	16:15	**Coffee break**	
16:15	17:30	**Poster presentations (6-P1-P17, continued)**	

Hall 439

Session 3 Symposia 3 and 5: Inorganic chemistry and technology. Catalysis

14:00	14:30	5-K1. Cobalt-based catalysts for volatile organic compounds removal	S. Todorova, I. Yordanova, A. Naydenov, G. Kadinov Bulgaria
14:30	14:45	3-O1. Non-equilibrium crystallisation in systems of the type $Na^+/Mg^{2+}/SO_4^{2-}/SeO_4^{2-}$-$H_2O$	Ch. Balarew, S. Tepavitcharova, S. Kamburov Bulgaria
14:45	15:00	3-O2. Nanotechnologies for next generation electrode materials in lithium ion batteries	S. Ivanova, E. Zhecheva, M. Mladenov, R. Stoyanova Bulgaria
15:00	15:15	5-O1. Catalytic behaviour in CO oxidation, CH_4 oxidation, and NO decomposition of rare-earth promoted alumina-supported copper cobaltites	B. Ivanov, I. Spassova, M. Milanova, M. Khristova Bulgaria
15:15	15:30	5-O2. Novel strategy for preparation of copper-modified SBA-15 and KIT-6 mesoporous silica catalysts	I. Genova, R. Nickolov, M. Dimitrov, M. Mihaylov, D. Kovacheva, K. Hadjiivanov, T. Tsoncheva Bulgaria
15:30	15:45	3-O3. Electrodeposition technique as a useful tool to obtain potential anode materials for Li-ion batteries with different nanoarchitectured morphologies	M. C. López, G. F. Ortiz, P. Lavela, R. Alcántara, J. L. Tirado Spain
15:45	16:15	**Coffee break**	
16:15	17:30	**Poster presentations (3-P1-P19, 5-P1-P5)**	

18:00	21:00	**Welcome reception at University of Chemical Technology and Metallurgy**

Friday, 27th June 2014

Room 210

8:30	18:00	**Registration and information**	CIM Company Conference Organiser

Asen Zlatarov Hall

9:30	10:15	PL4-Plenary lecture: A new approach to column apparatuses modelling	Ch. Boyadjiev Bulgaria
10:15	10:35	AQUACHIM: Innovative complex solutions in chemistry and industry	K. Arishtirova Bulgaria
10:35	11.00	**Coffee break**	
11.00	11:45	PL5-Plenary lecture: Polymer inclusion membranes: A novel tool for solventless extractive separation in industry and chemical analysis	S. D. Kolev Australia
11:45	12:30	PL6-Plenary lecture: Electrospinning of polymers: A versatile tool for fabrication of nanofibrous materials for a variety of applications	I. Rashkov, N. Manolova Bulgaria
12:30	13:30	**Lunch**	

Hall 424

Session 4 Symposium 1: Physical chemistry and electrochemistry

13:30	13:45	1-O1. Temperature dependence of inhibitor corrosion protection	A. Popova, M. Christov, A. Vasilev, T. Deligeorgiev Bulgaria
13:45	14:00	1-O2. Efficiency of galvanostatic formation of antimony oxide in oxalic acid solutions	Ch. Girginov, E. Lilov, E. Klein Bulgaria
14:00	14:15	1-O3. Estimation of kinetic parameters of oxide growth on stainless steel in high-temperature aqueous electrolyte: A sensitivity study	A. Alami, M. Bojinov Bulgaria
14:15	14:30	1-O4. Pulse electrolysis of alkaline solutions as a highly efficient method of production of hydroxygen gas mixtures	V. Karastoyanov, Tz. Tzvetkoff Bulgaria
14:30	14:45	1-O5. An electrochemical and surface analytical study of the degradation of electrode material during pulse electrolysis of water	D. Hristova, I. Betova, Tz. Tzvetkoff Bulgaria
14:45	15:00	1-O6. The dual protolytic ability of the stable semiquinone radicals	A. S. Masalimov, A. A. Tur, S. N. Nikolskiy Kazakhstan

15:00	15:15	1-O7. Electrochemical activity of two redox biocatalysts promoted by gold nanostructures: A proof of principle and applications in biosensing	N. Dimcheva, E. Horozova, T. Dodevska Bulgaria
15:15	15:30	1-O8. Frequency dependent glass transition of polystyrene: A combined photoacoustic and temperature-modulated differential scanning calorimetry study	Ch. Tzvetkova, Ts. Vassilev Bulgaria
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Hall 431

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13:45	14:00	4-O2. Surface modification of silica-coated $MnFe_2O_4$ magnetic nanoparticles applied as a sorbent for solid phase extraction of trace elements	D. Georgieva, N. Ivanova, V. Stefanova Bulgaria
14:00	14:15	4-O3. Methods for chemical analysis of undesired sediment formed in a high-pressure near zero sulphur diesel hydrotreater	A. Surleva, D. Stratiev, E. Todorova, K. Hristov, K. Stanulov, I. Shishkova, A. Pavlova Bulgaria
14:15	14:30	4-O4. Application of inductively coupled plasma optical emission spectrometry in the determination of platinum group elements in different materials	P. Petrova, N. Velitchkova Bulgaria
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Hall 439

Session 6 Symposium 2: Organic chemistry and technology

13:30	13:45	2-O1. Electrophilic cyclisation and addition reactions of 4-sulphinylated or 4-sulphonylated allene carboxylates	I. D. Parushev, I. K. Ivanov, V. C. Christov Bulgaria
13:45	14:00	2-O2. Metal-catalysed cycloisomerisation reactions of phosphorylated α- and β-hydroxyallenes	I. E. Ismailov, I. K. Ivanov, V. C. Christov Bulgaria
14:00	14:15	2-O3. Spectral and photochemical behaviour of unsymmetrical azines of 3-methyl-1-phenyl-pyrazol-5-ones derivatives after protonation	A. G. Chapkanov, I. K. Petkov, T. D. Dzimbova, S. M.Babanova Bulgaria
14:15	14:30	2-O4. Study on the synthesis, characterisation and bioactivities of substituted (9′-fluorene)-spiro-5-hydantoins	P. Marinova, M. Marinov, M. Kazakova, Y. Feodorova, D. Georgiev, A. Slavchev, S. Genova, V. Sarafian, N. Stoyanov Bulgaria
14:30	15:30	**Poster presentations (2-P1-P9)**	
15:30	16:00	**Coffee break**	

Asen Zlatarov Hall

16:00	17:30	**Discussion: Chemical science and energy sources of the 21st century**	V. Beschkov Bulgaria
17:30	17:45	**Closing session**	V. Beschkov Organising Committee

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PL1. Preparation of clean hydrogen by ammonia decomposition

L. A. Petrov

SABIC Chair of Catalysis, King Abdulaziz University, P.O. Box 80204, Jeddah 21589, Kingdom of Saudi Arabia

The preparation of clean hydrogen as an energy source has recently attracted great attention. Hydrogen storage, however, is a main obstacle for many H_2 applications. A possible solution is to prepare hydrogen by ammonia decomposition. Ammonia can easily be liquefied by compression under 1.0 MPa at room temperature. Liquid ammonia has a high gravimetric hydrogen density of 107.3 kg H_2 m^{-3}. The ammonia molecule contains 17.8 mass% hydrogen by weight, which is the highest among all other potential sources of hydrogen. Therefore, ammonia decomposition can be an excellent source of hydrogen for fuel cells in case one is able to carry out the process under mild conditions.

Supported ruthenium is so far the most active catalyst for ammonia decomposition, however, its scarcity in nature makes its wide application impossible. This lecture deals with a study of the catalytic properties of Ni and Co catalysts, supported on carbon materials, for ammonia decomposition.

Multi-wall carbon nanotubes (MWCNTs), single-wall carbon nanotubes (SWCNTs), grapheme, and activated carbons (AC) of different surface area were used. The catalysts were prepared by the incipient wetness impregnation method. The mass content of Ni and Co in the prepared samples was 5 and 10 wt.%, respectively. The supported catalysts were characterised by XPS, XRD, TEM, SEM, TPR, CO titration, and DTGA techniques. Catalytic performances of ammonia decomposition over these samples were tested in a fixed-bed reactor at ambient pressure.

Several factors play an important role for the formation of active catalysts. These include metal-support interaction and presence of functional groups on the carbon surface, electric conductivity, electron donation properties, surface area of the support, and thermal treatment of freshly prepared catalysts.

The characterisation techniques showed that carbon-nanotube surface functional groups have no significant influence on metal particle size and phase composition. Metal reducibility was slightly affected by the carbon nanotubes with different functional groups. Ammonia decomposition reaction tests have shown that catalysts supported on carbon nanotubes with different functional groups have close activity per gram catalyst. The $–NH_2$ group occupies the leading place in the preparation of most active catalysts.

Studies of the influence of thermal treatment in hydrogen and nitrogen ambience of Co precursors in the Co/MWCNTs system on the catalyst structure and catalytic activities in NH_3 decomposition have shown that the use of nitrogen is preferable. Cobalt-support interaction in MWCNTs-supported cobalt was controlled by varying the temperature of thermal treatment of the Co precursor and the reaction medium. Due to interaction of the cobalt species with MWCNTs, the Co/MWCNTs catalysts after pretreatment in nitrogen exhibited a much higher catalytic activity for NH_3 decomposition compared to that observed after hydrogen pretreatment. Co dispersion in MWCNTs-supported catalysts was found to be a function of the thermal pretreatment temperature. For AC supports, the use of large surface area supports leads to small cobalt particle sizes and high catalytic activity. However, cobalt catalysts supported on carbon nanotubes exhibited the highest catalytic activity for ammonia decomposition. Cobalt particle size had a significant impact on the catalytic activity in the ammonia decomposition reaction. The relationship between cobalt particle size and catalytic activity for ammonia decomposition plays a very important role. Data are summarised in Table 1. However, the use of carbon nanotubes as a support yielded a 4.7-nm cobalt particle size, which is much larger than that of CoAC-1, while the catalytic activity of CoCNTs reached a maximum value of 60.63% among all the catalysts under the same reaction conditions. The main effect was ascribed to peculiar electronic properties of the carbon nanotubes. Because of the electron donor properties of the carbon nanotubes, the ability of N_2 desorption from the metal surface was improved. Consequently, the N_2 molecule could easily desorb from the active sites on the surface.

Table 1. Surface area of carbon support and crystallite size of cobalt supported on different carbon supports

Catalyst	Specific surface area [a] (m^2/g)	NH_3 conversion (%) [b]	Cobalt crystallite size (nm)	
			XRD [c]	CO chemsorptions [d]
CoCNTs	169.3	60.63	4.4	4.7
CoAC-1	2954.0	33.59	3.7	1.9
CoAC-2	695.2	8.30	13.9	36.8
CoAC-3	71.3	7.23	18.8	54.5

a – corresponding to carbon supports; b – reaction conditions: T=500°C, GHSV=6000 h^{-1};
c – indicates Co_3O_4 crystallite size according to Scherrer's equation;
d – cobalt crystallite size from CO titration at 40°C.

PL2. Temperature-responsive polymer mesoglobules as templates for fabrication of nanocapsule carriers

Ch. B. Tsvetanov

Institute of Polymers, Bulgarian Academy of Sciences, Akad. G. Bonchev St., Bldg. 103A, 1113 Sofia, Bulgaria

A novel approach to the preparation of capsules using thermo-responsive polymer (TRP) templates is presented. TRPs are soluble in cold water and the phase separates upon heating above the phase transition temperature (PTT). In dilute aqueous solutions, the TRPs form stable monomodal spherical nano-aggregates, called mesoglobules (MSG), which disaggregate and dissolve at temperatures lower than PTT. Particle sizes can be tuned from 50 to 400 nm with a very narrow size distribution, making them potential candidates for core templates. The ability of the MSGs to disintegrate and dissolve upon cooling is the basis of the new approach. When MSGs are coated with a water-swellable polymeric membrane (i.e. formation of core-shell particles) by cooling the core starts to dissolve, and the dissolved macromolecules diffuse through the polymer membrane. A complete dissolution of the MSG template and extraction of the TRP can be carried out through centrifugation and dialysis thus producing a hollow sphere built of the outer polymeric membrane. Building the outer polymeric membrane was achieved by heterophase copolymerisation on the surface of the MSGs (e.g. seeded radical copolymerisation). Figure 1 presents the synthetic stages of the new method.

A major advantage of the method is the fact that all operations are performed only in an aqueous medium by simply changing the temperature, which is of particular importance when biomolecules have to be encapsulated. The possibility of adjusting the size of the template as well as the ease of formation of membrane shells of different thickness, porosity, and functional characteristics is a serious advantage of the proposed method.

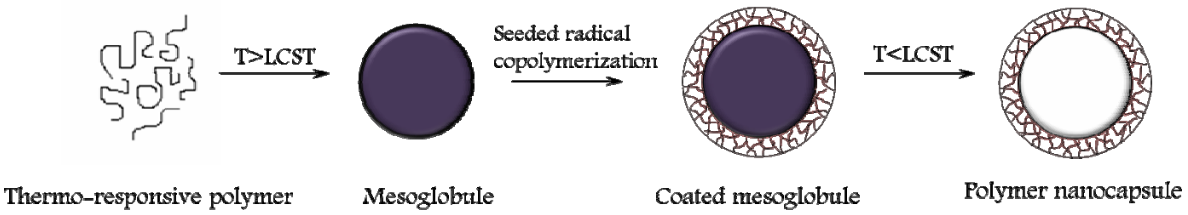

Fig. 1. Application of TRP core templates (mesoglobules) to preparation of nanocapsules.

This lecture highlights a thorough examination of both the successes and the problems associated with each stage of preparing hollow nano-spheres by using the technique described in figure 1.

Our approach provides a possibility for incorporation of biopolymers accompanied by the formation of a MSG core template. Thus, it enables a correct determination of the amounts of the biologically active substance to be encapsulated, or, in other words, to achieve the controlled load.

Our approach allows formation of structures that resemble an artificial cell structure or multi-compartment architecture as presented in figure 2.

Fig. 2. Sketch of sphere-in-sphere structure formation with two compartments A and B loaded by two different biomolecules.

This lecture is an attempt to persuade researchers of the opportunities for a further much deeper study of MSG as potential reservoirs, carriers, and transferring agents of biologically active substances.

PL3. 40 years ionic melt electrochemistry in Bulgaria

Tz. Tzvetkoff

University of Chemical Technology and Metallurgy, Holy Apostle and Evangelist Luka Institute of Hydrogen Technologies, 8 K. Ohridski Blvd., 1576 Sofia, Bulgaria
E-mail: *tzvetkof@uctm.edu*

The first systematic research on ionic melt electrochemistry in Bulgaria was initiated in the early 70s of the 20th century. Earliest studies in the field of ionic melt polarography were conducted at the Department of Electrochemistry and Corrosion Protection of the University of Chemical Technology and Metallurgy (UCTM) in Sofia. During the 80s, an extensive research in the field of high-temperature corrosion was performed at UCTM laboratory of ionic melt electrochemistry. It has been found that unstable metal peroxides with strongly oxidizing action, such as Na_2O_2 and KO_2, can be prepared in metal hydroxide melts.

In the last decade of the 20th century, systematic studies were carried out to achieve a practical application of ion melt technologies in industry. During this period, a number of inventions based on ionic melt electrochemistry were implemented in the military-industrial complex in Bulgaria. The end of this period marks an expansion of research in the field of thermodynamics and kinetics of electrode processes, physical chemistry of molten electrolytes, and electrolysis of ionic melts. Two fundamental review articles by the Sofia school appeared in 1995, namely ‘Electrodepositing of refractory metals (Ti, Zr, Nb, Ta) from molten salt electrolytes’ and ‘Corrosion of nickel, iron, cobalt, and their alloys in molten salt electrolytes’, both widely cited by leading research centres of ionic melt electrochemistry.

In 2003, a monographic chapter ‘High temperature corrosion in molten salts’ appeared in Molten Salt Forum Series. The first decade of this century was particularly useful for studies of the Bulgarian school of ionic melt electrochemistry, as evidenced by a DSc thesis ‘Mechanism of anodic oxidation of metals and alloys in molten electrolytes’ and four PhD theses in the field of physical chemistry and electrochemistry. During this period, anodic oxidation of nickel alloys and ferritic steels in hydroxide, and hydroxide-carbonate ion melts was studied and a mechanism for ion and electron transport was proposed in the resulting oxide films based on the mixed-conduction model (MCM). It was found that reactions of point defect generation and consumption at interfaces obey classical electrochemical kinetics, while transport is described by the generalised equations of diffusion-migration.

During the same period, studies were carried out on transpassive dissolution of ferric steels in industrial quasi non-aqueous electrolytes and ionic melts. Based on experimental data conclusions were made about the capacity of such electrolytes for use in nanostructured electrochemical processing. Similar studies have been conducted in ionic melts of KH_2PO_4. They suppose differentiated kinetics of transpassive dissolution of ferric alloys in the ionic melt to assume the existence of two different iron(III) intermediate products at the film-melt boundary: Fe^{3+} ad and Fe^{3+*} ad. This indicates that intermediates could result from the reaction of Fe(III) in the outermost layer of cations from the film with oxide or phosphate anions from the melt. At this stage, the reaction steps at the film/melt interface are regarded as electrochemical, i.e. their rate constants depend exponentially on the potential drop across the film-electrolyte interface. The reaction step of $Fe^{3+*}{}_{ad}$ is considered an autocatalytic reaction of the type:

$$\mathrm{Fe}_{\mathrm{Cr}}^{\mathrm{III}} + \mathrm{Fe}_{\mathrm{ad}}^{\mathrm{III*}} \xrightarrow{k_{34}} \mathrm{Fe}_{\mathrm{melt}}^{3+} + \mathrm{Fe}_{\mathrm{ad}}^{\mathrm{III*}} + \mathrm{V}_{\mathrm{Cr}}'''$$

Based on experimental results and performed calculations it is shown that the process of dissolution in transpassive regime in various types of electrolytes (quasi non-aqueous and molten) can be described by a similar kinetic scheme of the surface electrochemical reactions at the film/electrolyte interface.

PL4. A new approach to column apparatuses modelling

Ch. Boyadjiev

Institute of Chemical Engineering, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

The main problems of process modelling in chemical engineering are difficulties in the hydrodynamic part of the model and, in particular, the non-linearity of the differential equations of hydrodynamics and the inability to formulate boundary conditions between the phases. Many chemical, mass transfer, and heat transfer processes are realised in column apparatuses (except for plate columns) in one-, two-, or three-phase systems. The gas phase moves among the columns as a stream or bubbles. The liquid phase present in the column is as droplets, films, and jets. The solid phase forms are packed beds, catalyst particles, or slurries ($CaCO_3/H_2O$ suspension). Modelling of these processes in column apparatuses is difficult, because determination of velocities distributions in the phases is practically impossible.

A new two-step modelling approach is proposed to processes in column apparatuses, where the first step is a *convection-diffusion type model* and the second step is an *average concentration model*.

The former model allows to model processes in column apparatuses on the base of approximations of the mechanics of continua, where the mathematical point is equivalent to the medium elementary volume, which is sufficiently small with respect to the column volume and at the same time sufficiently large with respect to the intermolecular volumes of the medium. This model is used for qualitative analysis of the process and identification of the process mechanism, and to obtain mass transfer resistances in the phases.

The qualitative analysis of the model will be made using generalised variables, where the characteristic (inherent) scales are the maximal or average values of the variables. As a result, the unity is the order of magnitude of all functions and their derivatives in the model, i.e. the effects of the physical and chemical phenomena (the contribution of the terms in the model equations) are determined by the orders of magnitude of the dimensionless model parameters.

If all equations in the model are divided by a dimensionless parameter, which has the maximal order of magnitude, all terms in the model equations will be distributed in three parts: (i) the parameter is one or its order of magnitude is one, i.e. this mathematical operator represents a main physical effect; (ii) parameter's order of magnitude is 0.1, i.e. this mathematical operator represents a small physical effect; (iii) parameter's order of magnitude is <0.01, i.e. this mathematical operator represents a very small (negligible) physical effect, which must be neglected, because it is not possible to be measured experimentally.

The convection-diffusion type models are not suitable for quantitative description of the processes in column apparatuses, because the velocity functions in the convection-diffusion equations are unknown. This problem can be avoided at the second modelling step, if the average values of the velocities and concentrations over the cross-sectional area of the column are used. This means that the medium elementary volume (in the physical approximations of the mechanics of continua) will be equivalent to a small cylinder with real radius and a height, which is sufficiently small with respect to the column height and at the same time sufficiently large with respect to the intermolecular distances in the medium. As a result, the radial non-uniformities of the velocities and concentrations are presented by parameters, which is possible to be obtained experimentally.

The new approach to column modelling is used for theoretical analysis including: (i) one-phase systems – homogeneous chemical reactions in gas (liquid) systems; (ii) two-phase systems – physical and chemical absorption and adsorption processes and catalytic reactors modelling; (iii) three-phase systems – solutions of environmental problems (SO_2 absorption by $CaCO_3/H_2O$ suspension).

The new approach to column modelling leads to three main calculation problems. (i) The problem of two systems of coordinates in counter-current gas absorption is solved by MatLab and an iterative procedure. (ii) In cases of non-stationary processes in two-phase gas (liquid)-solid systems, the presence of mobile (gas, liquid) and immobile (solid) phases, under the conditions of long time processes, leads to a non-stationary process in the immobile phase and to a stationary process in the mobile phase. As a result, different coordinate systems should be used in the gas (liquid) and solid phase models. The solution of this problem is possible if MatLab and a multi-step procedure are used. (iii) The presented models for short columns are characterised by the presence of small parameters at the highest derivates and they have no exact solutions. Consequently, the use of conventional software to solve model differential equations is difficult. This difficulty may be eliminated by an appropriate combination between the conventional software and the perturbations (asymptotic) method, i.e. the solution of the differential equations is possible to be searched as a power series with respect to the small parameters.

Practical applications of the new approach to column apparatuses modelling are proposed.

PL5. Polymer inclusion membranes: A novel tool for solventless extractive separation in industry and chemical analysis

S. D. Kolev

School of Chemistry, The University of Melbourne, Victoria 3010, Australia
Fax: *+61-3-93475180, e-mail*: *s.kolev@unimelb.edu.au*

Separation based on polymer inclusion membranes (PIMs) offers an attractive alternative to conventional solvent extraction by eliminating the use of solvents and integrating the extraction and back-extraction processes into a single step [1,2]. PIMs consist of a base polymer and an extractant/carrier. In some cases, a plasticizer or modifier may be added to the membrane composition to improve the compatibility between the base polymer and extractant/carrier or to increase the solubility of the extracted species in the membrane liquid phase, respectively. These membranes have been used successfully for the extractive separation and preconcentration of both metallic and non-metallic species under laboratory conditions.

The present paper demonstrates the suitability of PIMs for applications involving industrial and analytical separation.

The potential of PIMs for industrial applications is illustrated with the development and testing of a PIM-based technology for the clean-up of gold mine tailings waters from thiocyanate. The presence of this anion, formed as a result of the reaction between cyanide and sulphidic minerals, does not allow the reuse of gold mine tailings waters in the production of gold. It has been demonstrated that a PIM consisting of the commercial extractant Aliquat 336, poly(vinyl chloride) (PVC) as the base polymer and 1-tetradecanol as a modifier is suitable for the separation of thiocyanate from its aqueous solutions [3]. The influence of the main parameters of the PIM-based system (i.e. initial thiocyanate concentration, membrane thickness, temperature and concentration of sulphate and chloride) for the separation of thiocyanate have been studied. Comprehensive mathematical models, describing the extraction and transport of thiocyanate, have been developed, numerically solved, and fitted to the experimental extraction data to determine the values of the extraction constant and the membrane diffusion coefficient of the thiocyanate ion-pair with the Aliquat 336 cation.

The potential of PIMs for use in chemical analysis is illustrated with two applications of these membranes in on-line separation and preconcentration in flow injection analysis (FIA) methods. The first application of PIMs in this area is for the determination of Zn(II) in aqueous samples in the presence of other metal ions, such as Mg(II), Ca(II), Cd(II), Co(II), Ni(II), Cu(II), and Fe(III) [4]. In this method the FIA system is equipped with a separation cell where a PIM, made of di(2-ethylhexyl) phosphoric acid as the extractant/carrier, PVC as the base polymer, and dioctyl phthalate as a modifier, separates two aqueous streams, i.e. a donor and an acceptor stream. The sample is injected into the donor stream and Zn(II) is transported selectively across the membrane into the acceptor stream where it is detected spectrophotometrically using 4-(2-pyridylazo) resorcinol. This FIA system has been applied successfully to the determination of Zn(II) in pharmaceuticals and samples from the galvanising industry. It has been shown that both the sensitivity and sampling rate of the proposed FIA method can be improved substantially by reducing the membrane thickness or by increasing the temperature of both the donor and acceptor streams and the separation cell [5].

A highly sensitive flow analysis system operating under FIA and continuous flow (CF) conditions has been developed for the trace determination of dissolved reactive phosphate in natural waters, which uses a PIM containing Aliquat 336 and PVC. The flow system, operating under CF conditions, has been successfully applied to the analysis of natural water samples containing concentrations of phosphate in the low $\mu g\ l^{-1}$ P range, using the multipoint standard addition method.

