



**RESEARCH INFRASTRUCTURE  
IN SUPPORT OF SCIENCE,  
TECHNOLOGY AND CULTURE**

**Scientific conference**

**Sofia, September, 29-30, 2020**

**On-line meeting**



Dear colleagues and collaborators of INFRAMAT,

Dear scientists joining our conference,

Dear guests,

INFRAMAT is a unique Research Infrastructure that integrates research equipment and experts from 16 educational, research and museum institutions, distributed in two Modules: Synthesis and Characterization of New Materials (Module I) and Analysis, Restoration and Conservation of Archeological and Ethnographic Artefacts (Module II).

Our present scientific conference is focused on the recent opportunities that equipment of INFRAMAT has offered to support advancements in different fields of materials science, technology development as well as for the preservation of cultural heritage.

I am thankful to all partners of INFRAMAT that responded to our invitation to share their current scientific results. I am glad that many young scientists and doctoral students joined the conference and have the opportunity to present their work.

In the extraordinary pandemic situation that we are all experiencing this is our first attempt to organize a conference in a quasi-virtual format. In fact, it will be a kind of hybrid event combining interactive on-line oral sessions and open air poster presentations (for Module I). We hope that despite this specific conference format we will all enjoy fruitful scientific exchange, vivid discussions, and motivating ideas for our forthcoming research activities.

I wish all participants success in their actual presentations and future scientific work,

Vessela Tsakova  
Coordinator of INFRAMAT

## **Organizing Committee**

**Prof. DSc Vessela Tsakova**  
**Prof. DSc Pavletta Shestakova**  
**Prof. DSc Tony Spassov**  
**Prof. DSc Yuri Kalvachev**  
**Dr. Kalin Dimitrov**  
**Kamenka Staykova**  
**Reni Andreeva**

**INFRAMAT is Distributed Infrastructure of Centers for Synthesis and Characterization of New Materials and Restoration and Conservation of Archeological and Ethnographic Artefacts**, part of *Bulgarian National Roadmap for Research Infrastructure*, supported by Ministry of Education and Science under contracts D01-155/2018 and D01-284/2019.

**INFRAMAT Coordinator:**  
**Institute of Physical Chemistry –**  
**Bulgarian Academy of Sciences**  
**Office INFRAMAT: [inframat@ipc.bas.bg](mailto:inframat@ipc.bas.bg)**  
**Web-site: [www.inframat.bg/en](http://www.inframat.bg/en)**

**Video presentation: [//inframat.bg/en/inframat-v-10-minuti/](http://inframat.bg/en/inframat-v-10-minuti/)**

# *Research Infrastructure in Support of Science, Technology and Culture*

## **PROGRAMME**

**29/09/2020**

9:30 – 9:40 **Opening**

### **MODULE I: Synthesis and Characterization of New Materials**

**Section A: Oral Presentations**

**Chair: Yuri Kalvachev**

09:40 – 10:00 ***A. Nakova, R. Ivanov, M. Ilieva, V. Tsakova***  
Electrode-assisted Electroless Metal Deposition – Palladium Nanocatalysts for  
Organic Fuel Oxidation

10:00 – 10:20 ***L. Mihaylov, E. Vasileva, St. Todorova, R. Stoyanova, T. Spassov***  
Microstructural Study of Porous Metals Obtained by Selective Dissolution

10:20 – 10:40 ***K. Maksimova-Dimitrova, E. Lefterova, G. Borisov, E. Slavcheva***  
Nanocomposite Catalysts Based on Mn, Ni, Co For Alkaline Water Electrolysis

10:40 – 11:10 **Break**

**Chair: Vessela Tsakova**

- 11:10 – 11:30 **B. Abrashev, M. Slavova, E. Mladenova, B. Burdin, G. Raikova, V. Terziev, K. Petrov, D. Vladikova**  
Electrochemical Properties of Optimised Electrode Materials for Rechargeable Zn-Air Batteries
- 11:30 – 11:50 **E. Petkucheva, G. Borisov, E. Lefterova, E. Slavcheva**  
Iron Modified Ni-Foam as a Self-Standing Electrode for Efficient, Durable Oxygen Evolution for Alkaline Water Splitting
- 11:50 – 12:10 **O. Kostadinova, V. Ilcheva, V. Boev, T. Petkova, B. Burdin, E. Mladenova, D. Vladikova, L.C. Costa**  
Electrochemical Impedance Behavior and Relaxation Processes in H<sub>3</sub>PO<sub>4</sub>-Enriched SiO<sub>2</sub>-TiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> System
- 12:10 – 12:30 **T. Cholakova, L. Kolaklieva, Hr. Bahchedjiev, V. Chitanov, S. Kolchev, R. Kakanakov**  
Improvement the Mechanical Properties of TiCN / ZrCN Multilayer Coating With Modulated Period for Industrial Applications