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PL6. Electrospinning of polymers: A versatile tool for fabrication of nanofibrous materials for a variety of applications

I. Rashkov, N. Manolova

Laboratory of Bioactive Polymers, Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 103A, 1113 Sofia, Bulgaria
Fax: *+359-2-8700309, e-mail*: *manolova@polymer.bas.bg*

Electrospinning enables the fabrication of continuous polymer fibres of high aspect ratio and of diameters in the nanoscale range. Nanofibres are produced under the action of a high voltage electrical field that draws a jet out of polymer solution or melt. Because of the exceptionally small jet diameter, the solvent has enough time to evaporate during the time of flight and solidified fibres are collected on an oppositely charged collector. Because of their high specific surface area, high porosity, small pore size, and 3D-structure, the nanofibrous electrospun materials may find a variety of applications. The ease of industrial scaling-up additionally contributes to the interest to electrospinning.

Our significant contributions to fabrication of electrospun materials and developed original appliances will be discussed. We pay attention to the efficiency of the obtained large range of new micro- and nanofibrous materials for application to biomedicine and pharmacy as a new generation of antimicrobial and haemostatic wound dressings, tissue-engineering scaffolds, implants for local postoperative chemotherapy, and systems for modified drug release. Further, applications to biotechnology as optimised substrates for immobilisation of enzymes, biologically active substances, microorganisms or cell cultures, to water and air purification, and to agriculture as environmentally friendly biohybrid materials are considered.

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D1. Chemical science and energy sources of the 21st century

V. Beschkov

Institute of Chemical Engineering, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

One of the greatest challenges of the present century is the replacement of the fossil fuels by new energy sources. It is provoked either by the fossil fuel exhaustion in future or by the threat of climate changes due to emissions of greenhouse gases in the atmosphere. Another drawback of the use of traditional fossil fuels is the impact of the resulting waste on the environment. These challenges require further applications of renewable energy sources, like wind, solar and water energy, biomass utilisation, hydrogen production and use, and new chemical processes.

Besides wind and water energy all other sources are more or less related to chemical processes, starting with traditional combustion, passing through electrochemical sources (batteries, fuel cells), hydrogen production and utilisation, and ending with photovoltaics for solar energy utilisation. The latter are also products of chemical science and technology.

The new energy technologies need advanced materials (as electrodes, catalysts), new energy carriers and net processes for hydrogen production and utilisation as a fuel as well as new types of fuel cells and equipment. All they require basic and applied research in chemical sciences.

The aim of the present round table discussion is to present the new trends and role of the chemical science in solving the problems with the complete or partial replacement of fossil fuels in the future.

1-O1. Temperature dependence of inhibitor corrosion protection

A. Popova [1], M. Christov [1], A. Vasilev [2], T. Deligeorgiev [2]

[1] Department of Physical Chemistry, University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd.,
1756 Sofia, Bulgaria
E-mail: apopova@uctm.edu
[2] Faculty of Chemistry and Pharmacy, University of Sofia, 1 James Boucher Blvd., 1126 Sofia, Bulgaria

Pickling in acids (HCl or H_2SO_4) is a usual surface treatment of metals prior to galvanisation. In order to reduce metal dissolution and acid consumption as well as corrosion, inhibitors are added to the pickling solution. Since elevated temperatures are usually used, it is important to be aware of the influence of temperature on metal dissolution and corrosion inhibition.

Two inhibitors, 3-methylbenzo[*d*]thiazol-3-ium bromide and 3,3′-(propane-1,3-diyl)bis[(2-methylbenzo[*d*] thiazol-3-ium) bromide], were investigated in the temperature range of 30−60ºC for corrosion of mild steel in 1M HCl. Impedance, polarisation resistance, and polarisation curves methods were used. Depending on temperature two structural models describing metal/(1M HCl + inhibitor) interface behaviour in the impedance spectra experiments were applied. Values of the model parameters were calculated by fitting the experimental curves. Temperature has different effect on the performance of the two inhibitors. The apparent activation energy was determined using the polarisation resistance and polarisation curves data.

Adsorption of the inhibitors is discussed as well.

1-O2. Efficiency of galvanostatic formation of antimony oxide in oxalic acid solutions

Ch. Girginov, E. Lilov, E. Klein

University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria
E-mail: *christian.girginov@gmail.com*

The galvanostatic isothermal formation of anodic oxide films on antimony was investigated in dilute solutions of oxalic acid. Special attention is directed to the efficiency of film growth in connection with the amount of dissolved metal. The latter is determined by the inductively coupled plasma optical emission spectrometry method in dependence of oxalic acid concentration, current density, and anodising time. For a given charge passed, the amount of dissolved antimony is found to increase at a higher oxalic acid concentration and anodisation time and to decrease on increasing current density. Theoretical thicknesses of anodic antimony oxide were calculated on the base of Faraday's law and compared to those obtained by optical methods. The calculations point to Sb_2O_3 as the most probable oxide composition. The results agree well with the established influence of current density on the amount of dissolved antimony.

The influence of the process parameters on the structure of the total current density is analysed. The anodic growth of Sb_2O_3 in oxalic acid solutions proves to take place at high electric fields within the oxide film. Film growth, however, is always accompanied by a dissolution process.

1-O3. Estimation of kinetic parameters of oxide growth on stainless steel in high-temperature aqueous electrolyte: A sensitivity study

A. Alami, M. Bojinov

Department of Physical Chemistry, University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria

In recent years, the mixed-conduction model (MCM) has been adapted to obtain the main kinetic and transport parameters for passive film growth on stainless steels and nickel-based alloys in high-temperature aqueous electrolytes. A procedure was elaborated to gain information on the rate-limiting steps of the process of oxide layer formation, growth and restructuring by quantitative comparison of the model equations with X-ray photoelectron spectroscopic data taken from the literature.

In the present paper, we focus on a sensitivity study of a range of parameters influencing the kinetics of growth and composition of the film, such as interfacial rate constants, field strength and diffusion coefficients in the inner and outer layers of oxide. The relative significance of the parameter values for the kinetics of the overall process of film growth and restructuring dissolution in the passive state is discussed and further steps towards a new version of the model are outlined.

1-O4. Pulse electrolysis of alkaline solutions as a highly efficient method of production of hydroxygen gas mixtures

V. Karastoyanov [1], Tz. Tzvetkoff [2]

[1] BG H2 Society, University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
[2] Hydrogen Technology Centre, University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria
vasko_kar@yahoo.com

Pulse electrolysis of water solutions is a highly efficient method of production of hydrogen and hydrogen/oxygen gas mixtures, sometimes called hydroxygen [1]. When pulse current is applied during electrolysis, the amount of hydroxygen formed is increased in comparison to the DC current regime [2]. The aim of the present paper is to investigate the effect of ultra short current pulses on the rate of hydroxygen gas mixture production as related to efficiency enhancement of the process by means of the reducing power consumption during electrolysis.

Pulse electrolysis was carried out in a laboratory electrolysis stack consisting of nine cells featuring electrodes of 316L stainless steel at a spacing of 10 mm. The volume of the used alkaline solution was 2 l of 0.5M KOH. Typically, the experiments were carried out for 1 min with current amplitudes of 0.7−1.0 A, frequencies of the signal 0.4−1.0 kHz and pulse saturation (duty cycle) within 2−95%. The volume of the produced hydroxygen gas mixture by pulse electrolysis was measured by gas flow meters and compared to the produced gas volume of the DC electrolysis in the same electrolyser and applied current of 5−10 A. Based on the results obtained, preliminary conclusions regarding optimisation of the pulse current regime are drawn and a discussion on a possible mechanism of rate enhancement is given.

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1-O5. An electrochemical and surface analytical study of the degradation of electrode material during pulse electrolysis of water

D. Hristova, I. Betova [1], Tz. Tzvetkoff

*Hydrogen Technology Centre, University of Chemical Technology and Metallurgy, 8 K. .Ohridski Blvd.,
1756 Sofia, Bulgaria
E-mail: dhristova@hotmail.com
[1] Department of Chemistry, Technical University of Sofia, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria*

Pulse electrolysis of water is a highly efficient method of production of hydrogen and hydrogen/oxygen gas mixtures, sometimes called hydroxygen. Under conditions of pulse electrolysis of water, the rate of the process is increased in comparison to the DC regime, which poses higher requirements to the corrosion resistance of the respective materials. The processes of their corrosion and degradation are crucial for the hydrogen generator's efficiency and are expected to depend on the electrical characteristics of the pulse (current/voltage, frequency, saturation).

The aim of the present paper is to investigate the effect of these characteristics on the electrochemical properties of AISI 316 stainless steel under pulse electrolysis operating conditions and to correlate these properties with the surface state obtained from SEM observations.

1-O6. The dual protolytic ability of the stable semiquinone radicals

A. S. Masalimov, A. A. Tur, S. N. Nikolskiy

*E. A. Buketov Karaganda State University, Republic of Kazakhstan
E-mail: masalimov-as@mail.ru*

The fast intramolecular tautomerism (FIT) in stable semiquinone radicals: 3,6-di-tert.butyl-2-oxyphenoxyl (I), 4,6-di-tert.butyl-3-clorine-2-oxyphenoxyl (II), and 4-triphenylmethyl-6-tert.butyl-3-clorine-2-oxyphenoxyl (III) due to nanosecond homolytic migration of a hydroxylic hydrogen atom between two oxygen atoms determines the specific dual protolytic ability for these paramagnetic acids. The FIT in radical (I) has degenerate nature and two reaction channels of acid-base interaction with different organic compounds: amines, alkaloids (Y), carbon acids, and primary and secondary amines (YH) in liquid medium are equivalent. Radical (I) may be used as a handy spin probe for EPR spectroscopic determination of rate constants of intermolecular proton transfer (IPT) reactions, $XH + Y \leftrightarrow XH\ldots Y \leftrightarrow XH^{-}\ldots Y^{-}$, and intermolecular proton exchange reactions (IPE), $XH + YH^* \leftrightarrow XH^* + YH$. Here * denotes acid proton spin orientation in the molecules.

The EPR investigations of rate constants of IPT reactions of radicals (I–III) with thebaine in toluene medium show that the values of their kinetic acidity decrease in the order I > II > III, but their thermodynamic acidity increases as I < II < III. It is obvious that the rate of IPT reaction is controlled by the values of activation entropy and the equilibrium of IPT is determined by specific structures and aggregations of the reactions products. It is showed that the ionic pairs of acid radical (I) form paramagnetic dimers in solution.

The dual protolytic ability of radicals (I–III) specified by FIT determines tautomerism in products and in intermediates of studied acid-base reaction in non-aqueous solutions. By using EPR spectroscopy and quantum chemical methods, the electronic structure and physicochemical properties of different protolytic systems with participation of spin probes (I–III) and different organic compounds were investigated.

1-O7. Electrochemical activity of two redox biocatalysts promoted by gold nanostructures: A proof of principle and applications in biosensing

N. Dimcheva, E. Horozova, T. Dodevska [1]

Department of Physical Chemistry, Paisiy Hilendarski University of Plovdiv, 24 Tsar Asen St., 4000 Plovdiv, Bulgaria
Fax: +359-32-261403, e-mail: ninadd@uni-plovdiv.bg
[1] Department of Inorganic and Physical Chemistry, University of Food Technologies, 26 Maritsa Blvd., 4002 Plovdiv, Bulgaria

The electrochemical activities of two oxidative biocatalysts, redox active protein myoglobin and enzyme ascorbate oxidase, have been examined on gold electrodes and on the same electrodes modified through electrodeposition with gold nanoparticles (GNPs). Both on smooth and GNPs-modified electrodes, the biocatalysts were attached to the electrode surface using the gold-thiol chemistry (also known as self-assembly process), which warrants monolayer formation. It was found that the self-assembled biocatalysts on GNPs exhibited both high electrochemical and electrocatalytic activity.

Alternatively, when biocatalysts are self-assembled onto a smooth gold electrode, although still active electrochemically, their electrocatalytic activities were found rather suppressed. This implies that the electrochemical and electrocatalytic activity of both redox-active biocatalysts was promoted by the gold nanostructures.

The established electrocatalytic activity of the two self-assembled redox proteins onto GNPs was successfully used to develop electrochemical biosensors for the assay of trichloroacetic acid herbicide (with myoglobin as bio-recognition element) and for vitamin C (with ascorbate oxidase enzyme as bio-recognition element).

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1-O8. Frequency dependent glass transition of polystyrene: A combined photoacoustic and temperature-modulated differential scanning calorimetry study

Ch. Tzvetkova [1], Ts. Vassilev [2]

[1] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Akad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria
E-mail: hrisi@svr.igic.bas.bg
[2] Rostislaw Kaischew Institute of Physical Chemistry, Bulgarian Academy of Sciences, Akad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria

The dynamic glass transition of polystyrene was investigated in a wide frequency range from 0.004 to 4500 Hz. Experiments were carried out using a new originally developed thermal wave technique called combined photoacoustic and temperature-modulated differential scanning calorimetry (PA-TMDSC). It was built based on a commercial model DSC Perkin Elmer 7 apparatus [1]. At a low frequency range (0.004 to 0.1 Hz) it uses the ability of standard-temperature modulated DSC (TM-DSC) calorimeters to measure complex heat capacity. At a higher frequency range (4–4500 Hz) it uses laser heating as a modulated heat source and microphone detection for photoacoustic signal which is proportional to thermal diffusivity. Both parts of the modulated PA signal, in-phase and out-of-phase components, were obtained by means of a lock-in amplifier. PA-TMDSC allows simultaneous measurements of both PA and DSC signals.

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2-O1. Electrophilic cyclisation and addition reactions of 4-sulphinylated or 4-sulphonylated allene carboxylates

I. D. Parushev, I. K. Ivanov, V. Ch. Christov

Department of Organic Chemistry and Technology, Faculty of Natural Sciences, Konstantin Preslavsky University of Shumen, 115 Universitetska St., 9712 Shumen, Bulgaria
Fax: +359-54-830371, e-mail: parushev.chem@abv.bg

A convenient and efficient method for regioselective synthesis of 4-sulphinylated or 4-sulphonylated allene carboxylates **1** and **2** has been found [1]. Reactions with different electrophilic reagents take place with 5-endo-trig cyclisation or 3,2-addition reaction depending on the kind of the substituent at the sulphur atom [2]. Treatment of 4-(benzenesulphinyl)-allenoates **1** with electrophiles gives 5-(benzenesulphinyl)-furan-2(5*H*)-ones **3** because of the neighbouring carboxylate group participation in the cyclisation. On the other hand, (3*E*)-4-(methansulphonyl)alk-3-enoates **4** were prepared by chemo-, regio, and stereoselective electrophilic addition to the C^2-C^3-double bond in the allenoate moiety of 4-(methanesulphonyl)-allene carboxylates **2**. When R^1=Me, the treatment with electrophiles gives mixtures of (3*E*)-4-(methanesulphonyl)alk-3-enoates **4** and (3*E*)-4-(methanesulphonyl)-2-methylene-alk-3-enoates **5** at a ratio of about 1.6 to 1 as a result of addition and elimination reactions.

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2-O2. Metal-catalysed cycloisomerisation reactions of phosphorylated α- and β-hydroxyallenes

I. E. Ismailov, I. K. Ivanov, V. Ch. Christov

Department of Organic Chemistry and Technology, Faculty of Natural Sciences, Konstantin Preslavsky University of Shumen, 115 Universitetska St., 9712 Shumen, Bulgaria
Fax: +359-54-830371, e-mail: ismail78@abv.bg

An efficient method for regioselective synthesis of phosphorylated α- and β-hydroxyallenes has been described [1,2]. Cycloisomerisation reactions [1,2] of α- and β-hydroxy-substituted allene phosphonates and allenyl phosphine oxides with the so-called coin metals ions, such as Ag(I), Au(I), Au(III), Pt(II), Pd(0), Pd(II), Cu(I), Al(III), Ni(II), Zn(II), and Sn(II) leads to formation of heterocyclic compounds with excellent yields. We established that the reaction of α-hydroxy-allene phosphonates and allenyl phosphine oxides **1** proceeds with formation of 3-phosphorylated 2,5-dihydrofuranes **3**. Metal-catalysed reactions of β-hydroxy-substituted allene phosphonates and allenyl phosphine oxides **2** give 4-phosphorylated 3,6-dihydro-2*H*-pyranes **4**.

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2-O3. Spectral and photochemical behaviour of unsymmetrical azines of 3-methyl-1-phenyl-pyrazol-5-ones derivatives after protonation

A. G. Chapkanov [1], I. K. Petkov [2], T. D. Dzimbova [3], S. M. Babanova [1]

[1] Department of Chemistry, Neofit Rilski South-West University, 66 I. Mihaylov St., 2700 Blagoevgrad, Bulgaria
Fax: +359-7-3885516, e-mail: chapkanov@swu.bg
[2] Faculty of Chemistry and Pharmacy, Sofia University, 1 J. Boucher Blvd., 1164 Sofia, Bulgaria
[3] Institute of Molecular Biology, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

Comparative UV-spectral analyses of some unsymmetrical azines originated from 4-acethyl-3-methyl-1-phenyl-pyrazol-5-one under different protonated conditions have been studied. The compounds can exist in four tautomeric forms: keto, enol, and two imino forms. The investigated compounds contain two structural fragments: 1-phenyl-3-methyl-pyrazol-5-one moiety and an azine moiety, which suggests a specific potential biological activities and practical application. The spectral and photochemical characteristics are depending on structural features, type of solvent, time of UV-light irradiation, and protonation. Two different protonation ways of the azines derived from 4-acetyl-3-methyl-1-phenyl-pyrazol-5-one in methanol solution were used: by means of 5% HCl and by 2,2,2-trichloro acetaldehyde after UV-light irradiation. The different spectral characteristics of the studied compounds depend on irradiation time and separated HCl amount as an active and protonated component. The presence of isobestic points in the spectra of studied compounds show the presence of mono protonated and non-protonated forms at ground state, probably at the di-methylamino group (aniline nitrogen atom). Increasing the time of irradiation leads to a possible protonation of other nitrogen atoms, which change spectral features. On the base of the obtained experimental results, a stabilisation and a predominant enol form in methanol solution were established.

2-O4. Study on the synthesis, characterisation, and bioactivities of substituted (9′-fluorene)-spiro-5-hydantoins

P. Marinova [1a], M. Marinov [2], M. Kazakova [3], Y. Feodorova [3], D. Georgiev [1b], A. Slavchev [4], S. Genova, V. Sarafian [3], N. Stoyanov [5]

[1a] Faculty of Chemistry, University of Plovdiv, 24 Tsar Asen St., 4000 Plovdiv, Bulgaria
E-mail: marinova@uni-plovdiv.bg
[1b] Faculty of Biology, University of Plovdiv, 24 Tsar Asen St., 4000 Plovdiv, Bulgaria
[2] Department of General Chemistry, Agricultural University, 12 Mendeleev Blvd., 4000 Plovdiv, Bulgaria
[3] Department of Medical Biology, Medical University, 15A V. Aprilov Blvd., 4000 Plovdiv, Bulgaria
[4] Department of Microbiology, University of Food Technologies, 26 Maritsa Blvd., 4002 Plovdiv, Bulgaria
[5] University of Ruse, Razgrad Branch, 3 Aprilsko Vastanie St., 7200 Razgrad, Bulgaria

The spirohydantoins are a class of organic compounds with a wide spectrum of biological activities. Their antiepileptic, anticonvulsant, and antitumour properties as well as their capability of inhibiting the aldoso-reductase enzyme have already been well documented. The aim of the present study was to synthesise, elucidate the structure, and investigate the biological properties of substituted fluorenylspirohydantoins: 3-methyl-(9'-fluorene)-spiro-5-hydantoin, 3-methyl-(9'-fluorene)-spiro-5-(2,4-dithiohydantoin, 1,3-dihydroxymethilene-(9'-fluorene)-spiro-5-hydantoin, 4'-bromo-(9'-fluorene)-spiro-5-hydantoin. We determined their cytotoxic effects on the human cell line (WERI- Rb-1) by WST-assay (Roche Applied Science). The antimicrobial activity against both Gram-positive and Gram-negative bacteria and *Candida albicans* yeast was also studied. The structures of the new compounds were discussed based on the performed spectroscopic measurements (UV-Vis, IR, Raman, ^{1}H- and ^{13}C-NMR spectroscopy) and the single-crystal X-ray diffraction method for 1,3-dihydroxymethilene-(9'-fluorene)-spiro-5-hydantoin. The compound was crystallised in monoclinic crystal system and $P2_1/c$ space group. We found that all studied spirohydantoins affected the viability of cells. Cell death was dependent on the compound concentration and incubation time. Our results imply that the four (9'-fluorene)-spiro-5-hydantoins act as potential anticancer agents inducing growth inhibition of retinoblastoma cells.

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2-P1. Competitive electrophilic cyclisation and addition reactions of 4-phosphorylated allene carboxylates

I. D. Parushev, I. K. Ivanov, V. Ch. Christov

Department of Organic Chemistry and Technology, Faculty of Natural Sciences, Konstantin Preslavsky University of Shumen, 115 Universitetska St., 9712 Shumen, Bulgaria
Fax: +359-54-830371, e-mail: parushev.chem@abv.bg

As a part of our long-standing programme on cyclisation reactions of mono- and bi-functionalised allenes we have prepared and investigated allene carboxylates **1** and **2** possessing a phosphoryl group at the 4th place in the allene carboxylic system [1]. A reaction of the 4-phosphorylated allene carboxylates **1** and **2** with different electrophilic reagents takes place with 5-endo-trig cyclisation or 3,2-addition reaction depending on the kind of substituent in phosphoryl group [2]. Treatment of the 4-(dimethoxyphosphopyl)-allenoates **1** with electrophiles gives mixtures of 2,5-dihydro 1,2-oxaphospholes **3** and furan-2(5H)-ones **4** as a result of the neighbouring group participation of phosphonate and carboxylate groups in the cyclisation. On the other hand, (3E)-4-(diphenylphosphoryl)-alk-3-enoates **5** were prepared by chemo-, regio, and stereoselective electrophilic addition to the C^2-C^3-double bond in the allenoate moiety of the 4-(diphenylphosphopyl)-allene carboxylates **2**.

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2-P2. Reactions of phosphorylated α-hydroxyallenes with electrophiles

I. E. Ismailov, I. K. Ivanov, V. Ch. Christov

Department of Organic Chemistry and Technology, Faculty of Natural Sciences, Konstantin Preslavsky University of Shumen, 115 Universitetska St., 9712 Shumen, Bulgaria
Fax: +359-54-830371, e-mail: ismail78@abv.bg

This work discusses the process of creating a comfortable and efficient method for regioselective synthesis of phosphorylated α-hydroxyallenes. The method includes a previously taken step where alkynes with protected hydroxyl group were isolated as well as subsequent steps of the synthesis of the desired 1,1-bifunctionalised allenes **1** and **2**. Electrophilic reactions of the prepared allene phosphonates **1** and allenyl phosphine oxides **2** with protected and unprotected hydroxylmethyl group at α-position were studied. Interaction of the allene phosphonates **1** with electrophilic reagents occurs with 5-endo-trig cyclisation by neighbouring participation of a phosphonate group only as an internal nucleophile to give 2,5-dihydro-1,2-oxaphosphol-2-ones **3**. On the other hand, the allenyl phosphine oxides **2** with electrophiles give mixtures of 2,5-dihydro-1,2-oxaphosphol-2-ium halides **4** and the (2E)-1-alkenyl phosphine oxides **5**.

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2-P3. Synthesis and electrophilic cyclisation and addition reactions of 3-vinylallenyl phosphine oxide

H. H. Hasanov, I. K. Ivanov, V. Ch. Christov

Department of Organic Chemistry and Technology, Faculty of Natural Sciences, Konstantin Preslavsky University of Shumen, 115 Universitetska St., 9712 Shumen, Bulgaria
Fax: +359-54-830371, e-mail: hasi__@abv.bg

A method for synthesis of the 3-methyl-penta-1,2,4-trienyl phosphine oxide **1** by [2,3]-sigmatropic rearrangement of the mediated alkenynyl phosphinite, formed in the reacton of 3-methylpent-1-en-4-yn-3-ol with diphenylchlorophosphine has been elaborated [1]. Electrophilic reactions of the 3-vinylallenyl phosphine oxide **1** occur *via* different pathways depending on used electrophiles [2]. Halogenation leads to the formation of 4-halo-5*H*-1,2-oxaphosphol-2-ium salts **2**, while reactions with sulphanyl and selanyl chlorides proceed with oxaphosphol (**2**) and thiophene or selenophene (**5**) heterocyclisation. Heating of the cyclic phosphonium salts **2** under reflux conditions provokes elimination of hydrogen halide and C^5-O bond cleavage of the ring with generation of the 3-methylenepenta-1,4-dienyl phosphine oxides **4**. On the other hand, 3-hydroxy-1,4-dienyl phosphine oxides **5** were prepared by elimination and hydrolysis reactions of the cyclic 1,2-oxaphosphol-2-ium halides **2**.

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2-P4. Electrophilic cyclisation reactions of vinylallenyl phosphine oxides

I. K. Ivanov, V. Ch. Christov

Department of Organic Chemistry and Technology, Faculty of Natural Sciences, Konstantin Preslavsky University of Shumen, 115 Universitetska St., 9712 Shumen, Bulgaria
Fax: +359-54-830371, e-mail: iivanov@shu-bg.net

Results of examined electrophilic cyclisation of vinylallenyl phosphine oxides **1** possessing a vinyl group at the 1st or 3rd place in the allenic system will be discussed [1,2]. We studied the reactions with different electrophilic reagents, such as chlorine, bromine, iodine, methane- or benzenesulphanyl chlorides and benzeneselanyl chloride [1,2]. It has been established that a heterocyclisation of vinylallenic system of double bonds proceeds in most cases. Halogenation of **1** occurs with formation of different products depending on the place of the vinyl group. We isolated the heterocyclic 4-halo-5*H*-1,2-oxaphosphol-2-ium salts **2** and **5** or the unsaturated trienyl phosphine oxides **3** and 3-hydroxy-1,4-dienyl phosphine oxides **4**. A reaction of the vinylallenyl phosphine oxides **1** with sulphanyl and selanyl chlorides proceeds with oxaphosphol (**2** and **5**), thiophen (**6** and **7**) or selenophen (**6** and **7**) heterocyclisation or with the unsaturated trienyl phosphine oxides **3** and the 3-hydroxy-1,4-dienyl phosphine oxides **4**.

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2-P5. Synthesis and bioactivity of new platinum and ruthenium complexes of 4-bromo-spiro-(fluorene-9,4'-imidazolidine)-2',5'-dithione

P. Marinova [1], M. Marinov [2], M. Kazakova [3], Y. Feodorova [3], V. Sarafian [3], N. Stoyanov [4]

[1] *Faculty of Chemistry, University of Plovdiv, 24 Tsar Asen St., 4000 Plovdiv, Bulgaria*
E-mail: *marinova@uni-plovdiv.bg*
[2] *Department of General Chemistry, Agricultural University, 12 Mendeleev Blvd., 4000 Plovdiv, Bulgaria*
[3] *Department of Medical Biology, Medical University, 15A V. Aprilov Blvd., 4000 Plovdiv, Bulgaria*
[4] *University of Ruse, Razgrad Branch, 3 Aprilsko Vastanie St., 7200 Razgrad, Bulgaria*

The most significant application of spirohydantoins is in the field of medicine and clinical practice as aldose reductase inhibitors. They reveal antitumour, anticonvulsant, antiepileptic, and antiarrhythmic action as well as inhibitory activities towards muscle and liver glycogen phosphorylase. On the other hand, compounds containing a fluorene ring have been proved as organic light emitting diodes (OLED) as applied in practice.

The aim of the current study is to present the synthesis and determination of the structure and biological properties of Pt(II), Pt(IV), and Ru(III) complexes with 4-bromo-spiro-(fluorene-9,4'-imidazolidine)-2',5'-dithione (L). The cytotoxic effect has been evaluated by WST-assay (Roche Applied Science). Although hydantoin compounds have been studied extensively, there is no much research on their antiproliferative effect.

The structure of complexes obtained was verified through elemental analysis and spectroscopic UV-Vis, IR, and FT-ATR, and Raman spectroscopy methods. We have shown for the first time a certain biological potential of the new complexes on a retinoblastoma human cell line (WERI-Rb-1). Further studies are needed to reveal their properties and exact mechanism of action.

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2-P6. Chemical modifications of inhibitors of M2 ion channel of influenza virus

K. Chuchkov, V. Zahariev, A. Galabov [1], I. Stankova

Neofit Rilski South-West University, 66 I. Mihaylov St., 2700 Blagoevgrad, Bulgaria
[1] *Angeloff Institute of Microbiology, Bulgarian Academy of Sciences, Sofia, Bulgaria*
E-mail: *chuchich@abv.bg*

Influenza spreads around the world in seasonal epidemics resulting in about three to five million yearly cases of severe illness and about 250 000 to 500 000 yearly deaths. In the 20th century three influenza pandemics occurred, each caused by the appearance of a new strain of the virus in humans, and killed tens of millions of people [1]. There are several specific antiviral agents against influenza viral infections: inhibitors of M2 ion channel and neuraminidase inhibitors. Inhibitors of M2 ion channel amantadine and rimantadine are the first antiviral drugs developed in the 70s of the last century [2]. The adamantan(amin)e derivatives amantadine and rimantadine have long been available for both the prophylaxis and therapy of influenza A virus infections, but their use has been limited because of the rapid emergence of drug resistance, the ready transmissibility of drug-resistant viruses, and particularly for amantadine, the occurrence of central nervous system (CNS) side effects. However, rapid emergence of M2 blockers resistance makes imperative the development of new anti-influenza drugs. In the last few years, several groups have synthesised and evaluated several analogues of amantadine and rimantadine. A new series of amantadine and rimantadine with amino acids cysteine was designed and examined for antiviral activity *in vitro* against influenza A virus. The esters were synthesised from the protected amino acid Fmoc-Cys(Acm)-OH and adamantan(amine)e analogues amantadine and rimantadine following a two-step procedure. The compounds exhibit an extremely low toxicity. Derivative of amantadine and rimantadine with Fmoc-Cys(Acm)-OH exhibit low activity against influenza A virus infections.

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2-P7. Application of waste glycerol from biodiesel production for obtaining modifiers for friction reduction

Z. Glavcheva-Laleva [1], L. Varadinova [2], S. Kerekov [3], D. Pavlov [4], I. Glavchev [2]

[1] *Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences,*
Acad. G. Bonchev St., Bldg. 9, 1113 Sofia, Bulgaria
[2] *University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria*
E-mail: ivgl@uctm.edu
[3] *NITIAT Ltd., Sofia, Bulgaria*
[4] *Angel Kanchev University of Ruse, Ruse, Bulgaria*

Glycerol mono oleate (GMO) was made from waste glycerol from biodiesel production by condensation of oleic acid in the presence of catalyst titanium alcoholates. The total acid number was determined by titration of the samples from GMO with alcohol solution of potassium hydroxide (ASKON). Neutralisation of extra oleic acid was performed by alcohol solution of methylamine and ASKON. The prepared sample from the obtained modifier was analysed by a standard method using a four-ball technique and the reduced friction was assessed.

2-P8. Nucleophilic reaction of sulphinic acids with conjugated alkenes and halonitroalkanes

S. Ivanova, M. Dimov, I. Nacheva

Department of Organic Chemistry, Prof. Asen Zlatarov University, 8010 Burgas, Bulgaria
E-mail: viperogr@abv.bg

Sulphinic acids are an unique example for reactants that undergo a facile nucleophilic addition to α,β-unsaturated alkenes, which results in the formation of Michael-type products [1].

Arylsulphonyl nitroethanes were prepared by a nucleophilic substitution reaction. The suggested method of synthesising arylsulphonyl nitroethanes has some important advantages over the methods known so far. It is a relatively fast one-stage process without by-products and there is no need of further procedure to isolate the main products from the reaction mixture. The final compounds possess sufficient purity [2].

Acknowledgement: This work was supported by the Research Centre of Prof. A. Zlatarov University of Burgas.

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2-P9. Study of the 4-hydroxymethylfurfural reaction with ozone

P. Karakashkova, S. Rakovsky, M. Anachkov

Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria
Fax: *+359-2-9712967, e-mail*: *petia.karakashkova@gmail.com*

4-Hydroxymethylfurfural (HMF) is a by-product of sugar production. The aim of this work is to investigate the possibility of its utilisation by treating its aqueous solutions with ozone. The peculiarities of ozone absorption during ozonolysis were studied by continuous monitoring of the ozone concentrations at the bubbling reactor outlet. The rate constant of the reaction was determined. The basic products of HMF ozonolysis were identified by using HPLC and ^{13}C NMR spectroscopy. It is demonstrated that the reaction proceeds according to the Criegee's mechanism and ozonolysis features, determined by the HMF structure, were discussed. It is shown that HMF can be transformed quantitatively to oxalic acid.

3-O1. Non-equilibrium crystallisation in systems of the type $Na^+/Mg^{2+}/SO_4^{2-}/SeO_4^{2-}$-$H_2O$

Ch. Balarew, S. Tepavitcharova, S. Kamburov

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
Fax: +359-2-8705024, e-mail:balarew @svr.igic.bas.bg

Many salts in systems of the type $Na^+/Mg^{2+}/SO_4^{2-}/SeO_4^{2-}$-$H_2O$ show a tendency to form supersaturated solutions or broad metastable zones, where no spontaneous crystallisation occurs. Thus, they are appropriate models for studying the crystallisation of metastable phases.

To illustrate unseeded non-equilibrium crystallisation for preparation of new salts hydrates, unknown so far, the double salt $Na_2Mg(SO_4)_2{\cdot}10H_2O$ [1] can be considered. The $Na_2Mg(SO_4)_2{\cdot}16H_2O$ salt [2] is obtained when blödite ($Na_2Mg(SO_4)_2{\cdot}4H_2O$) is exposed to sub-freezing conditions ($T \leq -10^oC$). By using seeded non-equilibrium crystallisation the new $Na_2SeO_4{\cdot}4H_2O$ [3] and $Na_2Mg(SeO_4)_2{\cdot}10H_2O$ salts [3] were obtained. As an example, the seeded non-equilibrium crystallisation of the metastable $Na_2SeO_4{\cdot}7.5H_2O$ using $Na_2SO_4{\cdot}7H_2O$ nuclei is given. Owing to the similarity found between some fragments of their structures, it was concluded that only a similarity between certain structural elements of both salts could be sufficient for nucleation [4].

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3-O2. Nanotechnologies for next generation electrode materials in lithium ion batteries

S. Ivanova, E. Zhecheva, M. Mladenov [1], R. Stoyanova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
Fax: +359-2-8705024, e-mail: svivanova7@gmail.com
[1] Acad. Evgeni Budevski Institute of Electrochemistry and Energy Systems, 1113 Sofia, Bulgaria

Lithium ion batteries based on $LiCoO_2$ and graphite electrodes are nowadays the most effective technology for energy storage. However, in order to meet the global challenges for future economic development, there is a need to elaborate new electrode materials that have a doubled specific energy and power. One chemical approach to achieve these requirements for electrode materials is by taking advantages of leading nanotechnologies. In this communication, we report new data on improving the electrochemical performance of manganese-based electrode materials by engineering of their particle size distribution. This approach is demonstrated to a lithium nickel-manganese spinel, $LiNi_{1/2}Mn_{3/2}O_4$, which is able to replace a $LiCoO_2$-based electrode due to its capability to intercalate lithium reversibly at a high voltage (at about 4.7 V) delivering a high specific energy (about 658 Wh kg^{-1}). It was found that the particle size distribution has a strong impact on rate capability for $LiNi_{1/2}Mn_{3/2}O_4$ and on its interaction with the electrolyte. After spinel storing in electrolyte solutions, the nanosized particles are covered by $LiF/Li_xPF_yO_z/P_2O_5$, while $Ni,MnF_2/Li_xPF_y$ compounds are deposited on the surface of the submicron particles. Ordered $LiNi_{1/2}Mn_{3/2}O_4$ with trimodal particle size distribution displays the best rate capability.

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3-O3. Electrodeposition technique as a useful tool to obtain potential anode materials for Li-ion batteries with different nanoarchitectured morphologies

M. C. López, G. F. Ortiz, P. Lavela, R. Alcántara, J. L. Tirado

Inorganic Chemistry Laboratory, University of Cordoba, Campus of Rabanales (C3), ES-14071, Cordoba, Spain
Fax: *+34-957-218 621, e-mail*: *p32carlo@uco.es*

Electrochemical deposition under galvanostatic regime was carried out using different solutions to obtain a variety of compounds suitable for anodic material in lithium-ion batteries. We report an optimised fabrication of copper-tin material in the form of nanowires perpendicular to the current collector with diameters ranging between 80 and 100 nm and 2 μm length, Co-P alloy films whose morphology can be controlled from leopard-like spots to hexagonal symmetric particles, and nanocomposite of NiO and Fe_2O_3 which forms a rough texture and seems to be made up of several nanosheets interconnected forming a microporous structure. All these different shapes can be attuned, even obtained different morphologies and compounds by simply varying the electrodeposition parameters (concentration of species in the dissolution, time and electrodeposition current, temperature, etc.). This approach aims to validate fabrication of thin films containing nanoparticles with different morphologies and taking the advantage of using an additive-free route for potential application in 3D-Li micro-batteries. The resulting films are examined in lithium test cells as potential anode materials for lithium-ion batteries.

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3-P1. Study on the composition of biogenic iron-containing materials obtained by cultivation of *Leptothrix genus* bacteria in different feeding media

M. Shopska, D. Paneva, G. Kadinov, Z. Cherkezova-Zheleva, I. Mitov, V. Groudeva [1]

Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria
Fax: *+359-2-9712967, e-mail*: *shopska@ic.bas.bg*
[1] Faculty of Biology, St. Kliment Ohridski University of Sofia, 8 Dragan Tsankov Blvd., 1164 Sofia, Bulgaria

Biogenic iron materials exhibit useful combination of electric, magnetic, adsorption, and catalytic properties and are widely investigated in the last years. Production of such materials does not require big investments and additional energy delivery because iron bacteria are normal cell metabolites. Bacteria from the *Leptothrix* genus develop intensively in *Sphaerotilus-Leptothrix* group bacteria isolation medium (SLGBIM), as in Fedorov and Lieske media. These media are quite different in their composition and could define the properties of biogenic material. The present study concerns the composition of biomass samples and an attempt is made to clear up the reasons for observed differences between laboratory obtained and natural biomasses from water sources in the Vitosha Mountains (Bulgaria). The biogenic materials were cultivated after 20 or 40 days in the respective medium. Control samples were obtained under the same conditions and procedures in bacteria-free nutrition media. FTIRS, XRD, and Mössbauer spectroscopy were used in the research. α-FeOOH, β-FeOOH, γ-FeOOH, and γ-Fe_2O_3 at different ratios were found in the biomass and in the control samples, together with SO_4, CO_3, and PO_4 groups. All the samples contained organic rest of bacterial origin. Comparative analysis showed that the increase of cultivation process duration resulted in formation of a larger amount of iron oxyhydroxides. Iron oxides were not found in the natural biogenic materials. Their availability in the studied samples is a result of ,chemical reactions that occur under the selected conditions: passive oxidation, H_2O_2 excretion due to bacterial metabolism, change of pH, competitive redox processes, disproportionation reaction, and asynchronous bacterial culture usage. Formation of various iron compounds by biotic and abiotic Fe^{2+} oxidation indicates that medium composition, incubation conditions, and presence of nucleation sites influence the produced biogenic materials.

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3-P2. Comparing extraction, synergism and separation of rare earths by use of acidic and neutral compounds in chloroform and one ionic liquid: Is the latter always 'better'?

M. A. Petrova [1], V. B. Kurteva [2], L. A. Lubenov [2], I. Billard [3]

[1] *University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria*
E-mail: ma@uctm.edu
[2] *Institute of Organic Chemistry with Centre of Phytochemistry, 1113 Sofia, Bulgaria*
[3] *Institute Pluridisciplinaire Hubert Curien, Rue du Loess 23, 67037 Strasbourg Cedex, France*

A new pyrazolone derivative, 3-methyl-1-phenyl-4-(4-trifluoromethylbenzoyl)-pyrazol-5-one (HL), was synthesised and fully characterised, and its complexation properties in solution were examined. Mixed ligand chelate extractions of trivalent lanthanoids (La, Nd, Eu, Ho, and Lu) with HL and 5,11,17,23-tetra-*tert*-butyl-25,26,27-tris(dimethylphosphinoylpropoxy)-28-hydroxy-calix[4]arene (S1) or 5,11,17,23-tetra-*tert*-butyl-25,27-bis(dimethylphosphinoylpropoxy)-26,28-dihydroxy-calix[4]arene (S2) as synergists were also carried out in chloride medium at constant ionic strength μ=0.1 and $CHCl_3$ as organic phase. Interactions between extractants in deuterochloroform were studied by ^1H, ^{13}C, and ^{31}P NMR spectra. The composition of the extracted species was established as $LnL_3{\cdot}HL$ (L represents HL anion) with HL as a single extractant, and as $LnL_3{\cdot}S$ in the presence of the phosphorus-containing calix[4]arene. Values of the equilibrium constants were calculated. The influence of the level of substitution of *tert*-butyl-calix[4]arene on the extraction process was discussed. Synergistic enhancement and separation factors between metals were evaluated. Finally, the extraction of La(III) and Eu(III) ions was performed by using an ionic liquid, 1-methyl-1,3-butylimidazolium-bis(trifluoromethanesulphonyl)imide, as a diluent and by varying the type of ligand.

3-P3. Rubidium and cesium Tutton compounds M2'M''(XO4)2·6H2O (M' = Rb, Cs; M'' = Mg, Co, Ni, Cu, Zn; X = S, Se): Preparation, X-ray powder diffraction and infrared spectroscopy

V. Karadjova [1], D. Stoilova [2]

[1] *University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria*
E-mail: *vkar@mail.bg*
[2] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Bldg. 11, 1113 Sofia, Bulgaria*

The solubility in a tricomponent systems of the type $M_2'(XO_4)_2$–$M''XO_4$–H_2O (M' = Rb, Cs; M'' = Mg, Co, Ni, Cu, Zn; X = S, Se) has been studied. Infrared spectra of the Tutton compounds are presented and discussed with respect to their crystal structure. Additionally, infrared spectra of mixed crystals of the type $M_{2-x}(NH_4)_xM(XO_4)_2{\cdot}6H_2O$ (x is approximately 0.2, 0.05, 0.10, or 0.15) are presented and analysed in the region of υ_4 of incorporated ammonium ions and water librations.

Analysis of the infrared spectra reveals that ammonium ions included in sulphate matrices exhibit three bands corresponding to υ_4. The same ions included in selenate matrices give rise to four bands. At that stage of our knowledge we assume that some kind of disorder of the ammonium ions included in the selenates occurs. The hydrogen bond strength in the mixed crystals decreases as compared to that in the neat compounds. This is deduced from the frequencies of the water librations due to a decrease in the proton acceptor strength of the SO_4^{2-} and SeO_4^{2-} ions because of the formation of hydrogen bonds between the host anions and the ammonium guest cations (anti-cooperative effect).

3-P4. Studies on the metastable zones in the Na_2SO_4-H_2O and Na_2SeO_4-H_2O systems

S. Kamburov, Ch. Balarew

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria
Fax: *+359-2-8705024, e-mail*: *s.kamburov@svr.igic.bas.bg*

Supersaturated solutions possess a state of supersaturation close to the equilibrium solubility, where no spontaneous crystallization occurs. Ostwald [1] named this zone a metastable zone. The recognition of the metastable zone is of substantial significance for the successful performance and optimisation of the crystallisation process.

The first detailed study on the metastable zones and the spontaneous crystallisation in the Na_2SO_4-H_2O system was made by Hartley et al. [2]. There are no studies so far on the width of the metastable zone of Na_2SeO_4-H_2O.

Since the width of the metastable zone depends on the cooling rate, two series of experiments were conducted with a view to determine the temperature of spontaneous crystallisation of the respective hydrates. Results from the study of spontaneous crystallisation in the Na_2SO_4-H_2O system showed that slow cooling and keeping the supersaturated solution overnight at an appropriate temperature leads to $Na_2SO_4 \cdot 7H_2O$ crystallisation in all cases. Crystallisation from its solutions at a concentration of 29.7 wt.% occurs at about 7.5ºC, and by dilution the temperature is lowered. Spontaneous crystallisation of $Na_2SO_4 \cdot 10H_2O$ occurs only at temperatures below −8ºC. The results of the spontaneous crystallisation in the Na_2SeO_4-H_2O system showed that by slow cooling and keeping the supersaturated solution overnight at an appropriate temperature, $Na_2SO_4 \cdot 7.5H_2O$ crystallises only in some cases, i.e., this is a probabilistic process. Under conditions of fast cooling of the supersaturated solutions (4ºC/min.) the metastable $Na_2SO_4 \cdot 7.5H_2O$ crystallises only in rare cases. In almost every case only $Na_2SeO_4 \cdot 10H_2O$ crystallises spontaneously in the temperature interval from −8 to −15ºC. Clearly, there is a trend of lowering the temperature of spontaneous $Na_2SeO_4 \cdot 10H_2O$ crystallisation or by dilution of its supersaturated solution.

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3-P5. Recovery of silver from zinc cakes

B. Lucheva, P. Iliev, V. Stefanova

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *plasma@dir.bg*

The present experimental study investigates the feasibility of thiosulphate recovery of silver from zinc cakes produced in the process of wet recovery of zinc calcine at KCM Ltd. in Bulgaria. The impact of various factors on the rate of silver recovery through thiosulphate leaching was studied. It was found that the rate of silver recovery was 70−74% within the temperature range of 30−50ºC at 20% pulp density and leaching time of 30 min irrespective of pH of solution. The behaviour of copper, lead, zinc, and iron during thiosulphate extraction was also observed. The pH of thiosulphate solution was kept at 7−8 to reduce the metals that have been transferred to the solution except for silver. After subsequent precipitation of the silver by means of Na_2S, silver concentrate was obtained. The possibility of regeneration of the thiosulphate solution is discussed. The solid residue from thiosulphate leaching contains 10−40 g/t silver and can be processed by a Wälz process.

3-P6. Recovery of valuable elements from TPS bottom ash using a combined method

D. Bojinova, R. Teodosieva

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *bojinova@uctm.edu*

Coal-fired power stations (TPS) over the world generate a large amount of solid wastes from the burning process, such as fly ash, bottom ash, or boiler slag and gypsum from flue gas desulphurisation process. The use of lignite in power generation has led to increasing environmental problems, related not only to gaseous emissions, but also to handling and disposal of ash residues. In this sense, these solid industrial wastes can be considered renewable secondary sources for recovery of valuable metals.

This study presents the results from our investigations, which integrated a thermo-hydrometallurgical method for treatment of bottom ash generated from Enel Maritsa East 3 (TPS). Leaching and extraction procedures were performed by using sulphuric acid (20, 30, and 40 wt.%) under autoclave conditions (100, 120, and 140ºC) and time (120, 240, 360, and 480 min), at a constant value of the liquid/solid ratio. After autoclaving, the samples were treated with water in a reactor by stirring at a constant temperature (50ºC) and time (60 min).

Based on the experimental data obtained the extraction degree of the valuable elements in the liquid after filtration were estimated. The extraction efficiency of aluminium increases significantly on increasing the temperature and achieves a maximum value of 70%. The highest values of extraction were determined as follows: Fe (86.4%), Ca (86.8%), Na (86.6%), Ni (83.3%), and Zn (95.5%). Other studied elements (Mg, K, Mn, Cu, and Cr) reach a maximum leaching value within 46–70%.

3-P7. Green method for Re extraction from oxide copper concentrate

Ch. Tzvetkova, O. Bozhkov

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Akad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria
E-mail: *hrisi@svr.igic.bas.bg*

The oxide copper concentrate produced in Asarel mines by bacterial bioleaching of low quality copper ore in sulphuric acid (pH=1.5–2.5), followed by cementation with iron turnings contains 135 g Re/t. The aim of the present study is to develop a simple green procedure for total extraction of Re from cementation copper concentrate. It is well known that rhenium is present in sulphide ores as ReS_2. The authors' assumption is that during copper bioleaching, probably, part of ReS_2 is also oxidised and present in the Cu concentrate as water soluble perrhenate ions (ReO_4^-). The experiments were carried out for a direct leaching of Re from oxide copper concentrate by water. Results showed that after soaking of the concentrate in cold water and stirring for 1 hour, 22% of the rhenium was leached. The same experiment with hot water resulted in a 44%-extraction of Re. Upon these procedures, copper was not leached from concentrate. For total extraction of Re, a full oxidation procedure of ReS_2 by simple additional treatment of the concentrate was necessary. For this purpose, the concentrate was heated in air at different temperatures and Re was leached by water. Heating the concentrate at 180−200ºC for 1 hour was sufficient for complete oxidation of ReS_2 to water soluble ReO_4^-. Analysis of the Re content in aqueous leaching solutions from pretreated concentrate confirmed a 100% yield of rhenium.

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3-P8. Removal of toxic ions from aqueous solution using raw coal fly ash

P. Vassileva, A. Detcheva

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Akad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria
Fax: *+359-2-8705024, e-mail*: *pnovachka@svr.igic.bas.bg*

High concentrations of metal ions in surface water are generally associated with disposal of industrial wastes. Metal-containing industrial effluents constitute a major source of metallic pollution of the hydrosphere. Metals are of special concern because they are non-degradable and therefore persistent. Adsorption is recognised as an effective and economic method for metal ions removal from wastewater especially if low-cost adsorbents are used.

Bulgarian power plants generate large amounts of highly alkaline fly ash. This waste product has a serious impact on the environment. On the other hand, the chemical composition of fly ashes makes them a potential material for adsorption of metal contaminants in water.