12:30 – 14:00 **Lunch time**

**Section B: Oral Presentations**

**Chair: Pavletta Shestakova**

- 14:00 – 14:20 **M. Ognyanov, Y. Georgiev, P. Denev**  
An Automated System for the Quantification of Uronic Acids and Neutral Sugars (Skalar San++ Analyzer) - Components, Advantages, Disadvantages, and Applications
- 14:20 – 14:40 **E. Mladenova, L. Dobрева, M. Slavova, G. Raikova, O. Kostadinova, B. Burdin, S. Danova**  
Study of Polarizable Dielectric Fluids - Cow and Soya Milk by Dielectric Impedance Spectroscopy
- 14:40 – 15:00 **E. Mladenova, I. Karadjova**  
Analytical Atomic Spectroscopy in Bee Honey Analysis

**15:00 – 15:30 Break**

15:30 – 17:00      **Poster Session A**

**A1 V. Chakarova, L. Mirkova, M. Monev**

Electrochemical Method for Studying the Process of Hydrogen Permeation into Metals during Aqueous Electrolysis. Hydrogen Permeation in Electroless Ni-P Coatings

**A2 R. Andreeva, E. Stoyanova, D. Stoychev**

Corrosion-Protective Ability of Chemically Deposited Conversion Layers on Technically Pure Aluminum, after Application of Specific Additional Treatments of the Aluminum Substrate and Formed on it Ceria Conversion Layer

**A3 M. Peshova, V. Bachvarov, St. Vitkova, N. Boshkov**

Corrosion Characterization of Environmentally Friendly Conversion Films on Zinc-based Protective Coatings by Electrochemical Impedance Spectroscopy

**A4 R. Ivanov, V. Tsakova, C. Czibula, C. Teichert**

Electroless Deposition of Pd on Carbon Substrates

15:30 – 17:00      **Poster Session B**

**B1 R. Mladenova, K. Aleksieva**

Effect of Gamma-Irradiation on Bee Pollen Antioxidant Activity and Free Radicals Studied by EPR Spectroscopy

**B2 M. Tavlinova-Kirilova, M. Kamenova-Nacheva, K. Kostova, V. Dimitrov**

Synthesis of Chiral, non-Racemic Aminonaphthols and Determination of their Chiroptical Properties Using a Polarimeter

**B3 M. Kamenova-Nacheva, M. Tavlinova-Kirilova, K. Kostova, V. Dimitrov**

Enantioselective Addition of Et<sub>2</sub>Zn to Aldehydes - Determination of Enantiomeric Excess by High-Performance Liquid Chromatography (HPLC)

**B4 P. Kardaleva, S. Todinova, D. Yancheva, M. Guncheva**

Study of the Conformation and Thermal Stability of Bovine Serum Albumin in Complexes with Ionic Liquids Containing Naproxen Anion

**B5 Y. Mitrev, D. Gerginova, S. Simova**

Quantitative NMR Spectroscopy of sugars – which experiment to choose?

**B6 N. Anastassova, N. Hristova-Avakumova, K. Radev, D. Yancheva**

New Indole Arylhydrazones and Study of their Protective Properties on Iron Induced Oxidative Damage of Biologically Important Molecules

**B7 M. Argirova, E. Cherneva, D. Yancheva**

New 2-Amino Benzimidazolyl Hydrazone Complexes: Synthesis, Spectroscopic and DFT Investigation

**B8 D. Gerginova, Y. Mitrev, S. Simova**

Are we Drinking a Real Wine? 1H NMR Metabolomic Profiling of Bulgarian Wines

**B9 A. Dolashki, A. Daskalova, N. Vasilev, S. Simova, M. Dangalov, L. Velkova,  
V. Atanasov, Y. Topalova, N. Kostadinova, E. Krumova, M. Angelova, T. Stoyanova,  
L. Woelki, D. Kaynarov, P. Dolashka**

Metabolites Isolated from Garden Snail Helix Aspersa with Antibacterial and Antifungal Activity Determined through 1HNMR and Mass Spectrometry

**30/09/2020**

**Section C: Oral Presentations**

**Chair: Yuri Kalvachev**

9:30 – 9:50 **S. Todorova, J. L. Blin, A. Naydenov, B. Lebeau, D. Karashanova,  
H. Kolev, A. Dotzeva, D. Filkova, L. Vidal, L. Michelin, L. Josien**  
Co-Mn Mixed Oxides Supported on Hierarchical Macro-Mesoporous Silicas for  
Co and VOCs Oxidation

9:50 – 10:10 **T. Todorova, P. Shestakova, T. Petrova, M. Popova, Hr. Lazarova,  
Yu. Kalvachev**  
Fluoride etching of AlZSM-5 and GaZSM-5 zeolites

10:10 – 10:30 **P. Shestakova, M. Popova, H. Lazarova, T. K. N. Luong, I. Trendafilova,  
J. Mihály, Á. Szegedi, T. N. Parac-Vogt**  
NMR Characterization of Hybrid Catalyst with Combined Lewis and Brønsted  
Acidity Based on ZrIV Substituted Polyoxometalate Grafted on MCM-41  
Mesoporous Silica for Esterification of Renewable Levulinic Acid

10:30 – 11:00 **Break**

11:00 – 11:20 **G. Issa, M. Dimitrov, R. Ivanova, T. Tsoncheva**  
Catalytic Behavior of Nanostructured Ceria Promoted Manganese in Vocs  
Elimination

11:20 – 11:40 **R. Ivanova, G. Issa, M. Dimitrov, T. Tsoncheva**  
Comparative Study of the Properties of Nanostructured Oxide Materials Based  
on Titanium Dioxide and their Application as Catalysts for Environmental  
Protection

11:40 – 12:00 **St. Kozhukharov, Ch. Girginov**  
The Electrochemical Impedance Spectroscopy as a Powerful Instrument for  
Corrosion Rate Determination

12:00 – 13:30 **Lunch time**



**Section D: Oral Presentations**

**Chair: Pavletta Shestakova**

13:30 – 13:50 ***R. Georgiev, K. Lazarova, M. Vasileva, B. Georgieva, T. Babeva***  
Micelles-Structured Bragg Stack of Nb<sub>2</sub>O<sub>5</sub> for Sensing Applications

13:50 – 14:10 ***St. Pereva, Ts. Sarafska, V. Nikolova, S. Angelova, T. Spassov, T. Dudev***  
Inclusion Compounds of NSAIDs with Cyclodextrins

14:10 – 14:30 ***Z. Todorova, O. Tumurbaatar, N. Koseva***  
Application for Analytical Ultracentrifugation and Dynamic Light Scattering for  
Study of the Specific Interaction between Con A and a Star-Shaped  
Glycopolymer

14:30 – 15:00 **Break**

15:00 – 15:20 ***E. Haladjova, M. Smolíček, I. Ugrinova, D. Momekova, P. Shestakova,  
Z. Kroneková, J. Kronek, S. Rangelov***  
DNA Delivery Systems Based on Copolymers of Poly (2-Methyl-2-Oxazoline)  
and Polyethyleneimine

15:20 – 15:40 ***M. Dangalov, Y. Mitrev, N. Toncheva-Moncheva, Ch. Novakov,  
N. G. Vassilev***  
In Situ Irradiation NMR Spectroscopy in the Design of New Functional Materials  
(LED-NMR)

15:40 – 16:00 **Break**

16:00 – 17:30 **Poster Session C**

**C1 *T. Todorova, P. Petrova, Yu. Kalvachev***  
Mordenite as Catalyst Support for Complete VOCs Oxidation

**C2 *M. Shopska, S. Todorova, I. Shtereva, H. Kolev, K. Aleksieva, G. Kadinov***  
Cobalt-Palladium Bimetallic System Behavior During CO Hydrogenation: Comparative  
Study of the Support Effect

**C3 *N. Lihareva, L. Dimowa, O. Petrov, Y. Tzvetanova, I. Piroeva,  
S. Atanasova-Vladimirova***  
Study of the Kinetics and Mechanism of Sr<sup>2+</sup> Sorption by Clinoptilolite

**C4 *P. Vassileva, A. Detcheva, I. Uzunov, S. Uzunova, D. Voykova***  
Investigation of Lead (II) Removal from Aqueous Solutions Using Waste Material Based  
on Rice Husk

**C5 A. Kosateva, B. Tsyntsarski**

Raman Spectroscopy of Water Samples

**C6 Ch. Girginov, St. Kozhukharov, A. Dishliev**

Hard Anodization as an Efficient Technique for Enhancement of the Mechanical Surface Properties of Aluminum and its Alloys

16:00 – 17:30

**Poster Session D**

**D1 I. Dionisieva, K. Buchkov, V. Marinova, I. Avramova, H. Dikov, D. Dimitrov**

Two-Dimensional Layers of PtSe<sub>2</sub> – Synthesis and Characteristics for Opto-Electronics Applications

**D2 G. Gerginov, S. Simeonov**

Green and Efficient Extraction of Shikimic Acid from Illicium Verum with Deep Eutectic Solvents