The aim of the present study was to investigate the efficiency of raw coal fly ash in the removal of some metal ions (Hg(II), Pb(II), and Cu(II)) from aqueous solutions and to estimate optimal operation parameters of the process. The fly ash used in the batch experiments was collected from the Bobov Dol coal-fired power plant. The effect of contact time, acidity, initial metal ions concentration on the adsorption was studied. Equilibrium experimental data were fitted to different mathematical equations. It was established that the Langmuir isotherm most adequately describes the adsorption process for all studied ions. A pseudo-first order, a pseudo-second order, and intraparticle diffusion models were used to analyse kinetic data. Maximum adsorption capacities were calculated. The obtained results demonstrate that the studied fly ash could be used as an effective low cost adsorbent for the removal of Hg(II), Pb(II), and Cu(II) ions from aqueous media.

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3-P9. Sulphuric acid autoclave dissolution of Ni-Co sulphide deposit

P. Iliev, V. Stefanova, B. Lucheva

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *pkiliev@uctm.edu*

Upon increasing use of Cu, Ni, and Co metals for different applications and fast depletion of natural land-based resources, worldwide efforts are being made to look for alternative resources for recovery of these metals. Such an alternative resource could be the vast oceans, containing these metals in the form of manganese nodules at a depth of about 4−5 km. Many research groups in different countries have been working for more than three decades on the development of copper, nickel, cobalt, and manganese recovery processes from manganese nodules by pyro-/or hydrometallurgical routes.

During processing deep ocean manganese nodules from the Clairon-Clipperton fraction zone of the Pacific Ocean by combined pyro-hydrometallurgical route the non-ferrous metals were concentrated in two sulphide deposits − copper and mixed nickel-cobalt. In the present work experimental results of sulphuric acid autoclave dissolution of the Ni-Co sulphide deposit, containing as mass.%: 30.37 Ni, 3.13 Co, 8.36 Fe, 0.08 Cu, 0.16 Mn, and 36.8 S, are presented. The effect of the main technological parameters of nickel and cobalt extraction and iron hydrolytic precipitation from solution were studied. The degree of nickel and cobalt extraction was 97.71 and 96.25%, respectively, at T= 363 K, Po_2 = 0.35 MPa, mol H_2SO_4/mol Ni+Co = 0.19, pulp density = 10%, and dissolution time = 240 min, while iron hydrolytic precipitation degree was 99.68%.

3-P10. A comparative study of the effect of different chemical activators on some parameters of activated carbons prepared from coffee husks

N. Ivanova, M. Genev, V. Toteva, R. Nickolov

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *nevena_ivanova89@abv.bg*

Different precursors of vegetable origin, as biomass from wood, oils, husks, pits and plant seeds, and fruits can be used for preparation of activated carbons. Utilisation of agricultural residues presents significant advantages because of their low cost and origin as renewable sources. Many studies have been reported in the recent years involving AC manufacture using agricultural residues, such as apricot or cherry pits, bean and rice husks, nut and corn husks, etc.

This study reports results of activated carbon preparations based on biomass (coffee husks) and of characterisation and comparison of their texture parameters. The laboratory technology is suitable for the purpose of involved carbonisation of the coffee husks: individual or in a mixture with 10, 20, or 30 mass% Bulgarian lignite coal and chemical activation by potassium hydroxide or phosphoric acid.

It was observed that activated carbons derived on the basis of the carbonised coffee husks upon chemical activation by phosphoric acid are characterised by a lower specific surface area as compared to those prepared by potassium hydroxide activation, the latter being characterised by a higher specific surface area (from 1533 to 1708 $m^2\ g^{-1}$).

3-P11. UV-protecting coatings for flexible solar cells application

E. Bubev, M. Machkova, V. Bozhilov, V. Kozhukharov

University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria
Fax: *359-2-8685488, e-mail*: *e.bubev@gmail.com*

It is well known that ultraviolet (UV) radiation protection is very important for numerous photo-sensitive products and devices. This high energetic region of the natural and artificial light spectrum causes various undesirable changes of the organic and polymeric materials, such as polymers, pigments, dyes, paints, and wood. Resulted degradation leads ultimately to a significant change of the physicochemical properties of the organic compounds. The sophisticated construction of flexible solar cells mainly consists of such light sensitive materials. One of the most common methods of UV protection refers to addition of compounds capable of absorbing light at wavelengths shorter than 400 nm. Aimed at depositing transparent layers of the corresponding UV protective coatings, a film forming polymer dispersion (C-700™) was used. UV absorbing benzophenone containing additives of different concentration were used: 2-hydroxy-4-methoxy-benzophenone-5-sulphonic acid (BP-4), under trade name Escalol 577, and 4-hydroxybenzophenone (4HBP). Like all organic compounds, the UV absorbers studied suffer from photodegradation, which is a very significant drawback. This is determined by formation of radicals causing autooxidation.

Film composition and thickness were evaluated to gain knowledge on absorption ability in the UV range, mean surface roughness, wettability, and durability behaviour under inert medium.

Experimental data were obtained by using AFM, UV-Vis spectroscopy, an irradiation test, a sessile drop test (Theta Light optical tensiometer from BiolinScientific equipped with a 60 FPS high speed camera), and a pull-off adhesion test (PosiTest AT-A by DeFelsko).

3-P12. Study of carbon-based nanocomposites with intermetallic nanoparticles (Co-Sn, Ni-Sn)

V. Milanova, T. Petrov, I. Markova, O. Chauvet [1]

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
[1] Institute of Materials, Nantes, France
E-mail: *vlpetrova_mil@abv.bg*

Intermetallic (Co-Sn, Ni-Sn) nanoparticles were synthesised through a borohydride reduction with $NaBH_4$ in a mixture of aqueous solutions of $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, and $SnCl_2.2H_2O$ at different mass ratios of Co to Sn and Ni to Sn. Subsequently, carbon-based nanocomposites were obtained. A ‘template’ technique which involves borohydride reduction of intermetallic nanoparticles on a support (carbon foam, carbon powder, graphite) was used. Samples were studied by scanning electron microscopy, energy dispersive spectroscopy, and X-ray diffraction analysis. The influence of the different used supports on morphology, structure, phase composition, and element composition of the synthesised composite materials was investigated. Phases of $CoSn_2$ (Co:Sn = 1:2), Co_3Sn_2 (Co:Sn = 3:2), Ni_3Sn_2 (Ni:Sn = 3:2), Ni_3Sn (Ni:Sn = 3:1) were found. Their composition corresponded to the phase diagrams of the Co-Sn and Ni-Sn binary systems.

Reductive precipitation by $NaBH_4$ using a template technique with different supports (C foam, C powder, and graphite) is a successful method to obtain nanocomposites of special type of inactive matrix/nanoparticles. Reaction parameters (i.e. concentration of precursors and reducing agent, reaction temperature, and complex agent) can easily be controlled. As a result, fine alloy powders were obtained. The morphology and phase composition of the investigated samples promise good electrochemical parameters. These materials can be used as electrode (anode) materials instead of graphite in Li-ion batteries.

3-P13. Aluminium-modified ZnO as thermoelectric materials

S. Harizanova, E. Zhecheva, V. Valchev [1], M. Khristov, R. Stoyanova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[1] Faculty of Physics, University of Sofia, 1164 Sofia, Bulgaria
Fax: *+359-2-8705024, e-mail*: *sonya@svr.igic.bas.bg*

The capability of thermoelectric materials to convert waste heat into electricity determines them as a key source of ‘clean’ energy for the future. Thermoelectric oxides are nowadays considered more stable and less toxic materials in comparison with conventionally used metals and semiconductors, however, their thermoelectric efficiency is still lower. The state-of-the-art research is mainly devoted to identify new oxide materials of higher thermoelectric efficiency. The aim of this contribution is to study the effect of aluminium additives on the thermoelectric properties of ZnO. All oxides were prepared by precipitation of hydroxide-carbonates followed by thermal treatment between 450 and 700ºC. Al concentration was varied up to 2.0%. The inclusion of Al into the crystal structure of ZnO was monitored by ^{27}Al MAS NMR spectroscopy. The thermoelectric efficiency of oxides was determined by the dimensionless figure of merit (ZT) calculated from the independently measured Seebeck coefficient, electrical resistivity, and thermal conductivity. Doping of ZnO with aluminium yields oxides with improved thermoelectric properties. The selective metal substitution opens new possibilities for optimisation of the thermoelectric activity of oxide-based ceramics.

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3-P14. Sodium deficient nickel manganese oxides as novel electrode materials for lithium ion batteries

M. Kalapsazova, E. Zhecheva, G. Tyuliev [1], R. Stoyanova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[1] Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
Fax: +359-2-8705024, e-mail: maria.kalapsazova@gmail.com

The development of safe and effective energy storage systems becomes a critical factor for future implementation of smart grid technologies. Lithium ion batteries are characterised by high specific energy and power, but they remain still expensive and unsafe. In this communication, we report new data on using sodium deficient nickel manganese oxides, $Na_xNi_{0.5}Mn_{0.5}O_2$, as cheaper and safe electrode materials for lithium ion batteries. For the preparation of the oxides, we have adopted a simple precursor method that involves thermal decomposition of mixed sodium-nickel-manganese acetate salts obtained by freeze-drying. At 700ºC, this method yields $Na_xNi_{0.5}Mn_{0.5}O_2$ with $0.5 \leq x < 0.75$ and a *P3*-type structure. A new structural feature of $Na_xNi_{0.5}Mn_{0.5}O_2$, as compared to well known *O3*-$NaNi_{0.5}Mn_{0.5}O_2$ and *P2*-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$, is the development of layer stacking ensuring prismatic site occupancy for Na^+ ions with shared face on one side and shared edges on the other side with surrounding Ni/MnO_6 octahedra. Lithium intercalation in $Na_xNi_{0.5}Mn_{0.5}O_2$ was carried out in model two-electrode lithium cells of the type $Li|LiPF_6(EC:DMC)|Na_xNi_{0.5}Mn_{0.5}O_2$. The stability of $Na_xNi_{0.5}Mn_{0.5}O_2$ in the electrolyte solution was examined by X-ray photoelectron spectroscopy. It was found that $Na_xNi_{0.5}Mn_{0.5}O_2$ displays a reversible lithium intercalation and a satisfactory rate capability, which determine their potential for use as cathode materials in Li-ion batteries.

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3-P15. Investigations on low-temperature preparation of iron phospho-olivines using dittmarite-type $NH_4FePO_4.H_2O$ precursor

T. Boyadzhieva, V. Koleva, R. Stoyanova, E. Zhecheva

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
E-mail: tanya_jb@svr.igic.bas.bg

Among the iron-based polyanion compounds, the olivine-type $LiFePO_4$ is the most promising cathode material for high-power lithium ion batteries with potential application in hybrid electric vehicles. It is characterised by high capacity, cyclic stability, excellent safety, and low cost. More recently, the thermodynamically unstable sodium analogue $NaFePO_4$ with an olivine-type structure becomes very attractive as a ‘green’ and cheaper electrode material suitable to replace $LiFePO_4$.

In this contribution, we have examined the preparation of both $LiFePO_4$ and $NaFePO_4$ phospho-olivines by topotactic reactions at low temperatures using $NH_4FePO_4.H_2O$ as a structure template. The phase composition in the $NH_4FePO_4.H_2O$-$NaCH_3COO.3H_2O$ reaction system was studied in the temperature range of 75−200ºC at different mole ratios of reagents and reaction times. It was established that under all experimental conditions the reaction yields a mixture of different phosphate phases instead of target $NaFePO_4$. The ion exchange of NH_4^+ from $NH_4FePO_4.H_2O$ for Li^+ is carried out in molten salts using $LiCl$-$LiNO_3$ and $LiOH$-$LiCl$ eutectic mixtures at 270 and 325ºC, respectively. Experimental conditions for the synthesis of high-purity $LiFePO_4$ were established. SEM images showed a plate-like morphology of target $LiFePO_4$, which is inherited from the precursor.

The plate-like aggregates were composed by nanoparticles of sizes below 80 nm, which is beneficial for facilitated lithium mobility.

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3-P16. Dicalcium phosphate dihydrate and tetracalcium phosphate derived cements

K. Sezanova, D. Rabadjieva, R. Ilieva, S. Tepavitcharova, R. Gergulova

Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria
E-mail: *ksezanova@abv.bg*

Formation of calcium phosphate cements starting from DCPD (dicalcium phosphate dihydrate) and TTCP (tetracalcium phosphate) powders was designed by thermodynamic modelling and experimental studies. A number of systems (DCPD/TTCP powders/inorganic acid/organic acid/water) were thermodynamically modelled. The influence of dissolution/crystallisation processes that occur on the grain surface was evaluated. The liquid phases for the experiments were K_2HPO_4, H_3PO_4, acetic acid, α-amino acetic acid, lactic acid, tartaric acid, citric acid, ascorbic acid or salicylic acid, all of them being at different concentrations. Xanthan gum and/or glycerin were used as a modifier to improve cement manipulation.

The obtained cements were compared with respect to registered phase transformation, initial and final setting times, and residual acidity. Best results were found in cases of diluted (30−40%) lactic, citric, and acetic acids. *In vitro* testing for SBF showed that they are prospective as biomaterials for bone defects feeling.

3-P17. Thermodynamic properties of tellurites of some d elements

L. Atanasova [1], G. Baykusheva-Dimitrova [2], G. Gospodinov [2]

[1] *Inorganic Chemical Technology Department, Prof. Dr. A. Zlatarov University of Burgas, 1 Prof. Yakimov St., 8010 Burgas, Bulgaria*
Fax: *+359-56-880249, e-mail*: *lgatanasova@btu.bg*
[2] *Inorganic and Analytic Chemistry Department, Prof. Dr. A. Zlatarov University of Burgas, 1 Prof. Yakimov St., 8010 Burgas, Bulgaria*

The aim of the present study is to evaluate specific molar capacities and the thermodynamic properties of the $CuTeO_3$ and $HgTeO_3$ compounds.

Studies on tellurites of some d elements from the first and second group of the periodic table are significant to gain information about an important field of inorganic chemistry, such as the chemistry of tellurium. Tellurites discussed in the present paper are used for preparation of optical glasses with special properties for optoelectronics, nuclear and power industries. Glasses containing TeO_2 have been studied for both scientific and practical purposes because their high refraction, good transmittance of infrared light and high dielectric constant make them suitable for use in optics. The TeO_2 compounds with transition metal oxides have semiconducting, electromagnetic, and other specific properties. Mercury tellurite is the base of many important semiconductor materials applied for far-infrared photodetectors.

Metal tellurites of $CuTeO_3$ and $HgTeO_3$ used for the experiments were synthesised from the corresponding metal oxide and high purity TeO_2 (99.999%). The synthesised tellurites were prepared for chemical analysis, differential thermal analysis, and X-ray analysis.

The specific heat capacity of the studied tellurites was determined by means of a DSC-III Setaram differential scanning calorimeter. The samples were finely ground and sieved (0.25 mm^2). For each tellurite, four samples were studied and the average was calculated. The relative error did not exceed 0.1%.

The method of regression analysis was used to process the experimental data on the dependence of specific heat capacity on temperature. By regression analysis, the coefficients in the following equation were determined: $Cp = a + bT - cT^{-2}$ in the temperature interval of 403−553 K. The calculated thermodynamic properties were entropy, enthalpy, and Gibbs function. The standard molar entropy $\Delta_0^{T'} S_m^0$, where $T' = 298.15$ K, was calculated by the method of Koumok. The use of the studied tellurites is related to their thermodynamic properties, like specific molar capacity ($C_{p,m}$), enthalpy ($\Delta_{T'}^{T} H_m^0$), entropy ($\Delta_{T'}^{T} S_m^0$), and Gibbs energy ($-\Delta_{T'}^{T} G_m^0$).

3-P18. Simulation of stable and metastable sea-type carbonate systems for optimisation of $MgCO_3.3H_2O$ precipitation from waste sea brines

A. Kovacheva, D. Rabadjieva, S. Tepavitcharova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Akad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria
E-mail: *antonina1975@abv.bg*

The thermodynamic simulation of the systems Na^+, Mg^{2+}/Cl^-, $CO_3^{2-}//H_2O$ and Na^+, Mg^{2+}/SO_4^{2-}, $CO_3^{2-}//H_2O$ using the Pitzer method at 25ºC revealed that both stable and metastable crystallisation can take place. On this basis, alkaline precipitation of metastable $MgCO_3.3H_2O$ from waste sea brines was thermodynamically simulated. Crystal chemistry and kinetic considerations of the crystallising salts showed that quick precipitation and re-crystallisation ensure $MgCO_3.3H_2O$ crystallisation without further transformation to metastable $4MgCO_3.Mg(OH)_2.4H_2O$ and stable $MgCO_3$. Optimum process conditions were found by laboratory and pilot-plant experiments and purified $MgCO_3.3H_2O$ was produced.

3-P19. Study of the bee family strength: Fertility of the queen bees and productivity of the family

Z. H. Garova

Asen Zlatarov Secondary School, 1 Chernorizets Hrabar St., Parvomay, Bulgaria
E-mail: *garova_69@abv.bg*

Our objective was to examine the laying activity of queen bees concerned with brood amount and food supplies. We constructed a combined cell transmission of queen bees and brood chamber. The tasks included experiments to proof the power of the bee family, problems of producing a combined cell, finding a relation between ecology and safety conditions of the bee families. Research activities done by students from the Asen Zlatarov Secondary School (town of Parvomay) involved four bee hives at the bee garden of the school course equipped with a combined cell transmission of queen bees and brood chamber.

Experiments, proposed by Associate Professor Plamen Petrov (Agrarian University, Plovdiv) were performed from 2nd August to 6th September 2011 and from 22nd to 18th April 2012. Four beehives, described above, were used for the experiments. Many students participated in these experiments, however, most of the work was done by Anelia Georgieva and Maria Trendafilova, and chemistry teacher Zlatka Garova.

Before experiment itself, we made a volumetric framework and made a dual cell for giving a queen bee.

The amount of brood was determined by the area that it occupies in the different honeycombs. It was measured using a volumetric framework. It was made of bee wires connected with tacks and has 12 squares (5×5 cm), each of which can fit about 100 workers' cells.

On 22nd March 2012 four strong colonies with give-Blatt hives (No 1, No 2, No 3, and No 4) were counted and the quantity of brood and food reserves were evaluated. The measuring frame was placed on each honeycomb and we counted only the number of the sealed brood. The number of the sealed brood was multiplied by 100 and divided into 12 squares for each frame where there was a brood. This attempt was made 3 times (4th April and 18th April) in 12 days (3rd day − pre-pupa, 9th − day pupa) to predict the number of bees that will hatch after 21 days. Thus, the average daily laying activity of the queen bees was calculated.

To evaluate the productivity of the bee family, we determined the amount of honey in each honeycomb. It is known that the amount of food in a honeycomb with a sealed honey was 3.5−4 kg and a beehive should not have less than 8−12 kg of honey.

The experiments were made three times in 12 days for a period from 2nd August to 6th September 2011. The purpose was to count the fertility of queen bees. The quantity of brood was counted by a volumetric framework and we also evaluated the food reserves.

In conclusion, the results prove that the power of the bee family provides brood and honey quality. The amount of brood is correlated with the area located on the bee combs. The quality of brood gives information about queen bee fertility, while the quantity of food reserves is defined according to the area of honeycombs.

4-O1. Possibilities and limitations of different inductively coupled plasma optical emission spectrometry systems in the determination of trace elements in matrices with various compositions

N. Velitchkova [1], S. Velichkov [2], N. Daskalova [2]

[1] Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Block 24, 1113 Sofia, Bulgaria
[2] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria
Fax: +359-2-8724638, e-mail: niaveli@geology.bas.bg

The present study presents conventional figures of merit such as detection limits, background behaviour, spectral and multiplicative interferences in the presence of matrices with different compositions depending on the various designs of the inductively coupled plasma (ICP) and spectrometer configurations. Various types/modes of sample introduction systems including conventional pneumatic and ultrasonic nebulisation are compared. The investigations cover determination of: (i) traces of Y, Sc, and rare earth elements in 'pure' rare earth matrices; (ii) Hg, As, Se, Zn, Be, Pt, Cd, Sb, B, Cu, Mn, Pb, Sn, Bi, Cr, U, Tl, and Ba in environmental materials (waters, sediments, and soils) containing Al, Ca, Mg, Fe, and Ti as a complex matrix; (iii) rhenium in molybdenum and copper concentrates containing Mo, Al, Ti, Fe, Mg, Ca, and Cu as matrix constituents and (iv) As, Hg, Se, Cd, Sb, Pb, and Tl in biological materials. An optimisation procedure of the operating conditions to lower the detection limits was applied in all cases.

It can be concluded that by using a 40.68-MHz ICP equipped with a spectrometer with practical spectral bandwidth within 5−10 pm for the spectral region from 160 to 800 nm and high dynamic detectors (photomultiplier tubes), one can select prominent lines free or negligibly influenced by line interference in the presence of the corresponding matrices. The selected prominent lines ensure detection limits, which satisfy the requirements of every day practice without the need of separation/preconcentration procedures.

4-O2. Surface modification of silica-coated $MnFe_2O_4$ magnetic nanoparticles applied as a sorbent for solid phase extraction of trace elements

D. Georgieva, N. Ivanova, V. Stefanova

Department of Analytical Chemistry and Computer Chemistry, Paisiy Hilendarski University of Plovdiv,
24 Tsar Asen St., 4000 Plovdiv, Bulgaria
E-mail: georgieva@uni-plovdiv.net

A method for surface modification of silica-coated manganese ferrite nanoparticles ($MnFe_2O_4$-α-SiO_2) was developed. Ammonium pyrrolidine dithiocarbamate (APDC) was used for impregnation and to improve the sorption capability of silica-coated magnetic nanoparticles towards V, Cr, Co, Ni, Cu, Zn, Cd, Tl, Pb, and Bi. Experimental conditions influencing APDC immobilization on the nanoparticle surface such as: nanoparticle conditioning; solution pH; contact time, and ligand quantity were optimized. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to monitor the modification by means of sulphur analysis. Modified nanoparticles ($MnFe_2O_4$-α-SiO_2-APDC) were tested as a sorbent for magnetic assisted solid phase extraction prior to inductively coupled plasma mass spectrometry (ICP-MS) analysis.

This sorbent preserved by a silica layer shows better stability in acidic media, compared to bare manganese ferrite nanoparticles, which leads to alleviation of matrix effects during ICP-MS measurement. Together with this, impregnation with APDC enhances complex formation of studied analytes on the nanoparticle surface, thus improving extraction efficiency.

4-O3. Methods for chemical analysis of undesired sediment formed in a high-pressure near zero sulphur diesel hydrotreater

A. Surleva [1], D. Stratiev [2], E. Todorova [1], K. Hristov [1], K. Stanulov [1], I. Shishkova [2], A. Pavlova [2]

[1] University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: surleva@uctm.edu
[2] Lukoil Neftochim, Burgas, Bulgaria

Formation of sediments in diesel hydrotreating installations has recently been considered a severe problem demanding fast and cost effective solutions. Salt formation in various refinery units and methods for sediment removal are discussed in the literature. Even now, there is no methodology and reliable data on identification of chemical species in sediments formed in middle distillate hydrotreaters. This study presents results of the application of several analytical techniques for determination of the composition of diesel hydrotreater heat exchanger deposits at Lukoil Neftochim Burgas upon use of Topsøe high activity Co-Mo TK-576 Brim catalyst. Analytical results from ion chromatography, argentometric titration, ICP-AES, thermogravimetry, DCS, X-ray and GC-MS techniques proved that studied samples contained 36.89% Cl^-, 23.28% NH_4^+, 9.6% NO_3^-, and less than 200 ppm of metals (Fe, Mn, Zn, Ca, and Na). The following composition of the deposit was supposed: 46.6% NH_4Cl, 9.6% NO_3, 13.6% organic Cl^-, and about 30% water, organic impurities (carboxylic acids and naphthenic hydrocarbons), and corrosion products. Numerical investigation of the temperature field in the area of deposit was performed in order to prove possibilities for NH_4Cl crystallization. Reliable data about chemical composition allowed this study of sediment origin and the development of appropriate technological solutions to start prevention.

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4-O4. Application of inductively coupled plasma optical emission spectrometry in the determination of platinum group elements in different materials

P. Petrova [1], N. Velitchkova [2]

[1] Faculty of Chemistry, Neofit Rilski Southwest University, 66 Ivan Mihailov St., 2700 Blagoevgrad, Bulgaria
[2] Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Block 24, 1113 Sofia, Bulgaria
E-mail: petya_dukova@yahoo.com

The economic and geological importance of platinum group elements has led to the development of analytical methods for their quantification in different types of samples: geological, environmental, and catalysts in catalytic converters. A spectral interferences database for selected prominent lines was obtained. For direct determination of Pt, Pd, and Rh the following detection limits were reached: platinum ores – 1700, 1440, and 900 ng g^{-1} for Pt, Pd, and Rh, respectively, road dust – 1540, 1150, and 740 ng g^{-1} for Pt, Pd, and Rh, correspondingly, and catalytic converters – 350, 550, and 300 ng g^{-1} for Pt, Pd, and Rh, respectively.