**D3 B. Napoleonov, D. Petrova, V. Marinova, B. Blagoev, V. Strijkova and D. Dimitrov**

Atomically Deposited Nanolayers of ZnO Doped with Al: Characterizations and Applications

**D4 G. Marinov, B. Georgieva, V. Strijkova, N. Todorova, T. Babeva**

Thin Nanocrystalline ZnO Films Doped with Al and Co Deposited by Electrospray: Properties and Applications

**The poster sessions of MODULE I will take place in the open air and located in the Campus “4-th km” of Bulgarian Academy of Sciences**

## **MODULE II Analysis, Restoration and Conservation of Archeological and Ethnographic Artefacts**

**29/09/2020**

**Oral presentations**

**Chair: Christo Popov**

09:40 – 10:00 **P. Penkova**

Investigation of Manufacturing Technology of Artifacts from a Tumulus Mound near the Village of Chudomir

10:00 – 10:20 **I. Hristov, I. Prokopov, V. Penchev, A. Vatov**

Analysis of Hellenistic and Celtic tetradrachms from the village of Terziysko, the Troyan region

10:20 – 10:40 **P. Y. Georgiev, K. Dimitrov**

Documentation of underwater archaeological excavation through digital photogrammetry

10:40 – 11:10 **Break**

11:10 – 13:00 **Poster Session**

**Chair: Christo Popov**

**M2.1 V. Fol, R. Preshlenova, R. Popova**

Creating the e-Database Encyclopaedia Ancient Thrace and the Thracians Aimed at Promoting the Cultural Heritage on the Territory of the Republic of Bulgaria

**M2.2 V. Bonev, B. Zlateva, T. Stoyanov**

Using of p\_XRF for Analysis of Archaeological Finds Made of Copper and Copper Alloys

**M2.3 V. Lyubomirova, R. Djingova, B. Todorov, V. Mihaylova, B. Zlateva, I. Belovezhdova**

Application of LA-ICP-MS for Investigation of Archaeological and Geological Samples

**M2.4 B. Todorov, V. Lyubomirova, R. Djingova, V. Mihaylova, B. Zlateva, I. Belovezhdova**

Application of Gamma Spectrometry for Dating of Archaeological and Geological Samples

- M2.5 N. Lumov, S. Belishki, S. Stoyanov, D. Yancheva, E. Velcheva, B. Stamboliyska**  
A technological study on the wall paintings in the Russian Church St Nikolay in Sofia:  
identification of the binding media by IR spectroscopy
- M2.6 S. Belishki**  
Application of multispectral imaging for the study of the painting Portrait of Alexander II  
by Stanislav Dospevski
- M2.7 I. Mishkova, G. Baykusheva**  
Case studies of the decorative elements of painted chests from the collection of  
IEFSEM-BAS
- M2.8 A. Vatov, Ts. Docheva, S. Hristova**  
Application of Reflectance Transformation Imaging (RTI) in the study of cultural artefacts  
from the fund of architectural complex - "Balchik Palace"
- M2.9 I. Borisov, D. Kyuranova**  
Solved conservation tasks on a shroud, owned by Historical Museum, Pomorie

**The poster session of MODULE II will take place virtually in the web-platform of  
the conference.**

# **MODULE 1**

# **ORAL PRESENTATIONS**

## Electrode-assisted Electroless Metal Deposition – Palladium Nanocatalysts for Organic Fuel Oxidation

A. Nakova, R. Ivanov, M. Ilieva and V. Tsakova

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*  
e-mail: [tsakova@ipc.bas.bg](mailto:tsakova@ipc.bas.bg)

Electroless metal deposition can be completed by using a reactive surface consisting of a redox active material that acts as electron donating medium and drives the metal ions reduction. In such an approach the reductant capacity is limited by the available surface-confined redox sites. Furthermore, re-reducing the oxidized reactive surface provides the opportunity to repeat the electroless metal reduction without dissolving the once deposited metal phase. To use this strategy for electroless metal deposition the reduced state of the reactive electrode surface should be kept at potentials negative enough with respect to the equilibrium potential of the depositing metal ions.

Conducting polymer materials are characterized by several intrinsic interconvertible oxidation states and may easily take the role of reducing agent in electroless metal deposition both as immobilized surface layer on a carrying substrate or as solute species in bulk solution. If deposited as a thin layer on an electrode surface they offer the opportunity to perform repeatedly redox-active surface-driven electroless metal deposition. Pd particles are observed to deposit also at bare pre-reduced carbon electrodes. It is suggested that in this case molecular hydrogen entrapped during reductive pre-treatment plays the role of reductant for electroless Pd deposition.

The conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) is deposited electrochemically as thin layer on graphite substrates. PEDOT-supported Pd catalysts with high-density homogeneous distribution of Pd nanoparticles (NPs) and sizes ranging between 4 and 12 nm are obtained by means of the above described strategy. The amount of deposited metal depends significantly on the pre-reduction potential of PEDOT whereas the observed surface density of the metal NPs is largely influenced by the doping ions (polystyrenesulfonate, PSS, or dodecylsulfate, SDS) used to obtain the PEDOT material.

Oxidation of glycerol and formic acid is studied in alkaline solutions under voltammetric and chronoamperometric conditions by varying the type of doping ions. It is found that at constant Pd loading PEDOT/PSS-supported catalysts have three times higher peak currents for both glycerol and formic acid oxidation. This effect is ascribed to the lack of overlap of the individual Pd NPs in the case of PEDOT/PSS in contrast to the strong clustering of the Pd observed on the PEDOT/SDS surface. The mass activity of Pd/PEDOT/PSS for both investigated reactions competes with the best performing single metal Pd catalysts.

**Acknowledgments:** Financial support of projects INFRAMAT (National Roadmap for Scientific Infrastructure) under contract D01-284/17.12.2019 of Ministry of Education and Science.

## Microstructural Study of Porous Metals Obtained by Selective Dissolution

L. Mihaylov, E. Vasileva, St. Todorova, R. Stoyanova, T. Spassov

*Sofia University "St. Kliment Ohridski" Faculty of Chemistry and Pharmacy*

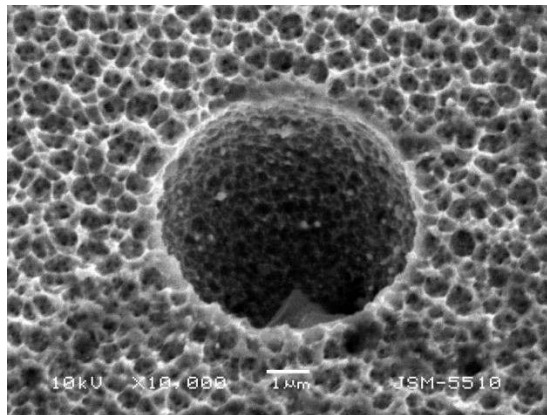
*1 J. Bourchier Blvd. Sofia 1164*

*e-mail: [tspassov@chem.uni-sofia.bg](mailto:tspassov@chem.uni-sofia.bg)*

Micro- and nanoporous metallic alloys obtained by electrochemical or chemical selective dissolution of metallic glasses and nanocrystalline alloys are of particular interest because of their valuable electrochemical and catalytic properties, as well as use for gas absorption and sensing. In a number of studies it is shown that their chemical and physical properties are strongly influenced by morphology, particle size and structure. Hence, the microstructure of these porous materials is crucial for their application. Among the most important methods used to characterize their structural and microstructural features are SEM, TEM and XRD, methods part of the scientific infrastructure supported by the Inframat project.

In the course of our studies on the synthesis of porous metals by de-alloying of amorphous and nanocrystalline precursors the present work was devoted to the influence of alloy composition and conditions of selective dissolution on the microstructure of the final porous material. Valuable information concerning the phase composition, crystallite size, pore and ligaments size distribution is obtained. Noticeable differences in the pores size and ligaments structure are found between the materials after chemical and electrochemical dissolution. This information was used to optimize the process of selective dissolution regarding the structure of the porous alloys.

High catalytic activity of the obtained porous structures with respect to Hydrogen Evolution Reaction is proven. They are also applied as binder- and carbon-free electrodes in Li-ion batteries.



Porous metal prepared by selective dissolution of Zr-based amorphous alloy (SEM)

## **Nanocomposite Catalysts Based on Mn, Ni, Co for Alkaline Water Electrolysis**

K. Maksimova-Dimitrova, E. Lefterova, G. Borisov, E. Slavcheva

*Institute of Electrochemistry and energy systems "Acad. Evgeni Budevski",  
Bulgarian Academy of Sciences, G. Bonchev St., Building 10, 1113 Sofia, Bulgaria  
e-mail: [katerina.maksimova@iees.bas.bg](mailto:katerina.maksimova@iees.bas.bg)*

NiMn, CoMn and NiCoMn catalysts are synthesized on a non-carbon support by the sol-gel method. The morphology, chemical and phase composition are characterized by SEM, EDX and XRD analyses. Electrochemical tests as cyclic voltammetry, steady state polarization and chronoamperometry were carried out for monitoring the effect of the composition on the catalytic properties. The catalysts were tested in an alkaline media (25% KOH) for the hydrogen and oxygen evolution reactions (HER, OER).

**Acknowledgments:** Distributed research infrastructure INFRAMAT (part of Bulgarian National roadmap for research infrastructures) supported by Bulgarian Ministry of Education and Science under contract D01-284/17.12.2019 was used in this investigation



## **Electrochemical Properties of Optimised Electrode Materials for Rechargeable Zn-Air Batteries**

B. Abrashev, M. Slavova, E. Mladenova, B. Burdin, G. Raikova, V. Terziev, K. Petrov,  
D. Vladikova

*Acad. E. Budevski Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences,  
G. Bonchev St., Building 10, 1113 Sofia, Bulgaria*  
e-mail: [babrashev@iees.bas.bg](mailto:babrashev@iees.bas.bg)

The current research work describes optimised and improved gas-diffusion electrodes (GDE) and Zn electrodes for zinc-air batteries that may have broad application in renewable energy systems. A new generation of Zn and GDE electrodes has been developed and tested in a half cell configuration. The GDE's carbon layer was developed by a heat treatment process of up to 300°C. The Zn electrode was also optimised as the optimal ration of Zn/ZnO was found to be at 30:70wt. %. Accelerated stress tests based on increase of the C- rate with respect to the exploitation conditions and determined by modelling have been introduced.

**Acknowledgments:** This work is partially supported by the Bulgarian Ministry of Education and Science under National Roadmap for Scientific Infrastructure (CMD No. 354 of 29.06.2017) "Distributed infrastructure of centers for synthesis and characterization of new materials and conservation of archeological and ethnographic artefacts, INFRAMAT" (Contract D01-284/17.12.2019) and National Science Found Project "Innovative Rechargeable Carbon-free Zinc-Air Cells, INOVI" (Contract KP-06-N27-15/14.12.2018).

## Iron Modified Ni-Foam as a Self-standing Electrode for Efficient, Durable Oxygen Evolution in Alkaline Water Splitting

E.Petkucheva, G. Borisov, E. Lefterova, E. Slavcheva

Acad. E. Budevski Institute of Electrochemistry and Energy System - Bulgarian Academy of Sciences,  
Acad. G. Bonchev Str.10, Sofia 1113, Bulgaria,  
e-mail: [e.petkucheva@iees.bas.bg](mailto:e.petkucheva@iees.bas.bg)

Alkaline water electrolysis is a key technology for large-scale hydrogen production powered by renewable energy. As conventional electrolyzers are designed for operation at fixed process conditions, the implementation of fluctuating and highly intermittent renewable energy is challenging.

In the present work, a concept for alkaline water electrolyzer with a "Dip and Drying" modified (DDM) nickel foam (NF) electrodes as anode, a pure NF cathode and a state-of-the-art Zirfon™ separator is presented. The geometric surface of the electrodes was 7 cm<sup>2</sup>.

The morphology and the chemical composition of the developed materials/electrodes were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively.

The electrocatalytic activities of the electrodes for the hydrogen (HER) and oxygen (OER) evolution reactions in 1M KOH are investigated by linear sweep voltammetry (LSV), cyclic voltammetry (CV), and chronopotentiometry (CP). Then, the electrodes were fixed in a laboratory made electrolysis test cell and separated by a 0.5 mm thick ceramic diaphragm Zifron Perl 500 (Fig.1). The doping of the diaphragm was performed directly in the cell by circulating 25% KOH solution for 24h at room temperature.

The single cell unit (DDM CoFe 250\_Zirfon PERL500\_NF-AW) operated in dynamic regime at room and elevated temperatures without any sign of degradation. The current density reached value of 0.150 A.cm<sup>-2</sup> at 80 °C and 1.94V cell voltage.

**Acknowledgments:** The research has been supported by the National Research Program " Young Scientists and Postdoctoral Fellows "-2020, Bulgarian Ministry of Education and Science.

Part of the experiments were performed on equipment of Research Infrastructure INFRAMAT (part of Bulgarian National Roadmap for Research Infrastructures) supported by Bulgarian of Education and Science under Contract D01-284/17.12.2019

[1] F. Song, M.M. Busch, B. Lassalle-Kaiser, C.-S. Hsu, E. Petkucheva, Michaë L Bensimon, Hao, M. Chen, C. Corminboeuf, X. Hu, An Unconventional Iron Nickel Catalyst for the Oxygen Evolution Reaction, *ACS Cent. Sci.* **2019**, 5, 558–568; <https://doi.org/10.1021/acscentsci.9b00053>.

[2] E. Petkucheva, G. Borisov, E. Lefterova, E. Slavcheva, Application of the "Dip and Drying" method (DDM) for the synthesis of electro-catalysts with application in industrial alkaline electrolysis, In: *Proc. of XVI National Youth Scientific-practical Conference*, 7-8 Nov. **2019**, Sofia, Bulgaria, pp. 17-22.