The detection limits for direct determination of Pt, Pd, and Rh in road dust are higher in comparison with requirements of the environmental science. An improvement of the detection limits in the determination of Pt and Pd in environmental materials by inductively coupled plasma optical emission spectrometry (ICP-OES) was achieved by development of a column method with 2-mercaptobenzimidazole immobilised on activated carbon for the preconcentration of Pt and Pd and separation of the matrix elements Al, Ca, Fe, Mg, and Ti. The interest in activated carbons is determined by their unique properties, such as large specific surface area, strongly developed micro porosity and the possibility to modify their surface and texture. The final sample solution was introduced into the ICP-OES by an ultrasonic nebuliser. The following detection limits were reached: Pt – 3.3 ng g^{-1} and Pd – 4.0 ng g^{-1}. These detection limits satisfy environmental requirements.

The accuracy of the analytical results was experimentally demonstrated by the analysis of three certified reference materials: SARM 7, Pt-ore, exhausted auto-catalyst certified reference material SRM 2556 and BCR-723 (road dust).

4-P1. Comparative study of the trace element content in Bulgarian bottled mineral waters

R. Velinova, A. Detcheva, S. Mitsiev, M. Karadjov [1], J. Jordanov, E. Ivanova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria
Fax: +359-2-8705024, e-mail: raligeorgieva@svr.igic.bas.bg
[1] Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 24, 1113 Sofia, Bulgaria

The contents of S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, As, Br, Rb, and Ba in several brands of Bulgarian bottled mineral waters (Gorna Banya, Kom, Thorn Spring, Devin, and Mihalkovo) were determined by total reflection X-ray fluorescence (TXRF) analysis using gallium as an internal standard using an optimised procedure. The content of S, Cl, K, and Ca was at a mg l^{-1} level, while that of Mn, Fe, Ni, Cu, Zn, As, Br, Rb, and Ba − at a lower µg l^{-1} level. Trace element content of the mineral waters did not considerably change (less than ±30%) over a storage period of approximately 2.5 years after bottling. This is an evidence for the stability of the trace element content of the bottled waters during prolonged storage. The precision of the TXRF results for trace element content in the analysed waters is characterised by an RSD of 5–16%. The natural purity and the stable trace element content of Bulgarian mineral waters make them a high-quality product on the local and European market of potable waters.

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4-P2. Colouration of medieval glass bracelets studied by total reflection X-ray fluorescence analysis

A. Detcheva, R. Velinova, M. Karadjov [1], E. Ivanova, J. Jordanov

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria
Fax: +359-2-8705024, e-mail: albena@svr.igic.bas.bg
[1] Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Block 24, 1113 Sofia, Bulgaria

The contents of 3d-transition metals in fragments of medieval glass bracelets were determined by total reflection X-ray fluorescence (TXRF) analysis using gallium as internal standard. The TXRF procedure was optimized and the certified reference material BAM-S005 (Soda-Lime-Glass Type A) was used for method validation. It was proved that Co and Fe elements are responsible for colour generation in the investigated glass samples. The precision of the determinations was characterised by an RSD of 7–10%.

Resulting data confirm the suitability of TXRF for colouration studies of archaeological glasses. Small sample amounts were required and any digestion procedure was avoided. A very important feature of TXRF is that it enables a quick and simultaneous determination of a large number of elements present in the glass artefacts, even if the concentrations, which have to be measured, range down to the trace level. Based on analytical data obtained, conclusions were drawn about the colouring technologies applied by medieval Bulgarian glassmakers.

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4-P3. Synthesis, characterisation, and adsorption properties of novel mesoporous hybrid materials

N. Velikova [1], P. Vassileva [2], A. Detcheva [2], R. Georgieva [2],Y. Vueva [1], Y. Ivanova [1]

[1] University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
Fax: +359-2-8685488, e-mail: nina.e.v@abv.bg
[2] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria

Mercury and its derivatives are among the most toxic contaminants of the industrial wastewater. One of the effective methods to remove inorganic Hg(II) ions from wastewater is the use of adsorbents modified by compounds incorporating sulphur containing organic groups. In the present study the adsorption properties of mesoporous silicas with intraframework functional group towards Hg(II) ions were studied. The new nanostructured materials were synthesized by sol-gel route by co-condensation of the organosilane precursors bis[3-(triethoxysilyl)propyl]tetra sulphide (BTPTS) and tetraethoxylsilane(TEOS) in the presence of non-ionic surfactant triblock copolymer (Pluronic P123). The surfactant was used as a template for improving the porosity of the hybrid gels. The synthesised materials have been characterised by FTIR, ^{13}C NMR, ^{29}Si NMR, DTA/TG, SEM, and BET analysis.

The adsorption properties of mesoporous silicas containing sulphur groups towards Hg(II) ions were investigated by the batch method. Experiments were carried out in acidic medium. Adsorption kinetics was also investigated. A pseudo-first order and a pseudo-second order models were used to analyse the kinetic data. Equilibrium data were fitted to linear Langmuir and Freundlich models and maximum adsorption capacities were calculated. The Langmuir equation showed a better correlation with the experimental data than the Freundlich model. Possibilities for desorption of Hg(II) ions were also estimated. All hybrid materials exhibited a high adsorption capacity for mercury ions and could be used for their removal from aqueous solutions in acidic medium.

4-P4. New method for indirect determination of ethylene bis(dithiocarbamates) by inductively coupled plasma optical emission spectrometry measurement of sulphur

D. Chakarova-Dimitrova, V. Kmetov

Department of Analytical Chemistry and Computer Chemistry, University of Plovdiv, Bulgaria
Fax: +359-32-261337, e-mail: dilldimitrova@yahoo.com

Dithiocarbamate fungicides are one of the most common classes of pesticides used in agriculture. The present work is focused on ethylene bis(dithiocarbamates) (EBDs) which are fungicides from the so-called ‘group of maneb’ − zineb, maneb, and mancozeb and their technical materials, which are produced in Agria S.A. factory near the city of Plovdiv. The production of these fungicides is based on synthesis of ethylenediamine, sodium hydroxide and carbon disulphide to yield Nabam. Precise measurements of the active substance in the formulated products have to be made before bringing them to the market. The official (CIPAC) method for determination of EBDs active substance is based on classical titrimetric determination of the carbon disulphide mass fraction produced after thermal degradation of ethylene bis(dithiocarbamates).

This study suggests a new method for EBDs determination by indirect measurements of sulphur bonded to the product. Two dissolution procedures in alkaline medium were examined using: (i) NaOH and (ii) ammonia. The latter was found more suitable for subsequent instrumental analysis. Atomic emission spectra of sulphur were measured by means of inductively coupled plasma optical emission spectrometer (Thermo scientific iCAP 6300 ICP-OES). Sulphur spectral lines in the near ultraviolet region at 180.731, 182.034, and 182.624 nm were observed using both radial and axial viewed plasma. Analytical parameters have been optimised in respect to achieve robust calibration and maximum signal stability with better repeatability of results.

The suggested inductively coupled plasma optical emission spectrometry method could be a better alternative to the conventional classical methods.

4-P5. Application of enaminones as new ligands for cloud point extraction of lanthanides

E. K. Varbanova, P. A. Angelov, K. K. Simitchiev, V. M. Stefanova

Paisiy Hilendarski University of Plovdiv, 24 Tsar Asen St., 4000 Plovdiv, Bulgaria
E-mail: *evarbanova@uni-plovdiv.net*

A representative of the enaminone class was used as a ligand for cloud point extraction (CPE) of rare earth elements (REEs) from aqueous medium. Extraction parameters such as water phase pH (2−12), heating temperature (30−70ºC), incubation time (15−75 min), and type and quantity of surfactant were optimized. After extraction, the analyte concentrations in the residual water and in the surfactant-rich phase were measured by inductively coupled plasma mass spectrometry (ICP-MS). Spectral interferences for all isotopes of REEs were studied by comparison of standard (no gas) and collision cell mode (He gas). Where possible, isotopes, free from interference, were selected or collision gas was applied to reduce interference. The separation procedure based on the new ligand shows a high selectivity for lanthanides towards alkali and alkaline earth metals, which makes it promising in respect to alleviation of interferences arising from concomitant components in natural waters. The non-spectral matrix effects were corrected by internal standardisation and matrix-matched calibration. Optimal conditions for ICP-MS analysis of lanthanides were established.

4-P6. D-ICP analysis of fluid inclusions in natural quartz from Madan ore district of Bulgaria

L. P. Ivanova, N. B. Piperov, A. N. Aleksandrova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria
Fax: *+359-2-8705024, e-mail*: *lidia@svr.igic.bas.bg*

The present study describes a D-ICP-AES analysis of fluid inclusions in quartz samples from the main ore vein of Krushev Dol Pb-Zn deposit of Madan ore district (Rhodope Mountains, Bulgaria). It reveals indisputable advantages of the D-ICP-method for analysis of fluid inclusions as a typical bulk technique. Comparison with LA-ICP-AES as a point method is made. Assembling of the main parts of the analytical line is shown. A 32-channel ICP spectrometer (SPECTROFLAME) was utilised. An additional aim of this study is the choice of the mineral sample, which can be used as a laboratory standard with respect to fluid inclusions. The study emphasizes on the choice of grain fractions, a correlation between grain size/masses and analytical signal, the sample preparation, and the results obtained by the D-ICP method in comparison with D(C)-leach-AAS and LA-ICP-MS. Results for X/1000 Na atomic ratios (i.e. mmol/mol) for some elements are presented. Somewhat idealised time-resolved curves of the analytical signal for 14 elements (Al, As, Ca, Cu, Fe, K, Li, Mg, Mn, Na, Pb, S, Si, and Zn) as a function of temperature are given. A brief comparison between the D-ICP and LA-ICP methods leads to a conclusion that both techniques have close, but not contradicting, fields of application.

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4-P7. Voltammetry of some aminohydantoin derivatives in the presence of Ni(II) ions at static mercury drop electrode

S. Georgieva [1], P. Todorov [2], Z. Genova [3], P. Peneva [3]

[1] Department of Analytical Chemistry, University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *st.georgieva@uctm.edu*
[2] Department of Organic Chemistry, University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
[3] University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria

A voltammetric determination of 3-amino-5,5-dimetylhydantoin and 3-amino-5,5-diphenylhydantoin using a Ag/AgCl (3-mol l^{-1} KCl) electrode as a reference electrode, a static mercury drop electrode as a working electrode, and a carbon electrode as an auxiliary electrode was investigated. The voltammetric behaviour of the aminohydantoin derivatives was studied under various experimental conditions, e.g. pH of the electrolyte solution, scan rate and sweep mode (direct current, differential pulse, and square wave). The complex formation between Ni(II) and aminohydantoin derivatives at a temperature of 20±1ºC in solutions of ammonium buffer (pH = 8.5±0.1) and different ligand concentrations was also studied by differential pulse polarography and cyclic voltammetry.

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4-P8. Investigation of the complex formation reaction between TiO^{2+} and gallotannin in excess of ligand

L. Costadinova, T. Kolusheva, P. Atanasova, E. Stefanov, A. Marinova

Department of Analytical Chemistry, University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *petiacv_atanasova@abv.bg*

We studied the equilibrium reaction of formation of the TiO^{2+}-tannin (T-tannin) complex at pH 4, maintained by formate buffer. A PMR spectrum of the ligand, hydrolysable tannin ($C_{76}H_{52}O_{46}$), with molar mass M = 1701.20 g mol^{-1} shows the formation of oligomers and confirms the composition of the tannic acid containing 10 galloil residues. By means of UV-VIS and IR spectroscopy we proved the formation of a complex compound with a coordination bond ($T{>}C{=}O \rightarrow TiO^{2+}$) and the formation of associates in solid phase. We found the composition of the complex $[TiOT]^{+}$ using the mole-ratio method with $C_{TiO}{}^{2+}$ = const and $C_{tannin}/C_{TiO}{}^{2+} = 0 \div 4$, along with the A= f ($C_{TiO}{}^{2+}$) function with $C_{tannin}/C_{TiO}{}^{2+} \geq 2$. The complex compound with distinctive yellow colour absorbs photons at $\lambda = 323$ nm. Its molar absorptivity is $\varepsilon^{323} = 4.43\times10^{4}$ l mol^{-1} cm^{-1}. The complex formation reaction is completed at $pH \leq 3$ ($\beta_{TiOT} > 10^{7}$). The stability constant of the complex at a temperature of 25±10ºC has a value of $\beta_{TiOT} \sim 10^{10}$.

4-P9. Metal ion directed template synthesis with 2-acyl-1,3-indandiones and ethylenediamine

A. Ahmedova, K. Ilieva, B. Nikolova, V. Chalakova

Faculty of Chemistry and Pharmacy, University of Sofia, 1 J. Bourchier Blvd., 1164 Sofia, Bulgaria
Fax: +359-2-9625438, e-mail: Ahmedova@chem.uni-sofia.bg

The unexpected regioselectivity of 2-acetyl-1,3-indandione in condensation reactions with different amines has already been noticed but remained less explored. On the other hand, reactions with diamines, aromatic or aliphatic, proceed with formation of three different types of products depending on the molar ratio of the reagents and the type of the side chain of the acyl group. Moreover, as cyclic β-triketones, the 2-acyl-1,3-indandiones are excellent complexation agents forming stable complexes with a wide range of metal ions. Herewith, we describe our attempts to exploit these two characteristics of the title compounds to obtain macrocyclic structures through metal ion directed template synthesis. The used 1,3-indandiones bear different acyl substituents that render distinctive optical properties of the compounds. Aliphatic ethylenediamine was used in order to obtain cyclam-like macrocycles conjugated with the 1,3-indandione ring. Two different metal ions were used as templating agents, namely Cu(II) and Ni(II). The synthetic procedures involve condensation under reflux either using the corresponding metal complexes of the 2-acyl-1,3-indandiones series, which were prepared before use, or by directly reacting all three components. The results will be presented with main emphasis on the optical properties of the formed macrocyclic compounds. The substituents effect and the reaction conditions will be discussed in view of the accomplishment of complete cyclisation. All products were characterised by vibrational (IR) and electronic (UV-Vis) spectroscopy as well as nuclear magnetic resonance (NMR) and mass spectrometric (MS) methods. The structure of the products will be discussed.

4-P10. Mixed-ligand ruthenium complexes of terpyridine and 2,4-dithiohydantoins

S. Asanova, A. Ahmedova, P. Marinova [1]

Faculty of Chemistry and Pharmacy, University of Sofia, 1 J. Bourchier Blvd., 1164 Sofia, Bulgaria
Fax: +359-2-9625438, e-mail: Ahmedova@chem.uni-sofia.bg
[1] Faculty of Chemistry, University of Plovdiv, 24 Tsar Asen St., 4000 Plovdiv, Bulgaria

The complexation ability of a series of cycloalkane-5-spiro-2,4-dithiohydantoins with some metal ions from the first transition row has recently been studied. Some general conclusions on the coordination modes of the used ligands could be drawn by employing an integrated approach of quantum-chemical and experimental spectroscopic methods. Recent data on new Pt(II) and Ru(II) complexes of 2,4-dithiohydantoins with bulky aromatic substituents at the 5th position in the hydantoin ring indicated a moderate anticancer activity against three types of human cancer cell lines. The structure description of the complexes, however, remained elusive due to expected formation of polymeric complexes through coordination of both thione groups of each ligand. Therefore, a new synthetic procedure was attempted with the use of tridentate terpyridine ligand (terpy) to obtain mixed-ligand complexes with some 2,4-dithiohydantoins that would have well-defined structure and composition by avoiding polynuclear complex formation. Complexes with cyclohexane-5-spiro-2,4-dithiohydantoin and 9'-fluorene-5-spiro-2,4-dithiohydantoin were obtained from Ru(terpy)Cl3, which was synthesised before use. In all cases, soluble cationic complexes were obtained. The latter were isolated through either counter ion exchange or precipitation by a nonpolar solvent. The products were characterised by means of vibrational (IR) and electronic (UV-Vis) spectroscopy as well as nuclear magnetic resonance (NMR) and mass spectrometric (MS) methods. Discussion on the structure of the complexes will be presented.

4-P11. Study of the chemical composition of mining waste by highly sensitive analytical methods

A. Penchev

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *alexandar.penchev@gmail.com*

The possibility of recuperation of various useful items from mining waste is gaining increasing interest worldwide. This study was initiated to prove the existence of elements in the waste with potential economic benefit. The aim of the investigation is to establish the presence of useful components and to evaluate their quantitative content in mining wastes as well as their behaviour and distribution in different technological products of the flotation process.

The study includes SEM (scanning electron microscopy) and EDX analysis, phase analysis, AAS analysis, ICP-OES analysis, and mineralogical analyses.

The results obtained by different analytical methods allow characterising the different mineral twins, micro inclusions of gold and other useful components as a part of different minerals, shape, size, and phase inhomogeneity. The presence of useful components and the purity of the analysed particles were determined.

5-K1. Cobalt-based catalysts for volatile organic compounds removal

S. Todorova, I. Yordanova, A. Naydenov [1], G. Kadinov

Institute of Catalysis, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
Fax: +359-2-9712967, e-mail: todorova@ic.bas.bg
[1] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

Volatile organic compounds (VOCs) are known to contribute to a number of environmental problems such as formation of ground-level ozone, photochemical smog and toxic air emissions. While there is no interest in recovering VOC, they are usually destroyed by deep oxidation. Among the techniques to decompose VOCs, catalytic oxidation is preferable to thermal oxidation because of its low energy consumption and lower temperature of operation. Metal oxides or supported noble metals are used in catalyst preparation. Metal oxides are an alternative to the high cost noble metals. Among all studied metal oxides the most active single metal oxides are those of Cu, Co, Mn, and Ni. Manganese and cobalt containing catalysts are less expensive and relatively highly active in VOCs combustion. The catalytic properties of MnO_x-based catalysts are attributed to the ability of manganese to form oxides of different oxidation states and their high oxygen storage capacity (OSC). Cerium has high oxygen storage capacity, associated with fast Ce^{4+}/Ce^{3+} redox process, making more oxygen available for the oxidation process.

The work presents the effect of Mn and Ce additives on the catalytic activity of silica-supported cobalt catalysts in the reaction of complete oxidation of *n*-hexane, ethyl acetate, and methane. *n*-Hexane and ethyl acetate were selected as VOC representatives of saturated aliphatic hydrocarbons and esters, respectively. The choice of methane is defined by its global warming potential (GWP), being 21 times higher than that of CO_2.

Co-M (M = Ce or Mn) samples were prepared by successive impregnation of silica with aqueous solution of nitrates. A series of Co-Mn samples were also prepared using a co-precipitation procedure. The catalysts were characterised by XRD, TPR, XPS, SEM, and FTIR.

Cobalt and manganese single component and bicomponent cobalt-manganese oxide catalysts are active in the complete oxidation of *n*-hexane. Both single component cobalt and manganese samples demonstrate a similar catalytic activity. A combination between the two elements (Co+Mn or Co+Ce) changes the activity and this depends on the method of preparation. Addition of Mn or Ce to a calcined Co/SiO_2 catalyst leads to a decrease in the catalytic activity in comparison with a single cobalt catalyst. An increase in the reduction temperature of Co_3O_4 is the main factor responsible for the low activity of the bicomponent samples prepared by consecutive introduction of the active components. A considerable increase in activity is established with all the samples prepared from a mixed solution. These results can be ascribed to: (i) formation of finely divided oxides, which are reduced at a lower temperature; (ii) enrichment in surface oxygen species as a result of low crystallinity; (iii) simultaneous presence of Mn^{4+} and Mn^{3+} in the manganese containing samples; (iv) close interaction between Co_3O_4 and CeO_2 in the catalyst prepared with a common solution of Co and Ce nitrates.

Bicomponent Co-Mn samples prepared by deposition-precipitation show a better catalytic performance than impregnated ones in the reaction of complete *n*-hexane and methane oxidation. This result is attributed to the formation of finely divided and easy reducible Co_3O_4, MnO_2, and mixed Co-Mn oxides. The formation of cobalt silicate on the surface of single component cobalt catalyst, prepared by deposition precipitation, is responsible for its low activity.

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5-O1. Catalytic behaviour in CO oxidation, CH_4 oxidation, and NO decomposition of rare-earth promoted alumina-supported copper cobaltites

B. Ivanov, I. Spassova, M. Milanova [1], M. Khristova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[1] Faculty of Chemistry and Pharmacy, Sofia University, 1 James Bourchier Blvd., 1164 Sofia, Bulgaria
Fax: +359-2-8705024, e-mail: b.ivanov @svr.igic.bas.bg

In order to improve catalyst activity, different additives have been tested, among them metal oxides of rare earths. Rare earth elements have been widely used in automotive exhaust catalysts, in particular, ceria compounds with their high oxygen storage capacity and lanthana with its proper basicity and large metal ion radius. Gamma-alumina supported copper cobaltite (CuCo/Al) impregnated with 1 wt.% Ln (Ln = La, Nd, Ce or Gd) nitrate solution was tested for efficiency in reactions of environmental importance, such as CO and CH_4 oxidation and NO decomposition. Ce/CuCo/Al and Nd/CuCo/Al demonstrated a certain catalytic activity in the oxidation processes, while La/CuCo/Al and Gd/CuCo/Al are less active than the parent CuCo/Al catalyst. The order of activity towards CO oxidation is Ce/CuCo/Al> Nd/CuCo/Al > CuCo/Al > Gd/CuCo/Al>La/CuCo/Al. Two temperature regions, below and above 300ºC, could be defined concerning the activity for CH_4 oxidation. Below 300ºC, the order of activity is Gd/CuCo/Al > Ce/CuCo/Al > Nd/CuCo/Al > CuCo/Al> La/CuCo/Al. Above this temperature, the order is Ce/CuCo/Al > Nd/CuCo/Al > Gd/CuCo/Al > CuCo/Al > La/CuCo/Al. In the process of NO reduction at temperatures above 300ºC, La/CuCo/Al and Gd/CuCo/Al exhibit a higher activity, while Ce/CuCo/Al and Nd/CuCo/Al demonstrate a lower activity than CuCo/Al. The selectivity to N_2 formation for the Ln/CuCo/Al catalysts is much higher than that of the parent CuCo/Al catalyst and can be explained by the stability of the intermediates formed in the process of NO decomposition.

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5-O2. Novel strategy for preparation of copper-modified SBA-15 and KIT-6 mesoporous silica catalysts

I. Genova [1], R. Nickolov [2], M. Dimitrov [1], M. Mihaylov [3], D. Kovacheva [3], K. Hadjiivanov [3], T. Tsoncheva [1]

[1] Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences,
Akad. G. Bonchev St., Bldg. 9, 1113 Sofia, Bulgaria
[2] University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
[3] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

A novel modified stepwise incipient wetness impregnation technique was applied for deposition of copper species into an ordered mesoporous silica host matrix (SBA-15 and KIT-6). The procedure included a stepwise copper deposition by alternating number of incipient wetness impregnation using aqueous solution of copper nitrate with changeable concentration and vacuum drying cycles. The state of the copper species was characterised by nitrogen physisorption, XRD, UV-vis, TEM-EDXS, FTIR of probe molecules (CO, NO, and N_2) and TPR. The catalytic behaviour of the materials was tested in methanol decomposition to hydrogen and carbon monoxide. Selected catalytic experiments were carried out under very low coverage of the surface with ^{11}C-radiolabelling methanol. *In situ* FTIR study of methanol decomposition was also performed. It was found that the pore topology of the mesoporous support controls significantly not only the dispersion of the active copper phase but also its accessibility to reactants. The optimal copper loading is also dependent on support pore topology. The highest catalytic activity was achieved at 8 and 15 wt.% copper loading for the SBA-15 and KIT-6 supports, respectively.

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5-P1. Catalytic reduction of NO over sol-gel prepared Cu/SiO_2-C composite catalysts

I. Spassova, R. Nickolov [1], N. Stoeva, M. Khristova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
Fax: +359-2-8705024, e-mail: n.stoeva@svr.igic.bas.bg
[1] *University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria*

Exhaust gases from stationary and mobile combustion sources contain nitrogen oxides that cause a variety of environmentally harmful effects. The most common approach to their elimination is the catalytic reaction using various reduction agents, such as NH_3, CO, and hydrocarbons. Supported copper catalysts are known as active in these reactions. We investigated the influence of support composition on the reduction activity of copper catalysts deposited on silica-carbon composite supports prepared by the sol-gel method. Four composite supports were obtained using different carbon materials in their specific surface area and texture: two active carbons (with a micro-mesoporous texture), soot (with a secondary porous texture), and graphite (non-porous texture). The catalysts were characterised by XRD, XPS, SEM-EDS, AAS, and BET analysis. The catalytic experiments were carried out in isothermal flow reactor in the temperature range 20–350ºC. Temperature-programmed desorption was carried out after catalytic tests. The transient response method was used to study the interaction of the gas phase with the catalyst surface. The influence of carbon materials, close in chemical nature and substantially different in texture, on the porosity of the prepared composites was investigated. The role of the interaction between the support and the active phase on catalyst activity in the studied reaction was discussed.