## Electrochemical Impedance Behavior and Relaxation Processes in $\text{H}_3\text{PO}_4$ -Enriched $\text{SiO}_2$ - $\text{TiO}_2$ - $\text{P}_2\text{O}_5$ System

O. Kostadinova<sup>1</sup>, V. Ilcheva<sup>1</sup>, V. Boev<sup>1</sup>, T. Petkova<sup>1</sup>, B. Burdin<sup>1</sup>, E. Mladenova<sup>1</sup>, D. Vladikova<sup>1</sup>, L.C. Costa<sup>2</sup>

<sup>1</sup>*Institute of Electrochemistry and Energy Systems Acad. Evgeni Budevsky,  
Bulgarian Academy of Sciences, Acad. G. Bonchev Str., bl 10, 1113 Sofia, Bulgaria,*

<sup>2</sup>*I3N and Physics Department, University of Aveiro, 3810-193 Aveiro, Portugal*

e-mail: [ofeliya.kostadinova@iees.bas.bg](mailto:ofeliya.kostadinova@iees.bas.bg)

Fast proton transfer is a key point for many processes that take place in various systems ranging from electrochemical energy conversion devices, through sensors to biological structures. Therefore, the mechanism that enables the fast proton transport, which is directly related to the molecular arrangement, is essential for improving the material's properties and its practical application. Phosphate materials have been known as fast ion conductors for long time ago [1]. Despite the fact that, above its melting point of 42 °C the pure liquid phosphoric acid has the highest intrinsic proton conductivity of any other known substance, when forming solid materials, phosphates suffer from chemical durability deficiency, which limits their practical applications [2]. To overcome this limitation, an effective approach is modification of chemical structure by bonding with other compounds such as SnO, PbO, ZnO, Al<sub>2</sub>O<sub>3</sub>, etc. in which the formation of Sn-O-P, Pb-O-P, Zn-O-P and P-O-Al bonds stabilizes the structure and leads to improvement in the chemical durability [3].

In this work we investigate the impedance behaviour, structural organization and new bond formation, as well as relaxation processes as a function of temperature and humidity of sol-gel derived  $x\text{H}_3\text{PO}_4$ -enriched  $85\text{SiO}_2$ - $9\text{P}_2\text{O}_5$ - $6\text{TiO}_2$ , ( $x = 0; 17.2; 35.0; 52.0$  mmol) system. The additional orthophosphoric could create more P-OH bonds, which in combination with water molecules is a prerequisite for the enhanced proton conduction. Furthermore, a non-Debye relaxation process was identified and fitted with Cole-Cole model. It was found that the dielectric relaxation parameters of the investigating materials depend on H<sub>2</sub> exposition and percentage of humidity. Finally, a proton conducting mechanism was proposed.

Keywords:  $\text{SiO}_2$ - $\text{P}_2\text{O}_5$ - $\text{TiO}_2$ ,  $\text{H}_3\text{PO}_4$ , sol-gel, impedance spectroscopy; dielectric relaxation, hydrogen detection, infrared structural investigation

**Acknowledgments:** This work was partially supported by the Bulgarian Ministry of Education and Science under National Research Programme E+: Low Carbon Energy for the Transport and Households, grant agreement D01-214/2018 and National Roadmap for Scientific Infrastructure (CMD No. 354 of 29.06.2017): Distributed infrastructure of centers for synthesis and characterization of new materials and conservation of archeological and ethnographic artefacts, INFRAMAT, (Contract D01-284/17.12.2019).

[1] Steve W Martin, *J Am Ceram Soc* 74 [8] **1991** 1767-84

[2] L. Vilciauskas, *Universität Stuttgart*, **2012** DOI: 10.18419/opus-6782

[3] P.Y. Shih, S.W. Yung, T.S. Chin, *J Non-Cryst. Solids* 244 **1999** 211-222

## Improvement the Mechanical Properties of TiCN / ZrCN Multilayer Coating with Modulated Period, for Industrial Applications

T. Cholakova, L. Kolaklieva, Hr. Bahchedjiev, V. Chitanov, S. Kolchev, R. Kakanakov

Central Laboratory of Applied Physics, Bulgarian Academy of Sciences, Plovdiv, Bulgaria  
e-mail: [st\\_kolchev@abv.bg](mailto:st_kolchev@abv.bg)

This work presents results from the investigation of the properties of nanostructured multilayered TiCN/ZrCN coatings with different bilayer periods deposited by cathodic-arc evaporation from Ti and Zr targets in nitrogen atmosphere onto stainless steel and high-speed steel substrates. TiCN and ZrCN monolayers were also prepared, for comparison. The samples were obtained at different rotation speed of the specimen holder as other deposition conditions were kept the same. The total coating thickness was in the range of 6.4 - 6.6  $\mu\text{m}$ , while the thickness of TiCN-ZrCN bilayers varied from 12 to 34 nm depending on the rotation speed of the holder. The thickness, nanohardness, adhesion strength and coefficient of friction were analyzed using Calotester, Nanoindentation Tester and Micro Scratch Tester.