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5-P2. Copper-based layered double hydroxides as catalysts for water-gas shift reaction

I. Ivanov, T. R. Reina [1], S Ivanova [1], T. Tabakova, M. A. Centeno [1], J. A. Odriozola [1], V. Idakiev

Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria
Fax: +359-2-9712967, e-mail: bogoev@ic.bas.bg
[1] *Departamento de Química Inorgánica e Instituto de Ciencia de Materiales de Sevilla, Centro mixto*
Universidad de Sevilla-CSIC, Avda. Américo Vespucio 49, 41092 Sevilla, Spain

Presently, investigations on water-gas-shift (WGS) catalytic activity grow significantly in number due to increasing demand of pure hydrogen for fuel-cell power systems. In this aspect, the development of novel active and stable WGS catalysts is of great importance. Traditional copper-based catalysts used in the industry for low temperature WGS are not suitable for automobile exhaust application due to the contact with air and/or condensed moisture during start-up and start-down operation.

Novel copper catalysts with a layered double hydroxides (LDHs) structure were synthesised by a new co-precipitation method with different Cu/(Zn+Al) atomic ratios in the synthesis mixture. Depending on the copper content, the samples were denoted as CuHT1, CuHT2, and CuHT3.

The obtained CuZnAl-LDH catalysts were studied in the water-gas shift (WGS) reaction and characterised by X-ray diffraction (XRD) and temperature-programmed reduction (TPR). The state of copper before and after the WGS reaction and the reduction behaviour of the catalysts clearly show differences that depend on copper content. The maxima of the TPR peaks in the profiles of CuHT1 and CuHT2 were shifted to lower temperatures (245ºC), while the sample with the highest copper content CuHT3 demonstrated a complex peak with T_{max} at 367ºC. The catalytic measurements revealed a promising WGS activity and stability during the catalytic operation. The results are interesting and additional research is in progress for optimization of copper content and modification with various additives in order to obtain highly active and stable catalysts for WGS reaction.

5-P3. Effect of the duration of mechanochemical treatment on the photocatalytic activity under UV light irradiation of nanosized zinc oxide synthesized by precipitation

K. Zaharieva, K. Milenova, Z. Cherkezova-Zheleva, S. Dimova [1], B. Kunev, A. Eliyas, I. Mitov, I. Stambolova [2], V. Blaskov [2]

Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria
Fax: +359-2-9712967, e- mail: zaharieva@ic.bas.bg
[1] Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 103A, 1113 Sofia, Bulgaria
[2] Institute of General and Inorganic Chemistry, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria

Zinc oxide, synthesised by precipitation method, has been treated mechanochemically to obtain nanosized ZnO particles. The milling time interval was varied for the different samples – 15, 30 min or 4 hours using an agate or stainless steel milling container at a velocity of 300 or 600 rpm and mass sample to balls ratio of 1:6 or 1:13. XRD and FTIR measurements have been made. The mechanochemical treatment leads to a decrease in the mean crystallite size of the ZnO phase (9.9 nm), compared with the initially precipitated nanostructured ZnO (14.6 nm). The so prepared ZnO powders were tested as photocatalysts in the photocatalytic degradation of Reactive Black 5 dye under UV irradiation. The results give evidence that the time interval of mechanochemical treatment causes some changes in the photocatalytic activity of the ZnO samples. The ZnO treated mechanochemically for 15 min manifests the highest rate constant (35.5×10^{-3} min^{-1}) compared to those of the other samples decreasing in the following order: ZnO (15 min) (35.5×10^{-3} min^{-1}) > precipitated ZnO (30.4×10^{-3} min^{-1}) > ZnO (30 min) (26.4×10^{-3} min^{-1}) > ZnO (4 h) (19×10^{-3} min^{-1}). The conversion degree of RB5 dye degradation over the ZnO samples after 120 min of illumination is varying in the range 82–96%.

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5-P4. Comparison between zirconium catalysts for the oxidation of sulphide ions according to the method of production

N. Dermendzhieva, E. Razkazova-Velkova, L. Ljutzkanov, V. Beschkov

Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria
Fax: +359-2-8707523, e-mail: nastemi1@abv.bg

The catalytic oxidation of sulphide ions in seawater model solutions was studied. Two types of zirconium catalysts obtained by impregnation of active carbon with zirconium salt are used. The impregnation was carried out on a dry and pre-wetted support and subsequent pyrolysis was applied. Thus, the obtained ZrO_2, incorporated in the matrix of activated carbon, was characterised by iodine adsorption.

Experiments are performed by varying the sulphide concentration and temperature while keeping constant catalyst amount and mixing rate. A two-fold higher oxidation rate was registered with the catalyst prepared using pre-wetted active carbon. We explain these results by uniform distribution of the active sites on the catalyst surface and zirconia cluster size.

5-P5. Purification of crude polydextrose by immobilised glucose oxidase and catalase

M. Kamburov, T. Ivanov, I. Lalov

Department of Biotechnology, University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd.,
1756 Sofia, Bulgaria
E-mail: *m_kamburov@yahoo.com*

Crude polyglucose can be prepared by heating 89% dextrose, 10% sorbitol and 1% citric acid in the presence of acid catalysts. The improved polydextrose has less than 3% monomeric glucose. Bearing in mind that there is a growing interest in good-quality soluble food fibres, which have as low calories as possible, immobilised glucose oxidase (GOD) and catalase were applied for investigation of the process of removing residual glucose from crude polydextrose.

The present study deals with a potential application of immobilised glucose oxidase and catalase for purification of crude polydextrose. Styrene, maleic anhydride, and a divinyl benzene copolymer were prepared by suspension polymerisation method in a batch type reactor at 70ºC and continuous stirring for 3 h. Then glucose oxidase (GOD, beta-D-glucose:oxygen-1-oxidoreductase, EC 1.1.3.4) and catalase (H_2O_2:H_2O_2 oxidoreductase, EC 1.11.1.6) were immobilised on the polymer under optimised conditions (incubation time, pH 6.5, GOD 5 mg ml^{-1}). The enzymatic activity of free and immobilized GOD were assessed in terms of the oxidation of d-glucose to d-gluconic acid carried out under stirring by air. The enzyme immobilisation yield was 87% with the immobilised GOD activity of 125 U mg^{-1} protein. The Michaelis constant for immobilised GOD was evaluated to 26.3 mmol l^{-1} by Lineweaver-Burk plot at 25ºC. The highest enzymatic activity was achieved at pH ~7.0 of the medium. Storage stability of the GOX samples was investigated for two months and the retained activity was 67.5%, being higher than that of the free enzyme (9.3%).

6-O1. Indicators describing pressures on environment from industry

L. Ilchev, N. Davcheva-Ilcheva

Faculty of Economics and Business Administration, St. K. Ohridski University of Sofia
E-mail: *lubomirilchev@abv.bg*; *davcheva_ilcheva@abv.bg*

The paper surveys an urgent need for creation a set of indicators describing big pressures on environment from industry (chemistry, metallurgy, etc.). Basic air polluting emissions and greenhouse gases with biggest contribution to climate changes are discussed. This set of indicators is suggested to comply with the ten policy fields adopted by the European Union. It is recommended to specify it according to specific characteristics of every single branch and plant. It is necessary to elaborate proper methods for defining those indicators for which such methods are missing.

6-O2. Catalytic conversion of sulphides into energy in sulphide-driven fuel cell

V. Beschkov, E. Razkazova-Velkova, M. Martinov

Institute of Chemical Engineering, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
E-mail: *vbeschkov@yahoo.com*

Hydrogen sulphide is frequently found in nature as a component and pollutant of water and air. It is an inevitable component of natural gas and oil, in some marine waters (like those in the deep Black Sea waters), in some mineral water springs, etc. Its removal in the oil and gas processing practice leads to considerable expenses. One valuable approach is to utilise hydrogen sulphide or its corresponding sulphide ions as raw materials or as a source of energy. Direct combustion is not feasible because of secondary pollution as sulphur dioxide in air.

The present work considers the utilisation of hydrogen sulphide (or sulphides) as a source of energy converting the chemical energy of sulphide-assisting reactions into electrical energy in newly designed fuel cells using sulphide ions as a fuel. A fuel cell was designed to operate at room temperatures in aqueous media, thus being energetically very efficient.

The idea of such a fuel cell is based on the increase of the energy, resulting from the oxidation of a sulphide to sulphur, to a sulphite, and, consequently, to a sulphate. This energy could be converted into electrical one and used afterwards for different purposes, i.e. for hydrogen production by water splitting, for mechanical purposes, etc.

The variable chemical properties of sulphur and the variety of resulting compounds lead to very complicated situations for operating of such a fuel cell. For this purpose, different catalysts have been tested and studied. Usually these catalysts contain ions of transient metals (i.e. manganese, zirconium) or ones from the iron group: cobalt, nickel, iron.

Different types of catalysts containing cobalt, manganese, and zirconium have been tested. Specific techniques have been applied to attain the desired selectivity, high activity and inertness against the sulphide ions.

Different factors with impact on fuel cell performance have been studied: sulphide concentrations, pH of the media, operation under electrochemical conditions, flow pattern, and cell design. Kinetic studies in batch and continuous stirred tank reactor have been carried out. Best results have been obtained by cobalt-containing catalysts.

It was established that under certain conditions the fuel cell efficiency, based on the created electro-motive force, might lead to 80–90% depending on the electrochemical reactions taking place within it.

The proposed approach combines energy production with removal of harmful pollution by hydrogen sulphide. The products (i.e. sulphur, sulphites or sulphates) have practical applications. The process does not require any use of toxic and harmful chemicals. On the other hand, the proposed method relies on almost inexhaustible resources such as hydrogen sulphide that is considered sometimes a renewable one.

6-O3. Denitrification of wastewater by immobilised cells of Pseodomonas denitrificants

T. Ivanov, I. Lalov, L. Jotova

Department of Biotechnology, University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd.,
1756 Sofia, Bulgaria
E-mail: *todorvelikovivanov@abv.bg*

Nitrate contamination is one of the major problems in wastewater. In order to eliminate nitrate ions from wastewater a biological denitrification technology can be applied for which a carbon-containing and energy source are needed. Addition of an external carbon source helps in increasing the denitrification rates and enhances nitrogen removal.

In this study, a pure culture of *Pseudomonas denitrificans* (NBIMCC 1625) was used. The bacterium from agar slants was inoculated into YPD liquid medium. The activated culture was transferred to 100 ml of medium with the following composition (as g/l): potassium aspartate 15, yeast extract 14, KNO_3 8, $MnSO_4$ 0.0025, $(NH_4)_6Mo_7O_{24}.4H_20$ 0.0025, $FeCl_3.6H_2O$ 0.006, pH 6.75. After cultivation by weak shaking for 24 h at 30ºC, cells were harvested by centrifugation (15 min, 4000 g), washed twice in saline solution and stored at 4ºC. A preliminary study was carried out with batch fermentation and free cells in shake flasks containing nitrate as 1−3 mM KNO_3 and carbon source 6−18 mM methanol, the C/N ratio being 6.

Complete nitrate removal was achieved within 2 to 3 h. After 60- to 120-min accumulation, nitrite was detected, but the final nitrite concentrations were low. To determine the kinetics of the process the influence of the initial nitrate concentration on nitrate removal was examined. By applying a linear fit to the denitrification rate *vs*. the initial nitrate concentration Michaelis-Menten constants K_m and V_{max} were found to be 63 mg NO_3-N/l and 0.671 mg NO_3-N/min/g cells, respectively.

Further investigation of the denitrification process was performed with cells immobilised on different synthetic supports. In the batch mode, lower denitrification rates were observed and after 24 h 80% of the nitrates were converted. Denitrification was carried out in a continuous-flow column reactor. A column with ID=50 mm was packed with 25 g of support and solution of 42.4 mg NO_3-N/l was pumped through the column. After 3 hours, a steady state was reached with on output concentration of 30 mg NO_3-N/l. The result of this study demonstrated that nitrate concentrations up to 45 mg NO_3/l could be removed from wastewater. In the continuous column process with immobilised cells of *Pseudomonas denitrificans* at HRT = 6 h a high denitrification rate was achieved.

6-O4. CFD simulation of the hydrodynamics of external loop airlift reactor. Effect of gas sparger construction and location

R. A. Stoykova, D. K. Moutafchieva, D. S. Popova, S. N. Tchaoushev, V. D. Iliev

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *rosica2136@abv.bg*

In this research, the hydrodynamics of two-phase air-water flow in an external-loop airlift reactor was simulated using a CFD program. Experiments and simulations were aimed at obtaining global flow characteristics (gas hold-up and liquid interstitial velocity in the riser and in the downcomer) in the airlift configurations investigated. The experiments and simulations were performed for different cross sectional areas of riser to downcomer and different gas sparger location and construction.

The aim of this study was numerical analysis of the influence of the sparger construction and location on the fluid flow characteristics in an external loop airlift column. An ANSYS CFX 12 solver was used for the simulations. Unsteady state simulations of air-water flow in the airlift reactor were performed using two-fluid Euler-Euler numerical approach. The gas hold-up in the riser and the downcomer was measured experimentally by U-tube manometers. The obtained results from the numerical simulations showed that the gas hold-up in the riser and the downcomer get higher on increasing the superficial gas velocity. A good agreement between the averaged results of numerical simulations and the experimental data was achieved.

6-P1. Biodegradation of acetamide from *Pseudomanas aeruginosa L10*

G. P. Naydenova [1], J. A. P. Coelho [2], D. S. Yankov [1], R. P. Stateva [1]

[1] *Institute of Chemical Engineering, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*
Fax: +359-2-8707523, e-mail: greta_naydenova@abv.bg
[2] *Chemical Engineering and Biotechnology Research Centre, Instituto Superior de Engenharia de Lisboa (ISEL), Lisbon, Portugal*

The aim of this work is to explore the influence of some process parameters on the hydrolysis of aliphatic amides by an amidase from *Pseudomonas aeruginosa L10*. The aliphatic amidase (acylamide amidohydrolase; EC 3.5.1.4.) catalyses the hydrolysis of aliphatic amides, such as acetamide, producing the corresponding acid and ammonia.

The influence of enzyme, substrate concentrations, and pressure on the hydrolysis process was investigated.

The reaction mixture contained appropriate amounts of acetamide in TME buffer pH 7 (25 ml) and a 10-µl cell culture from *Pseudomonas aeruginosa L10*. Hydrolysis was carried out at a pressure within 1 to 120 bar at $T = 22^{\circ}$C.

Aliquots (1 ml) were taken from the batch reactor at suitable time intervals (each for 3 min) and the substrate and product of the reaction were analysed by ion-selective electrode.

The kinetic constants (V_{max}, K_m) of the hydrolysis process were determined as follows: $V_{max} = 0.1026$ mM/min and K_m=0.668 mM for the reaction at p = 1 bar and $V_{max} = 0.06248$ mM/min and $K_m = 9.228$ mM for the reaction at p = 60 bar.

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6-P2. Study on the solubility of C-tetraalkylcalix[4]resorcinarenes in supercritical CO_2

P. P. Petrova [1], G. P. Naydenova [2], J. A. P. Coelho [3], S. M. Miloshev [1], C. P. Novakov [4], D. S. Yankov [2], R. P. Stateva [2]

[1] *University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria*
[2] *Institute of Chemical Engineering, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*
Fax: +359-2-8707523, e-mail: greta_naydenova@abv.bg
[3] *Chemical Engineering and Biotechnology Research Centre, Instituto Superior de Engenharia de Lisboa (ISEL), Lisbon, Portugal*
[4] *Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

The present contribution is the first in a series of studies devoted to the application of polymers as a co-solvent to a supercritical fluid (supercritical carbon dioxide, $SCCO_2$) in an efficient environmentally friendly and benign new green route for *in situ* product removal of inhibitory bio-products, like organic acids and some antibiotics.

Two representatives of calix[4]resorcinarenes were studied, namely C-tetramethylcalix[4]resorcinarene and C-tetrapenthylcalix[4]resorcinarene. They were synthesised and characterised by gel permeation chromatography and NMR spectroscopy. The solubility of the cyclic oligomers in $SCCO_2$ was measured applying a flow apparatus. The equipment permits carrying studies at temperatures up to 393.2 K and pressures up to 600 bar.

Solubility measurements were performed at temperatures of 313.2, 323.2, and 333.2 K and pressures within 120–350 bar. The solubility was calculated from HPLC chromatograms of the corresponding quantities of resorcinarenes dissolved in $SCCO_2$. The chromatograms were taken at 210 nm on an Agilent 1100 gas chromatograph equipped with a diode array UV detector (DAD). The individual peaks of the chromatograms were attributed to different stereo specific isomers of C-tetraalkylcalix[4]resorcinarene by their characteristic UV spectra.

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6-P3. Comparison of different pretreatment methods for reducing sugars production from distillery-spent grains

B. I. Ilieva, V. S. Bankova, D. S. Yankov

Institute of Chemical Engineering, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
Fax: +359-2-8707523, e-mail: bilqna_1984@abv.bg

This work focuses on different chemical and enzymatic methods for pretreatment of distillery-spent grains.

Alkaline and acid hydrolysis were applied as well as enzymatic hydrolysis with amylases and cellulase. An attempt for ultrasonic intensification of the hydrolysis process was made.

The influence of acid and base concentration, liquid to solid ratio, time and pressure on the degree of hydrolysis was examined.

Enzymatic hydrolysis was carried out in simultaneous or consecutive manner and the influence of temperature and time on reducing sugars yield was investigated.

An ultrasonic disintegrator was used to improve the hydrolysis process and the influence of sonification time and intensity was studied.

Different schemes of the hydrolysis process realisation were compared and an optimal procedure, which provides higher reducing-sugars content, was suggested.

6-P4. Liquid-liquid equilibria in aqueous two-phase systems based on modified C-tetraalkylcalix[4]resorcinarenes

B. I. Ilieva, S. N. Yankova, C. P. Novakov [1], S. M. Miloshev [2], R. P. Stateva, D. S. Yankov

Institute of Chemical Engineering, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
Fax: +359-2-8757023, e-mail: bilqna_1984@abv.bg
[1] Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia Bulgaria
[2] University of Chemical Technology and Metallurgy, Sofia, Bulgaria

This work is a part of a study devoted to the examination of the applicability of aqueous two-phase systems (ATPS) based on modified C-tetraalkylcalix[4]resorcinarenes, namely tetrasulphonatoethyl-C-tetramethyl-calix[4]resorcinarene and tetrasulphonatoethyl-C-tetrapenthylcalx[4]resorcinarene, designed for separation of valuable bio-products. We expected that the presence of water soluble modified C-tetraalkyl-calix[4]resorcinarenes in ATPS would enhance the partition coefficient of low molar mass organic acids or antibiotics produced *via* fermentation. The underlying hypothesis is that, owing to their specific molecular structures, the modified resorcinarene will bind the target compound either in its cavity or by a hydrogen bond with the arene's pending group.

We studied the liquid-liquid equilibria of a number of ATPS composed by tetrasulphonatoethyl-C-tetramethylcalix[4]resorcinarene and polyethylene glycol (PEG), and by tetrasulphonatoethyl-C-tetrapenthyl-calix[4]resorcinarene and PEG at T = 20−40ºC and atmospheric pressure. Polymer distribution among the equilibrium phases was determined by HPLC and size exclusion chromatography (SEC). Light scattering measurements were used to determine cmc of modified arenes and particle size of obtained aggregates in solution. Phase equilibria data obtained will be an important indicator for selecting the most appropriate ATPS for a green *in-situ* extractive fermentation of a valuable target component like lactic acid.

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6-P5. Recovery of resveratrol from grapevine stems

G. Angelov, L. Boyadzhiev, S. Georgieva

Institute of Chemical Engineering, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Block 103,
1113 Sofia, Bulgaria
E-mail: *gang@bas.bg*

The methods for producing natural resveratrol are of great interest because of many health benefits of this substance and its increasing use in functional foods and food supplements. Generally, resveratrol is extracted from different natural sources, most of them being usually produced for consumption purposes (grapes, nuts).

This paper presents a method for recovery of resveratrol from largely available raw material − grapevine stems, which are wastes from vine pruning. An efficient extraction scheme is developed, by which more concentrated extracts of resveratrol are obtained.

The method is based on the different solubility of the extracted substances. After a simple extraction, the extract is additionally separated to two fractions containing water and ethanol soluble compounds, respectively. Using this approach, the low water-soluble resveratrol is isolated from other water-soluble substances. The resulting product is almost ten times more concentrated in resveratrol than the initial total extract. Additionally, a fraction containing water-soluble polyphenols is obtained, which might be used for water-based pharmaceutical and cosmetic products.

6-P6. Dimensional changes of vegetal particles in contact with a solvent

G. Angelov, P. Guiraud [1], L. Boyadzhiev

Institute of Chemical Engineering, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Block 103,
1113 Sofia, Bulgaria
E-mail: *gang@bas.bg*
[1] *National Institute of Applied Science* (*INSA*), *Toulouse, France*

Soaking with liquid is the first step of a common process of solid-liquid contact preceding the principal solid-liquid extraction process. This paper investigates volume changes of vegetal particles submerged in liquid. The spatial dimensions of cuboid vegetable particles were measured in the course of time as a function of water salinity. Positive volume changes (swelling) were registered at low salinity, while negative volume changes (shrinkage) were observed at high salinity. Both processes were intensified by agitation of the liquid. The dimensional changes have shown to be different in three space dimensions even at apparently homogeneous structure of the tested material.

A kinetic model was used for process description. It was found that both processes of swelling and shrinking have analogous mechanisms and could be described by the same model. The kinetic parameters were identified from experimental data.

Shrinkage is an equivalent of a non-thermal dehydration process. This low-temperature elimination of water has potentials to prevent degradation of thermally unstable substances, to preserve the nutritional qualities, and to save a lot of energy usually consumed by a conventional drying process.

6-P7. Screening of strain for butyric acid production

S. P. Hristoskova, S. K. Antonova-Nikolova [1], L. D. Yocheva [2], D. S. Yankov

Institute of Chemical Engineering, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
Fax: +359-2-8757023, e-mail: siiis@abv.bg
[1] *General and Industrial Microbiology, Faculty of Biology, Sofia University, Sofia, Bulgaria*
[2] *Biology, Medical Genetics, and Microbiology, Faculty of Medicine, Sofia University, Sofia, Bulgaria*

In the recent years, there is a growing interest in the fermentative production of butyric acid because of its wide application to chemical, food, pharmaceutical, and fuel industries. The purpose of this study was to make screening of 15 strains of the genus *Clostridium* isolated from raw chickpea grains. Experiments were carried out with the purpose to select a strain of high production capacity for butyric acid. Fermentation was carried out under strictly anaerobic conditions, which were maintained by using Anaerocult A (Merck). The strains were grown in an anaerobic chamber and cultivated at 37ºC. Different media were used for cultivation: meat-peptone broth with different carbon source (glycerol, glucose, arabinose, and xylose), a triptone-thiogluconate medium (TTM), and a chickpea grain medium.

Results showed that the strain 4A1 grown on TTM with 5% glucose produced the higher quantity of butyric acid (2.45 g l^{-1}). The experiments will continue on optimising medium composition for higher butyric acid production with selected strain.

6-P8. Optimisation of medium composition for butyric acid production by *Clostridium 4a1*

S. P. Hristoskova, S. K. Antonova-Nikolova [1], L. D. Yocheva [2], D. S. Yankov

Institute of Chemical Engineering, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
Fax: +359-2-8757023, e-mail: siiis@abv.bg
[1] *General and Industrial Microbiology, Faculty of Biology, Sofia University, Sofia, Bulgaria*
[2] *Biology, Medical Genetics, and Microbiology, Faculty of Medicine, Sofia University, Sofia, Bulgaria*

Butyric acid has many uses in different industries and currently there is a great interest for use as a precursor to biofuels. After initial screening of several strains, it was found that the strain *Clostridium 4a1* was the best producer of butyric acid (2.45 g l^{-1}).

The objective of this study was to optimise medium composition in view to increase the amount of the produced butyric acid by anaerobic fermentation with the selected strain. Experiments were conducted to determine the optimal medium for increasing the concentration of the target product. For this purpose, several different media were used by varying concentrations of the following components of the media: carbon source (glucose, glycerol, and xylose), KH_2PO_4, K_2HPO_4, yeast extract, $MgSO_4.7H_2O$, $CaCl_2.2H_2O$, $FeSO_4.7H_2O$. An optimal composition was determined and the amount of produced butyric acid was increased.

6-P9. Comparison of the effectiveness of two types of sulphide-driven fuel cells

M. Martinov, E. Razkazova-Velkova, V. Beschkov

Institute of Chemical Engineering, Bulgarian Academy of Sciences, Akad. G. Bonchev St., Bldg. 103, 1113 Sofia, Bulgaria
Fax: +359-2-8707523, e-mail: msmartinov@yahoo.com

The present study is an attempt for sulphide removal from the deep Black Sea water by oxidation to sulphites or sulphates in electrochemical way. The process was carried out in a sulphide-driven fuel cell and, as a result, energy is released which can be used. The aim of the work was to improve the energy efficiency of the fuel cell by optimising its design.

A comparison between the obtained electrical power and the oxidation rate of two different constructions of sulphide-driven fuel cells was considered. One of them consists of two separated compartments divided by a membrane. Sel Gard 3501 was used as a membrane. Oxidation of the sulphide ions took place in the anodic space. The working electrodes in this space were made of graphite fabric. Graphite rods were used as electrodes in the cathodic compartment and its volume was filled with charcoal. In another configuration, the anodic space was the same like the former one. The difference was that instead of membrane gas, a diffusion electrode was used and the cathodic space was directly aerated.

The experiments are carried out at the same initial concentrations of 75 mg l^{-1}. To improve the conductivity of the solution sodium chloride at a concentration of 165 g l^{-1} was used as an electrolyte.

Material balance and balance by the generated electrical power according to the Faraday's law is presented.

6-P10. Influence of temperature and salinity on the specific chemical reactions in a sulphide-driven fuel cell

S. Stefanov, P. Panajotova, I. Georgieva, V. Beschkov

Institute of Chemical Engineering, Bulgarian Academy of Science, Acad. G. Bonchev St., Bldg. 103, 1113 Sofia, Bulgaria
E-mail: stefanmartinov@yahoo.com

The present study is a part of our efforts for sulphide removal from the deep Black Sea water by oxidation to sulphates in an electrochemical way. The process was carried out in a fuel cell and the resulting electrical energy is released that can be used for a variety of purposes. The aim of the study was to enhance the efficiency of the fuel cell by reducing the secondary reactions.

The influence of temperature and varying salinity on the levels of electrode potentials, directly dependent on the specific chemical reaction in the fuel cell, was investigated. The experiments were carried out by two model solutions of seawater: distilled water with NaCl and tap water with commercial sea salt. In the fuel cell, graphite rods as electrodes for the anode compartment and a gas diffusion electrode (GDE) for the cathode compartment were used. The voltammetric characteristics of the system showed that there is a slight hysteresis and the equilibrium potential corresponds to sulphide to sulphite/sulphate oxidation.

6-P11. Concentration effect on flux and rejection in nanofiltration of plant extracts

I. I. Tsibranska, V. I. Karabozhikova, Z. Zheliazkov

Department of Chemical Engineering, University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria

This study examines flux and rejection during membrane separation/concentration of polyphenols and flavonoids from alcoholic extracts of herb tea (*Sideritis spp. L*) and waste tobacco leaves (*Nicotiana tabacum L.*). For the latter, results of real extracts and model solutions were compared. Two membranes, resistant to organic solvents, were used: Starmem^{TM} 240 (polyimide) and Duramem^{TM} 200 (modified polyimide). The choice of membrane was based on previous investigation concerned with rejection dependence on membrane molecular weight cut-off. A flux and rejection decline was observed and calculated during long-term nanofiltration in batch (dead-end) mode. The influence of polyphenols/flavonoids concentration on the process resistance due to osmotic pressure and concentration polarisation is evaluated.

6-P12. Treatment of landfill leachate in a two-stage vertical-flow wetland system with/without additional carbon source

S. Lavrova, B. Koumanova

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *engeco2001@uctm.edu*; *bkk@uctm.edu*

Landfill leachate consists of various inorganic and organic substances, which may be suspended or dissolved. Chemical oxygen demand (COD), biochemical oxygen demand (BOD), and ammonium nitrogen (NH_4-N) are at high concentrations typical of this wastewater. Wetland systems can be suitable for landfill leachate treatment.

The aim of this study was to investigate the treatment efficiency of two laboratory scale vertical-flow wetland systems (VFWS) with/without additional carbon source to affect the denitrification process. The systems consisted of two type-VFWS laboratory reactors, which were continuously connected. They were filled with different gravel size in height. Wastewater passed through the wetlands at a recirculation regime of 1:1 and 1:2 (1-h water movement through the media and 1 or 2 h water resting in the system). During the experiments the parameters COD, BOD, [NH_4^+-N], [NO_2^--N] and [NO_3^--N] were determined by standard methods. A significant removal efficiency was achieved according to COD (94.69±2.5% without methanol addition and 92.96±2.52% with methanol addition) and BOD (95.96±2.5% without methanol addition and 91.61±9.06% with methanol addition). Complete nitrification of ammonium nitrogen into nitrite and nitrate was realised in both systems. Denitrification occurred only in the wetland system where methanol was added.

6-P13. Photocatalytic oxidation of paracetamol by Fenton's reagent with nanostructured magnetite

F. Velichkova [1,2], C. Julcour-Lebigue [2], B. Koumanova [1], H. Delmas [2]

[1] Department of Chemical Engineering, University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *fvelichk@uctm.edu*; *bkk@uctm.edu*
[2] Université de Toulouse, Laboratoire de Génie Chimique, 4 allée Emile Monso, 31432 Toulouse, France

Nanostructured iron oxide (magnetite) was used as a heterogeneous catalyst in Fenton reactions for paracetamol degradation in aqueous solutions. For this purpose, the paracetamol conversion and mineralisation yield, total organic carbon (TOC) removal, were evaluated.

The influence of reaction parameters, such as hydrogen peroxide dosage, temperature, and pH was investigated as well as the effect of UV and visible irradiation. Paracetamol mineralisation was improved by the presence of both UV and visible irradiation, a higher temperature, and a low oxidant dosage due to radical scavenging effects. Under best conditions (a stoichiometric amount of H_2O_2, a temperature of 45ºC, a catalyst concentration of 1 g l^{-1}, UV and visible irradiation, and low pH), paracetamol was fully degraded after 5 h and the TOC removal reached about 70%. The iron oxide exhibited low iron leaching (<1%), the leached iron activity was evaluated, and a comparison between the homogeneous and heterogeneous reactions was made using equivalent quantities of homogeneous and heterogeneous catalyst.

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6-P14. CFD simulation of the hydrodynamics of external loop airlift reactor with different cross sectional area of riser to downcomer. Effect of sparger gas construction and location

R. A. Stoykova, D. K. Moutafchieva, D. S. Popova, S. N. Tchaoushev, V. D. Iliev

University of Chemical Technology and Metallurgy, 8 St. K. Ohridski, 1756 Sofia, Bulgaria
E-mail: *rosica2136@abv.bg*

In this research, a two-phase air-water flow in an external loop airlift reactor was simulated using CFD. The experiments and simulations were aimed at obtaining global flow characteristics (gas hold-up and liquid interstitial velocity in the riser and in the downcomer) in our airlift configurations. Experiments and simulations were made for different cross sectional area of riser to downcomer and different sparger gas location and construction. The aim of this study was numerical analysis of the sparger construction and location influence on the fluid flow characteristics in an external loop airlift column. An ANSYS CFX 12 solver was used for the simulations. Unsteady simulations of air-water flow in the airlift reactor were performed using a two-fluid Euler-Euler numerical approach. The gas hold-up in the riser and the downcomer was measured experimentally by U-tube manometers. The obtained results of the numerical simulations showed that the gas hold-up in the riser and the downcomer increased at a higher superficial gas velocity. A good agreement was achieved by comparison of the averaged results of numerical simulations with the results of experimental investigations.

6-P15. Isolation of microbial chitosan from waste fungal biomass

I. Lalov, M. Kamburov, T. Ivanov, O. Bozadzhiev, I. Dimitrov [1]

Department of Biotechnology, University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd.,
1756 Sofia, Bulgaria
E-mail: ivo.lalov@abv.bg
[1] *Faculty of Pharmacy, Medical University of Sofia, 2 Danube St., 1000 Sofia, Bulgaria*

Chitosan has emerged as a new biomaterial for food, pharmaceutical, textile, and other industries as well as for wastewater treatment. Chitosan is commercially produced from shrimp and crab shell chitin deacetylated by strong alkalis at high temperatures for long periods of time. However, supplies of raw materials are variable and seasonal and the process is laborious and costly. Furthermore, chitosan derived from such a process is heterogeneous with respect to its physiochemical properties. Chitin and chitosan production from fungal mycelium has recently received increased attention due to significant advantages. Fungal mycelium can be obtained by a convenient fermentation process that does not have geographic or seasonal limitations. It has a lower level of inorganic materials compared to crustacean wastes. Additionally, fungal chitosan exhibit relatively consistent properties because of the controlled fermentation conditions.

Waste fungal mycelia can become a free and rich alternative source of chitin-chitosan materials beside the traditional industrial source.

The purpose of this work was to develop a method for laboratory scale production of chitosan from waste fungal mycelium. Waste *Aspergillus niger* mycelium obtained as a by-product of microbial xylanase production was used as a source of chitosan.

Chitosan extraction was carried out according to a well-known procedure, described in literature, at a relatively high temperature (90ºC) resulting in extracted chitosan of 7.2 mg g^{-1} of dry mycelium. After partial optimisation of the extraction procedure, the yield of the extracted chitosan reached 36.3 mg g^{-1} of dry mycelium. FTIR spectra of the extracted product showed a typical chitosan spectrum, which confirmed that the extracted product was chitosan. The average molecular weight, measured viscosimetrically, and the degree of deacetylation were 48.2 kDa and 72%, respectively.

6-P16. Biocompatible ionic liquids in liquid-liquid extraction of lactic acid. A comparative study

K. Tonova [1], I. Svinyarov [2], M. G. Bogdanov [2]

[1] *Institute of Chemical Engineering, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*
Fax: +359-2-8707523, e-mail: zlazar@bas.bg
[2] *Faculty of Chemistry and Pharmacy, St. K. Ohridski University of Sofia, 1164 Sofia, Bulgaria*

Ionic liquids consisting of pairs of imidazolium or phosphonium cation and a chloride or saccharinate anion were synthesised and compared with respect to their extraction efficiency towards the fermentative L-lactic acid. Acid partitioning in the equilibrated biphasic systems of ionic liquid and water was quantified through the extraction degree and the partition coefficient. Water transfer from the aqueous phase into the ionic liquid-rich phase was also always followed. The effect of pH, which determines the state of lactic acid in the aqueous source, was studied. The effect of other salting-out substances that modify the ionic liquid/water equilibrium were also investigated to reveal the best liquid-liquid system with respect to low toxicity, high extraction, and back extraction efficiencies and performance simplicity.

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6-P17. Energy integration and stochastic optimisation for sustainable autothermal thermophilic aerobic digestion systems

R. K. Vladova, N. G. Vaklieva-Bancheva, E. G. Kirilova

Institute of Chemical Engineering, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 103, 1113 Sofia, Bulgaria
Fax: *+359-2-8707523, e-mail*: *raika_vladova@abv.bg*

Autothermal thermophilic aerobic digestion (ATAD) is a wastewater treatment process, which produces class A biosolids. The process is carried out by the help of thermophilic aerobic microorganisms with exothermic metabolism. The ATAD process conducts in parallel series of consecutively connected batch bioreactors, where wastewater is treated at different operational temperatures. Biochemical oxidation of organic compounds in treated sludge leads to heat release. Heat retention in the ATAD system results in an increase of the operational temperatures, hence the process stabilisation and pasteurisation of treated sludge is realised. However, on incoming to the first bioreactor each new portion of raw sludge causes a decrease of the operational temperatures at the first bioreactors stage and subjects the thermophilic microorganisms to the thermal shock. Therefore, it provokes the fluctuation in the operational temperatures of the entire system. The problem could be overcome by utilising the wasted low potential heat in the system by energy integration of the processes. However, the integration process is complicated by the presence of uncertainties in the parameters of the incoming raw sludge into the system, i.e. temperature, amount and composition of the raw sludge. Thus, to capture the uncertainties and maximise recovery of the wasted heats we have proposed a methodology for designing the energy integrated ATAD system operating under uncertainties. The proposed methodology includes a model of heat exchanger-integrated system and one heat storage, which is involved within a stochastic optimisation framework. The problem is defined as a problem of two-stage stochastic optimisation with an economic optimisation criterion. Heat exchangers areas and the volume of the heat storage are selected as the first-stage control variables, while flow rates constitute the second stage variables. To approximate the solution, a multi-scenarios decomposition and genetic algorithm are used. The results obtained demonstrate a certain efficiency of the designed energy-integrated ATAD system to deal with uncertainties in the parameters of raw sludge incoming into the system. Reduction of the thermal shock by 5−6 grad is reached and more sustainable operational temperatures in both bioreactors, closed to the required, are achieved. Finally, the acquired stable operational conditions affect a decrease of the retention time and reduction of the energy consumption in the entire system.

7-O1. Utilisation of waste single-based propellants to compositions of liquid fertilisers

Tz. Tzvetkoff, I. Glavchev

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *tzvetkof@uctm.edu*

The utilisation of waste single-based propellants (SBP) to compositions of liquid fertilisers was made in laboratory, semi-industrial and industrial equipments. Alkaline hydrolysis of SBP was used to obtain liquid fertilisers. The kinetics of alkaline hydrolysis was investigated at 19 and 40ºC in a glass reactor supplied with a stirrer, a reflux condenser, and a thermometer. Further laboratory investigation was made applying the same equipment, however, at 95ºC with different amount of SBP and aqueous solution of sodium hydroxide to complete hydrolysis of propellants. Semi-industrial experiments were made in a 200-l steel reactor. The industrial experiments were made in a 2500-l steel reactor supplied with a stainless steel reflux condenser, a stirrer, and a thermometer. An effectve technology was elaborated to obtain liquid fertilisers.

7-O2. Processing and performance characteristics of elastomeric composites with addition of epoxy resin as a filler

D. Zaimova [1,2], E. Bayraktar [2], N. Dishovsky [1], D. Katundi [2]

[1] *University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria*
E-mail: *dishov@uctm.edu*
[2] *Supmeca/LISMMA-Paris, School of Mechanical and Manufacturing Engineering, France*

In different industrial applications of elastomeric composites, variation in the mixing process is one of the basic tools for process optimisation as well as performance requirements. Various components taking part in a particular formulation play an important role on the final properties (these variables are compound consideration, etc.).

The focus of this work lies on the nature of unconventional additional elements (epoxy resin) on the mechanical properties of elastomeric composites based on a mixture of natural and butadiene rubber.

The influence of an accelerator-vulcanising agent system and the replacement of a certain amount of carbon black with epoxy resin (used as fillers) were determined by a comparative study of the mechanical properties. An equilibrium swelling technique was applied to characterise rubber cross-linking density. In addition, a dynamic mechanical thermal analysis and micro-indentation tests were applied. Results of scanning electron microscopy were used to investigate the structure of the vulcanisates and the damage mechanism leading to the final rupture.

7-O3. Comparative analyses of keratin biocomposites with composites based on collagen

D. Zheleva

University of Chemical Technology and Metallurgy, Department of Textile and Leather, Sofia, 8 Kl. Ohridsky
E-mail: *jelevad@uctm.edu*

Keratin and collagen are among the most abundant proteins which can be used in a variety of biomedical applications due to their biocompatibility and biodegradability. Even though, keratin and collagen biomaterials are of very high potential for tissue engineering applications. However, the major disadvantages of the natural biomolecules are their poor mechanical properties. Therefore, they should be modified or combined with synthetic polymers. Most of the synthetic polymers have good mechanical properties and thermal stability.

Numerous studies of biocomposites based on collagen or keratin and a synthetic polymer have been performed. Polyurethanes are considered the most promising class of polymers for *in vivo* studies and fulfil all the criteria for application to medical practice.

Keratin biomaterials have many various advantages over conventional biomolecules including unique chemical properties due to a high content of sulphur in their structure, high biocompatibility, having ability to intracellular recognition, and tendency to self-configure. There have been a lot of studies for the composites based on the keratin and one of the following synthetic polymers: polyethylene oxide, polyamide (PA6), polyvinylacetate, polymethylmethacrylate, poly(L-lactic acid), etc., with application to tissue engineering and drug delivery in the form of gels, sponges, foams, films, fibres, and mats. In the literature, however, there are no investigations for composites based on keratin/polyurethane for biomedical applications. It is not clear why such biocomposites cannot be used in this field, for example, various composites based on collagen/polyurethane, for which abundant information is available about their use.

7-O4. Lignocellulosic biomass as a resource for bioethanol production in Bulgaria

V. Blyahovski, S. Petrin, I. Valchev, S. Nenkova

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *ventsib_g@abv.bg*

The main guideline of the European energy production is the using of fuels from renewable sources. Chemical and biotechnological processing of agricultural and wood wastes is one of the main aspects of their comprehensive utilisation as valuable natural raw materials. The products obtained from them, such as sugars, alcohols, yeast, organic acids, and biologically active substances, etc., have an important practical application. Having in mind the rise in the price of fossil fuels it becomes clear that the development of a technology for utilisation of lignocellulose for biofuel production is very important for this country.

This investigation was performed to examine lignocellulosic biomass supplies in Bulgaria and to determine the chemical composition and potential for bioethanol production from available raw materials.

In our study, the potential of producing sugars from lignocellulosic materials are estimated by treatment through dilute acid, hydrothermal and steam-exploded pre-treatment, and cellulase hydrolysis at the second step.

In Bulgaria, each year about 3.5 million tons of lignocellulosic materials that are suitable for processing to bioethanol become waste. Biomass from plantations of fast growing tree species and annual fibre crops can also be an alternative and attractive.

The glucose yield after cellulase hydrolysis of steam-exploded fast growing paulownia is up to 55%. This result is approximately 10% higher compared to a corresponding treatment of maize stalks, while comparable glucose yield is obtained for poplar and wheat straw.

The generated agriculture residues and the plantation harvesting make that lignocellulosic biomass perspective and suitable for bioenergy production in Bulgaria.

7-O5. Improvement of the physical-mechanical properties of printing production with biodegradable printing varnishes

Ya. Nedelchev, T. Bozhkova, I. Spiridonov, R. Boeva, A. Ganchev

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *t.bozhkova@uctm.edu*

Due to limited fossil resources and an increased need for environmentally friendly and sustainable technologies, the importance of using renewable resources in ink and coating industries will increase in years to come. Other than traditional water-based coatings, which are based on petroleum derivatives, biodegradable coatings focus on resins and waxes from nature.

Biodegradable coatings are based on natural resources for more than 90% and according to ISO-9888 they should be biodegradable by more than 75%. To be able to fully replace the conventional water-based coatings, whose main components are acrylate and styrene acrylate polymers, the biodegradable coatings should be able to cover the main quality requirements: stable running characteristics on the printing press, scuff and scratch resistance, block resistance, wet block resistance, and satisfying optical properties. This research highlights the primary quality differences between biodegradable and conventional coatings and their optical, chemical, and physical characteristics.

7-P1. Potential of fast growing poplar, willow, and paulownia for bioenergy production

N. Yavorov, S. Petrin, I. Valchev, S. Nenkova

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *nyavorof@gmail.com*

The use of renewable energy sources is one of the possible prospects offering a real alternative to mineral fuels in combination with various eco-oriented advantages. In Bulgarian forests, there exists an extensive set of fast growing tree species with a potential for low-cycle-of-rotation management. The most preferred are intensive forest plantations and short-rotation systems from selected clones of poplar, willow, paulownia, acacia, etc. Biomass from plantations of fast growing tree species can be an alternative and attractive base for bioethanol production.

This investigation was performed to determine the potential of fast growing hardwood species in Bulgaria (*Paulownia elongata, Populus alba,* and *Salix viminalis rubra*) as energy crops.

The highest cellulose content was found for poplar, while the amount of lignin was the lowest in paulownia. The obtained lowest calorific value for *Paulownia elongata* was related to the determined content of lignin. The glucose yield after cellulase hydrolysis of steam-exploded paulownia was up to 55%. This result was approximately 15% higher in comparison with a corresponding treatment of poplar and willow.

The obtained result can be explained by a specific structure of paulownia. The chemical composition of wood and especially the cellulose content has no direct effect on the glucose yield.

The plantation harvesting, the calorific value and the glucose yield from fast growing poplar, willow, and paulownia in Bulgaria make these tree species perspective and suitable for bioenergy production.

The structural features of wood are important for cellulosic bioconversion to bioethanol, while chemical content affects the calorific value.

7-P2. Energy potential of hardwood tree species in Bulgaria

P. Tsekova, S. Petrin, V. Gyuleva [1], Y. Dodev [1], A. Dimitrova [2], S. Nenkova, I. Valchev

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
[1] Forest Research Institute, Bulgarian Academy of Sciences, Sofia, Bulgaria
[2] ESF-GTS, Svishtov, Bulgaria
E-mail: *cekovapetya@gmail.com*

The use of renewable energy sources is one of the possible prospects offering a real alternative to mineral fuels in combination with various eco-oriented advantages. Forest fast growing tree species are a promising alternative to agrarian entities in their use of deserted agrarian land or land adjacent to forest stock; they reduce the dependence on fuels import and are considerably more cautious about environment. In this country, experimental research has been conducted and intensive forest plantations from selected clones of poplars and willows and varieties of locust have been created, but mostly for production of construction timber and pulpwood. Biomass properties that affect its use for bioenergy include chemical composition, polymer composition, amount and ratio of cellulose, hemicelluloses, and lignin, which vary depending on the tree species as well as on the age. For this reason, it is important to study the chemical composition of wood by species as well as their calorific value.

The aim of this paper is to determine the energy potential of various hardwood tree species growing in Bulgaria.

Chemical analyses of tree species from acacia, willow, hornbeam, poplar, and paulownia from different regions of Bulgaria were determined. The highest cellulose content was found for poplar and acacia, while the amount of lignin was the lowest in hornbeam.

The highest calorific value was established for willow and poplar, while the lowest results were obtained for paulownia and acacia. However, a certain relationship between the chemical composition and the calorific value, which increases with lignin content, was found.

The results of the chemical analysis and the calorific value of fast growing tree species in Bulgaria may be a basis to create new energy crops grown in plantations.

7-P3. Artificial ageing of composites based on modified cellulose fibres and polyurethane prepolymer

Ts. N. Ilieva [1], S. Nenkova [1], M. Herzog [2]

[1] University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
[2] University of Applied Science Wildau, Hochschulring 1, 15745 Wildau, Germany
E-mail: *ilieva246@gmail.com*

Composite materials reinforced with natural short fibres have a number of advantages compared to other composites. These materials have high moulding flexibility, lightweight properties and they are environmentally friendly. By fibre modification, obtained materials are applicable in different areas, such as automotive industry, conductive composites, building construction, etc.

The ultimate goal of this work is to study the properties of produced composite materials. This research focuses on the production of highly filled polymer composites from short paper fibres from de-inking process and polymer matrix. The properties of these newly created composites are unknown, which forms a principle basis for further research.

In this communication, a method for use of waste fibres is reported. The fibres were mixed with a liquid polyurethane prepolymer to form the composite. The samples were exposed to artificial ageing for 72, 144, 288, and 384 h at 90ºC and 50% relative humidity. The mechanical properties before and after ageing were studied.

7-P4. Copper-based nanostructured lignocellulose materials with antibacterial activity

N. Rangelova, S. Nenkova, N. Lazarova, N. Georgieva

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *nenkova@uctm.edu*

In this study, wood fibre (WF) and technical hydrolysis lignin (THL) were used as lignocellulosic materials. To produce copper sulphide lignocellulose nanocomposites and a two-component Cu(I) reduction system at a saturated steam were used. The modification process was at a module of 1:6, and the ratio of $CuSO_4.5H_2O$ to $Na_2S_2O_3.5H_2O$ components was 1:2 for 45% of lignocellulose materials. Copper content in the samples was determined by inductively coupled plasma optical emission spectrometry, and thermal and acid decomposition methods. The linkage of the cupro ions with lignocelluloses were studied by infrared spectroscopy. The thermal behaviour of the raw and modified materials was investigated by differential thermal analysis. The surface morphology and the shape and size of the formed copper nanoparticles were observed by scanning electron microscopy and transition electron microscopy. The antibacterial activity of the modified lignocelluloses was tested against gram-positive (*Bacillus subtilis* 3562) and gram-negative (*Escherichia coli* K12 407) bacteria. The results showed that the THL-based material exhibits a better antibacterial activity compared to the WF material. The obtained modified materials can be used to prepare lignocellulose-based fibre boards with good antibacterial properties.

7-P5. Chemical specificity of the main Bulgarian forest types

S. Petrin, E. Velisarova [1], P. Tsekova, I. Valchev, S. Nenkova, T. Stankova [1], M. Glushkova [1], D. Dimitrov [1]

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
[1] *Forest Research Institute, Bulgarian Academy of Sciences, Sofia, Bulgaria*
E-mail: *stoiko_petrin@abv.bg*

Forest fires behaviour depends strongly on the forest fuels across a given landscape. The chemical properties and spatial configuration of forest fuels affect ignition, intensity, spread, and fuel consumption of a wildland fire. Therefore, the objective of this study was to characterise the chemical composition of needles and leaves as well as forest litter for assessing the role of the biomass of different woody species for forest fire occurrence and behaviour and associated post-fire chemical changes in the surface soil layer. So far, no systematic research on this topic has been performed in Bulgaria.

The chemical composition of needles, leaves, and litter of the main Bulgarian forest types were analysed. The contents of nitrogen, carbon, and hydrogen as well as solid organic components (lignin, cellulose, and ash), extractable elements, and calorific values were determined.

The concentration of carbon in needles of the coniferous trees slightly exceeds that in forest litter. The hydrogen content followed the same trend. Analyses for solid organic compounds showed that lignin concentration was lower in the needles of the coniferous, while an opposite trend was observed for the cellulose concentration. Plant materials from the crown part of the coniferous forests exhibited about 10% higher calorific values in comparison with the deciduous ones, which suppose a more intensive burning in coniferous forests.

The quantitative chemical composition analysis of plant materials from Scots pine, Austrian pine, beech, and oak forests showed a predominant content of cellulose in the needles of coniferous plant materials compared with their forest litter. On the contrary, a predominance of lignin in the forest litter was documented that could increase the quantity of tars and char formed in result of a fire.

7-P6. Ecological utilisation of printed waste paper

S. Kotlarova, V. Lasheva

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *s_kotlarova@abv.bg*

The use of printed waste paper as a source of secondary fibrous material for the production of paper and paperboard is related to its de-inking by flotation. A perspective and ecological method for de-inking waste paper is flotation with enzymatic treatment at neutral pH that contributes to modification of the cellulose fibres.

Under this condition, we studied the influence of two enzymes: cellulose and lipase, and combinations of these enzymes, in a flotation for de-inking printed waste paper.

At the first step of pulping, printed waste paper flexibility regeneration of fibres begins at a concentration of 4%. The determination of the behaviour and characteristics of the obtained fibre material was based on kinetic drainage, which was determined on a Schopper-Riegler apparatus.

Enzymatic flotation was carried out in a flotation cell. This cell provided a set of hydrodynamic conditions of mixing the paper slurry with a surfactant and enzymes and separation of the ink particles.

The physical and mechanical properties of the paper samples, the latter being received in a Rapid-Keten apparatus, were characterised by the following indicators: tensile strength and breaking, tear resistance, bending resistance, and bursting strength. ISO brightness of the paper samples, prepared by bio-modified de-inked recycled fibre material, was measured.

The papermaking properties of secondary fibres were recovered through bio-modification with enzymes. This bio-modification contributes to an increase of the series of cycles to use recycled paper and to improve some characteristics of the paper produced from recycled fibres.

7-P7. Effect of dry-heating ageing on label paper quality

V. Radkova, P. Tsekova, T. Ivanova, I. Valchev

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *v_radkova@uctm.edu*

Paper ageing can be defined as a sum of all irreversible physical and chemical processes which appear in the material during time. Brightness reversion is of importance for high brightness paper producers. Reversion is the result of chromophores generated by condensation reactions.

The aim of this study was to determine the impact of dry-heating ageing on the quality of label paper properties.

The influence of dry-heat ageing on strength and optical properties of label paper was studied. Three types of pigment-coated label papers were used. One of the samples was characterised by a denser pigment surface layer. Pc number dependence on reaction time for three different temperatures was examined.

Studies on aging with respect to the Pc number for the three types of paper showed that it increases significantly in the paper with a denser surface layer. This was determined by the chromophore structures in the pigment surface layer. The applicability of different kinetic equations valid for heterogeneous processes was verified. The kinetics of the ageing process was described most precisely by an exponential kinetic equation for all types of the sample papers.

Heat is one of the main factors to affect the stability of colour prints. That is why a second examination was taken to determine the colour stability of aged digital prints of photographic quality. The label papers were printed by colour proofing device and artificially aged using the same technique of accelerated ageing. Prints on non-aged label papers, aged prints and differences between aged paper types were analyzed. Their colorimetric characteristics are represented by means of colour density, colour difference, and colour gamut.

7-P8. Investigation on the influence of chemical additives on the behaviour of paper furnish from recycled fibre material

S. Bencheva, D. Todorova

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *todorova.dimitrina@uctm.edu*

The use of secondary fibres from waste paper itself is a major trend in the production of various types of paper and cardboard, which has a very positive environmental effect; it saves water, electricity, steam, and wood raw material. On the other hand, regenerated fibres exhibit reduced sheet-forming properties and induce problems by the appearance of the so-called ‘stickies’. These substances are undesirable components since reduction and in some cases interfere with the action of the cationic chemical additives (CCA) added for a specific purpose. To solve these issues papermakers use CCA.

What is used primarily in the paper production processes are high-molecular weight hydrophilic synthetic polymers (polyelectrolytes) of different chemical nature. Their role is to cause colloid-chemical changes at the barrier surface of the system ‘fibre-to-water’ and especially to affect the values of the electrokinetic potential. The obtained larger and smaller agglomerates are better retained onto the web. As a result, dewatering is accelerated, the retention of the components in the paper sheet is improved, and this provides clarified white waters.

The behaviour of the paper furnish during dewatering basically depends on the type of fibre material and the degree of its beating (pulp, chemical pulp, and waste paper), fillers, sizing agents, and used chemical additives.

The purpose of this study was to investigate the effect of cationic synthetic polyelectrolytes of different chemical nature and charge on the behaviour during dewatering of paper furnish from recycled fibre material from waste paper.

The recycled fibre material is from waste newsprint paper and it mainly consists of chemical thermo-mechanical pulp. Six types of cationic chemical additives of different chemical nature and charge density were used. The dewatering ability was measured and the turbidity and conductivity of the white waters was determined.

Due to this study, it was found that a chemical additive based on polyacrylamide was the best for use to improve dewatering and clarification of the white waters.

7-P9. Thermoforming process of biopolymer composites

K. Dimitrov, A. Matev, M. Herzog [1], S. Nenkova

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
[1] *University of Applied Science Wildau, Hochschulring 1, 15745 Wildau, Germany*
E-mail: *nenkova@uctm.edu*

The main object of this work was to investigate the forming properties of two-dimensional composites during the thermoforming process. The composites were prepared from polylactic acid films with the aim to improve the viability of such films by reinforcing by various fibre types. The composites thus obtained were used for the production of a packaging compound by means of vacuum thermoforming. The products were manufactured by KIV Kreis GmbH. The mechanicals properties of the composite materials were investigated. The morphology of the materials was investigated by means of optical microscopy. Technical parameters of the thermoforming process were investigated. A consumptions test showed that added glass fibres improved the bearing capacity of the packaging.

7-P10. Kinetic aspects of the enzyme hydrolysis of cellulose fibre materials

P. Tzvetkov, N. Yavorov, S. Petrin, I. Valchev, G. Radeva

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *grradeva@uctm.edu*

A kinetic dependence of the enzyme hydrolysis of cellulose fibre materials (bleached kraft pulp and populus pulp) on different cellulasic enzyme complexes was studied. It was found that the topochemical mechanism provides a satisfactory interpretation of cellulase action. The kinetics of the process was described by a modified topochemical equation of Praut-Tompkins, which is applied for processes taking place on the most accessible outside surface of the pulp and gradually penetrates inside the capillary system of the fibre matrix. The rate controlling factors include structural features of the pulp-enzyme system. During the process, the activation energy of the hydrolysis was constant. This shows that the energy characteristics of the cellulose-enzyme complex were the same for the surface and inside the fibre system. The pre-exponential factor accounts for the accessibility and dimensions of the reaction area, which is formed based on cellulose-enzyme complexes and changes during the process.

7P-11. Investigation of the thermal ageing of chemical mechanical pulps obtained from different types of hardwood

R. Boeva, I. Spiridonov, R. Nikolov, G. Radeva [1]

Department of Pulp, Paper and Printing Arts, University of Chemical Technology and Metallurgy,
8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *r_boeva@abv.bg*
[1] Department of Physical Chemistry, University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd.,
1756 Sofia, Bulgaria

The basic raw materials used in papermaking processes are obtained from fibrous materials produced by chemical treatment of various types of wood or annual plants.

In this research, chemical mechanical pulps (CMP) of wood chips from *Paulownia tomentosa* and *Populus deltoides clon-235-15* with higher density (474 kg m^{-3}) were obtained.

The main goals of the present work were to study artificial thermal aging of bleached and unbleached CMP obtained in the laboratory from poplar and paulownia wood and microscopic analysis of fibrous masses.

The obtained chemical mechanical pulp was bleached in two stages by using hydrogen peroxide and formaldehyde-hydrosulphite. Changes of whiteness and yellowness of samples in the process of artificially thermal ageing at 105ºC were observed.

7-P12. Investigation of the effect of different tone value sum of inks on colour reproduction accuracy of heatset web offset images

I. Spiridonov, R. Boeva, T. Bojkova, Ya. Nedelchev

Department of Pulp, Paper and Printing Arts, University of Chemical Technology and Metallurgy,
8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *spiridonov@abv.bg*

The goal of the present study was to define a correlation between the tone value sum (total area coverage, TAC) and colour reproduction accuracy on heatset web offset images printed on LWC paper. In case of incorrect value use at relatively high or low levels of tone-value sum, press problems, such as big amount ink consumption, poor ink trapping, back-transfer, and set-off due to insufficient ink drying might be encountered. That is why it is necessary to find and determine the optimal values of colour separation parameters for each inks/paper/printing press combination.

A test form was that contained different control strips for densitometric, colorimetric measuring, and test charts used for ICC profiles.

The reflection spectra of measured colour patches in the entire visible range were used to determine the effect of different TAC values. To study the effect of TAC values on colour gamut and colour accuracy, we calculated colour differences ΔE*ab, surface area and volumes of 2D cross-sections, and 3D shape body in a CIE L*a*b* colour system.

The results achieved are important from a scientific and practical point of view. For the first time in an experimental way, a well-grounded proof was achieved with regard to the limits of the tone value sum and variation from the optimal TAC values for heatset offset press by provision of colour differences in compliance with international standards.

7-P13. Structural transformations of polystyrene/polyether block copolymer core-shell particles investigated by diffusion-ordered NMR spectroscopy and TEM

E. Haladjova, P. Shestakova [1], D. Karashanova [2], Ch. B. Tsvetanov, Ch. P. Novakov

Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 103A, 1113 Sofia, Bulgaria
[1] *Institute of Organic Chemistry with Centre of Phytochemistry, 1113 Sofia, Bulgaria*
[2] *Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*
Fax: *+359-2-8700309, e-mail*: *ehaladjova@polymer.bas.bg*

The aim of the present work was to investigate structural transformations and size changes of amphiphilic block copolymer particles induced by addition of hydrolytic agents to their solutions. Aggregates were prepared by dissolving a series of previously synthesised diblock copolymers consisting of hydrophobic polystyrene (PS) with randomly distributed short diene moieties and hydrophilic polyether or polyglycidol (PEO or PG) blocks in selective solvents. An attempt to induce structural changes of the preformed aggregates was made by addition of a hydrolytic agent (strong acid and ferric salt) to the system.

The structure and size of the PS/PEO (PS/PG) block copolymer core-shell particles were investigated by conventional and diffusion NMR spectroscopy (DOSY). The broadening and disappearance of the PS signals in the ^{1}H NMR spectra upon increase of water content in mixed organic/aqueous solutions evidenced a possible reversal of the core-shell structure. The DOSY spectra indicate an increase of particle size in parallel with the increase of water content. Detailed information on morphology, shape and size distribution of the aggregates was provided by TEM. For comparison, the change of the particle size under identical conditions for objects of preliminary stabilised core-shell morphology was monitored as well. In addition, size exclusion chromatography was used to follow changes in copolymer molecular weight and molar mass distribution, while dynamic light scattering was applied as a complementary technique for particle size determination.

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7-P14. Green synthesis of novel amphiphilic triblock polyglycidol-poly(allyl glycidyl ether)-polyglycidol copolymers and study of their aggregates in solution

B. Stoyanova, Ch. P. Novakov, S. Rangelov, Ch. B. Tsvetanov

Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 103A, 1113 Sofia, Bulgaria
Fax: *+359-2-8700309, e-mail*: *bstoyanova@polymer.bas.bg*

Three series of original triblock copolymers of polyglycidol-poly(allyl glycidyl ether)-polyglycidol (PG-PAGE-PG) were prepared by ring-opening anionic polymerisation. The copolymers differ in their overall molecular weight and ratio of the constituent units. The polymerisations were carried out in bulk, that is, in the absence of organic solvents. They were found to proceed in a controllable and predictable way.

Bifunctional PAGE homopolymers of molecular weights of 2200, 3700, and 5700 Da were initially synthesised by ring-opening anionic polymerisation of allyl glycidyl ether. They were used as macroinitiators for anionic polymerisation of ethoxyethyl glycidyl ether (EEGE, protected glycidol). After successful cleavage of the protective ethoxyethyl groups, nine linear amphiphilic triblock PG-PAGE-PG copolymers, in which the hydrophilic (polyglycidol) fraction was set at 30, 45, and 60 mol%, were prepared. The resulting copolymers were of total molecular weight within the range of 3000 to 8900 Da and dispersity below 1.4.

The ability of the newly synthesised copolymers to self-associate in aqueous solution was investigated. Fundamental parameters, such as critical aggregation concentration, size and size distribution of particles as well as thermodynamic parameters of self-association and particle morphology were determined.

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7-P15. Influence of lipoid structure and polymer chain length on the properties of DPPC liposomes grafted with novel polyglycidol-lipoid conjugates

P. Bakardzhiev, S. Rangelov, D. Momekova [1], S. Shaheen

Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 103A, 1113 Sofia, Bulgaria
[1] Department of Pharmaceutical Technology and Biopharmacy, Faculty of Pharmacy, Medical University,
2 Dunav St., 1000 Sofia, Bulgaria
E-mail: *pavettoo@abv.bg*

Liposomes are promising carriers for both hydrophilic and hydrophobic drugs. Due to some interactions with the reticulo-endothelial system they are characterised by fast clearance and short half-life in the bloodstream, which can be overcome by grafting poly(ethylene glycol)-conjugated lipids on the liposomal surface, thus creating sterically stabilised or *Stealth* liposomes. Polyglycidol is a hydrophilic and flexible polyether-polyol bearing a hydroxyl group in each monomer unit. The aim of the present contribution was to reveal its ability to provide steric stabilisation of liposomes. For this purpose we synthesised a series of lipoid anchors (1R,3R′-propane-2-ol), where R and R′ are C_{12}-C_{18} linear, saturated or unsaturated aliphatic groups, linked to the glycerol skeleton *via* ether bonds, which are conjugated to polyglycidol chains of different molar masses. The polymers were characterised by ^{1}H-NMR and GPC, and their self-assembly in water was studied as well. Liposomes, based on dipalmitoylphosphatidylcholine (DPPC), grafted with the novel polyglycidol-lipoid conjugates, were prepared and their properties studied. Furthermore, the polyol nature of the polyglycidol gives a platform for functionalisation by specific molecules, such as monoclonal antibodies, vitamines, peptides, etc., which can be used as targeting ligands of the grafted liposomes.

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7-P16. Cross-linked star (co)polymers containing a core of C-tetraalkylcalix[4]resorcinarene

P. P. Petrova, S. M. Miloshev, Ch. P. Novakov [1]

University of Chemical Technology and Metallurgy, 8 K. Ohridsky Blvd., 1756 Sofia, Bulgaria
[1] Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
E-mail: *stuci@uctm.edu*

The aim of the present contribution was to synthesise a series of new star block copolymers containing a core of C-tetraalkylcalix[4]resorcinarene that can be sensitive in response to changes in environment.

Several approaches were employed to obtain star-like structures. In one case, an ATRP polymerisation technique was used to form regular star polymers that consist of a symmetrical structure comprising radiating linear chains (arms) with identical chemical composition. The 'core-first' controlled polymerisation approach was conducted from C-tetraalkylcalix[4]resorcinarene macroinitiator and vinyl monomers, e.g. acrylic acid derivatives and/or NIPAM. Experiments for the preparation of cross-linked stabilised structures were made with the addition of a cross linking agent (e.g. divinylbenzene) at a certain stage of the process. Another approach to synthesise star block copolymers was based on coupling to a method where linear functional homo- and copolymers were reacted with a preformed C-alkylcalix[4]resorcinarene core.

Various star block copolymers with well-defined architecture were prepared using the above approaches. Their structure and molecular mass characteristics were studied by conventional instrumental methods, e.g. NMR spectroscopy and size exclusion chromatography (SEC). The process of self-association of various copolymers in solution as well as some variation in their behaviour in response to changes in stimuli were investigated using complementary techniques, such as dynamic light scattering and coupled SEC/multi angles laser light scattering.

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7-P17. Self-assembly of calix[4]pyrrole nanostructures in an acryl-methacrylic copolymer matrix

S. I. Nikolov, S. M. Miloshev

University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *stuci@uctm.edu*

Over the past several decades a large number of acyclic and macrocyclic compounds have been synthesised as ion receptors. As a consequence, both cation and anion recognition are now well-established branches of supramolecular chemistry. Of significant interest are the amphiphillic cyclic structures which are capable of forming simultaneously both cation and anion complexes. These so-called pair receptors might also permit a higher level of control over ion recognition, extraction from specific media, and much effective through-membrane transport than simple ion receptors.

It is shown that polymeric matrices, containing anion and cation recognition groups, which are capable of forming cyclic oligomers, containing pyrroles or benzo-crown units, can be used. They are capable of binding halide anions in organic media and forming a 2:1 sandwich complex with the K^+ cation.

Classical heterocyclic oligomeric compounds, calix[4]pyrroles, were synthesized and used. Their behaviour in an acrylic-metacrylic polymer matrix was investigated. It is shown that the calix[4]pyrrole itself forms well defined clusters which effectively form complexes with cations of alkaline metals and some noble metals and their nanoparticles. An increased level of ion recognition was observed in the cases of forming a three-dimensional network between the cyclic oligomer and the polymer matrix on interaction with suitable agents. The obtained compounds and their supramolecular structure were characterised by ^{1}H NMR, FTIR, UV-vis, HPLC, SEC, DLS, and TEM) and feasible mechanisms for the obtained supramolecular structures are proposed.

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7-P18. Siloxane composition coatings reducing marine biofilm formation

D. Akuzov [1], T. Vladkova [1], A. Klöppel [2], F. Brümmer [2]

[1] University of Chemical Technology and Metallurgy, 8 K. Ohridsky Blvd., 1756 Sofia, Bulgaria
[2] Biology Institute, Stuttgart University, Stuttgart, Germany
E-mail: *akuzov@gmail.com*

Biofilm formation is the initial stage of marine biofouling with own negative impact on various submerged surfaces. In most cases, it acts as a substrate to which macro-foulers, such as barnacles, tube worms, algae, etc. attach and develop their fouling communities. Therefore, fighting with marine biofilms attracts continuous research interest.

Marine biofilm formation is a dynamic process involving a large diversity of microbial material and molecules. In addition, it depends on the environmental conditions and irrespective habitants. Thus, the combat with marine biofilms is a significant challenge and requires complex approaches adjusted to the matching surface in the corresponding equatorial. A biofilm develops even on a biocide antifouling paint coated surfaces under high shear stress.

Siloxane fouling release coatings are currently the only viable commercial alternative of the toxic biocide containing antifouling paints that were banned in 2008. We are trying now to develop a totally preventing hard foulers settlement, siloxane coatings that reduce sharply marine biofilm formation.

Our study demonstrates that some low toxic additives, such as oils, non-ionic surfactants, antioxidants, and their combinations included in siloxane composition coatings reduce biofilm formation down to 3 to 7 times. This depends on evaluating parameter and additive type and amount. A possible explanation of this effect is presented.

7-P19. Preparation of poly(ethylcyanoacrylate) nanofibres by vapour phase polymerisation using alcohol initiators

N. Marinov, M. Simeonova

Department of Polymer Engineering, University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *msimeonova@uctm.edu*

Anionic initiators, containing either hydroxyl or thiohydroxyl group as initiating moieties, were used for preparation of a poly(ethylcynoacrylate) (PECA) nanofibre by vapour phase polymerisation. The hydroxyl (alcohol) and thioalcohol groups as nucleophilic entities are capable to attack the double bond of monomer resulting in polymerisation in the vapour phase and formation of nanofibres at a high relative humidity. Different techniques, such as scanning electron microscopy (SEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), size exclusion chromatography (SEC), and FTIR spectroscopy were used for characterisation of the morphology, thermal behaviour, molecular weight and structure of the polymer nanostructures (nanofibres).

The results obtained show differences in the properties of the PECA nanofibres formed *via* vapour phase polymerisation most likely due to different nucleophilicity of both initiating species.

7-P20. Surface-modified poly(butyl cyanoacrylate) nanoparticles loaded with indomethacin: Preparation and physicochemical characterisation

V. Staneva, G. Ivanova [1], M. Simeonova

Department of Polymer Engineering, University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
[1] REQUIMTE, Departamento de Quımica, Faculdade de Ciĕncias, Universidade do Porto, 4169-007 Porto, Portugal
E-mail: *msimeonova@uctm.edu*

Poly(butylcyanoacrylate) nanoparticles (PBCN) as biodegradable and biocompatible devices have gained interest as a colloidal drug delivery system. Their main technological advantage is the possibility for preparation by anionic polymerisation in aqueous medium without addition of any initiator that could have undesirable toxic effects. Unfortunately, under such conditions there arises a problem of the difficulty of encapsulating low water-soluble drugs.

We have investigated the modifying ability of hydroxypropyl-beta-cyclodextrin (HPBCD) in the preparation of PBCN loaded with indomethacin. Surface modified HPBCD-PBCN were prepared by an interfacial polymerisation of the monomer. The loading of indomethacin was performed simultaneously with the formation of nanoparticles.

The physicochemical characterisation of indomethacin-loaded surface-modified PBCN was made by DLS (particle size analysis), laser Doppler electrophoresis (zeta potential measurement), and NMR spectroscopy, which verify the presence of the drug into a nanoparticle polymer matrix.

7-P21. Investigation of dynamic-mechanical properties of vulcanisates based on natural rubber filled with pyrolytic silica in the presence of different types of zinc soaps

Y. Kolev, M. Mihaylov, M. Ivanov

Department of Polymer Engineering, University of Chemical Technology and Metallurgy, 8 K. Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: *m_c_mihaylov@uctm.edu*

There is a tendency towards a massive implementation of the so-called ‘green’ tires. The reinforcing filler in them constitutes mainly of silica. It provides lower rolling resistance and therefore lower fuel consumption compared with mixtures filled with carbon black. The object of the study was a new material containing silica and carbon black with nanosized particles (SiO_2D), produced by recycling of scrapped ‘green’ tires *via* pyrolysis, as a filler in rubber composites based on natural rubber. Studies have been made on mixtures and their vulcanisates based on natural rubber stuffed with a filler, pyrolytic silica (SiO_2D), in the presence of different types of zinc soaps without zinc oxide.

A Goodrich flexometer and a dynamic mechanical thermal analyser (MK III, Rheometric Scientific) were used to determine the dynamic-mechanical properties of the vulcanisates from the studied compounds cured for both an optimal and a 4-fold optimal time. It was established that vulcanisates containing zinc soaps had a lower heat build-up than control samples, which is dependent on zinc stearate content. The presence of zinc soaps did not lead to a substantial change in the glass transition temperature, but the dynamic module (E') of the vulcanisates containing zinc soaps was lower for the glass transition temperature.

There was no substantial change in tg δ in the temperature range from 0 to 100ºC in the vulcanisates formed in the optimum curing time. In vulcanisates formed for 4x optimum curing time, tg δ rises with the increase of temperature. This shows that for a longer curing time destructive processes of the already formed crosslink network begin to develop.

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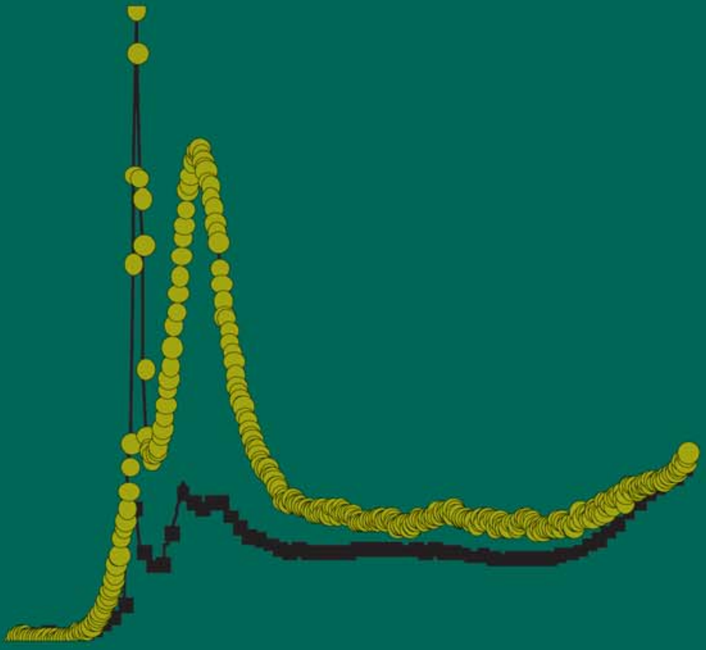
40 YEARS IONIC MELT ELECTROCHEMISTRY IN BULGARIA



$$\mathrm{Fe}_{\mathrm{Cr}}^{\mathrm{III}} + \mathrm{Fe}_{\mathrm{ad}}^{\mathrm{III}*} \xrightarrow{k_{34}} \mathrm{Fe}_{\mathrm{melt}}^{3+} + \mathrm{Fe}_{\mathrm{ad}}^{\mathrm{III}*} + \mathrm{V}_{\mathrm{Cr}}'''$$

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Bulgarian Hydrogen Society

Union of Chemists in Bulgaria
108 G. Rakovski St.,
1000 Sofia, Bulgaria
tel/fax: +359-2-9875812
web site: http://www.unionchem.org

Company for International Meetings Ltd.
18 Christo Belchev St., 1000 Sofia, Bulgaria
tel: +359-2-981931, +359-2-9860806
fax: +359-2-9806074
web site: http://www.cim.bg