The nanoindentation was performed by a triangular diamond Berkovich pyramid in the loading interval 20–500 mN. The nanohardness and elastic modulus were calculated from nanoindentation load-displacement data using the Oliver & Pharr method [1]. The adhesion strength to the substrate material and the friction coefficient were evaluated using a spherical Rockwell indenter. The character of the resulting damages was assessed by observations with an optical video microscope equipped with a CCD camera.

The Ti-TiN-TiCN/ZrCN-ml coatings demonstrated high hardness of 32-38 GPa, very good adhesion to the substrates in the loading interval 1-30 N and, low coefficient of friction ( $\mu=0.15-0.17$ ) against a diamond indenter. The results obtained show that the mechanical properties of multilayer TiCN/ZrCN coatings are improved in comparison to those of the monolayer TiCN and ZrCN coatings [2-4], which exhibit the hardness of 30 GPa. The study revealed a dependence of the mechanical properties on the bilayer period. The maximum hardness of 38 GPa, was determined for the coating with 12 nm bilayer period. This coating exhibited also good plastic deformation resistance of 0.22.

**Acknowledgments:** Research equipment of distributed research infrastructure INFRAMAT (part of Bulgarian National roadmap for research infrastructures) supported by Bulgarian Ministry of Education and Science under contract D01-284/17.12.2019 was used in this investigation.

[1] W. Oliver and G. Pharr, *J. Mater. Res.*, **1992**, 7, pp.1564–1583.

[2] M. Balaceanu, M. Braic, V. Braic, G. Pavelescu, *Surf. Coat. Technol.*, **2005**, 200, pp. 1084-1087.

[3] J.D. Gu, P.J. Chen, *Surf. Coat. Technol.* **2006**, 200, pp. 3341-3346.

[4] P. Siow, J.Ghani, M. Jameelah Ghazali, T. Jaafar, M. Selamat, Che Haron, *Ceramics International*, **2013**, 39, pp. 1293–1298.

## An Automated System for the Quantification of Uronic Acids and Neutral Sugars (Skalar San<sup>++</sup> Analyzer) - Components, Advantages, Disadvantages, and Applications

M. Ognyanov, Y. Georgiev, P. Denev

*Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences,  
Laboratory of Biologically Active Substances, 139 Ruski Blvd., 4000 Plovdiv, Bulgaria  
e-mail: [mogn@orgchm.bas.bg](mailto:mogn@orgchm.bas.bg)*

The auto-analyzer uses *m*-hydroxydiphenyl and orcinol-sulfuric acid colorimetric methods for determination of uronic acids [1, 2, 3] and neutral sugars [4], respectively. The San<sup>++</sup> system [5] is equipped with a sample collector with an injector, and a module consists of a peristaltic pump, a chemical reactor, a condenser, and a detector measuring absorption at two wavelength - 530 and 420 nm, respectively. The analyzer is controlled by friendly software. The automated version of the methods has advantages over the manual analyses, such as higher sensitivity, specificity, and reproducibility. The dangers posed by using a highly corrosive sulfuric acid, harmful chromogens, and boiling water are minimized. The system is compact, productive (50-100 samples), fast, and accurate because it avoids careless errors, made by the user, by strict control of the parameters. However, the necessity of continuing for a long time sample preparation and conditioning of the apparatus before each analysis is not precluded. The periodic run of a series of standards due to a detector drift, constant visual observation, periodic inspection, and replacement of corroded parts complicates the usage, as well. These lead to higher chemical, reagents, and consumables consumption, which costs a lot to maintain. Nevertheless, the device is used successfully to determine the content of uronic acids and uronic acid-containing polysaccharides (pectin, etc.), and neutral sugars in plant (cell wall) materials and extracts.

**Acknowledgments:** The Skalar San<sup>++</sup> analyzer was purchased with the financial support of the European Regional Development Fund, Ministry of Economy and Energy under the Operational Programme for “Development of the Competitiveness of the Bulgarian Economy” 2007–2013 by Project BG161PO003-1.2.04-0007-C0001 “Renovation of the equipment of IOCCP-BAS for utilization of medicinal and aromatic plants by green technologies.”. The system is a part of distributed research infrastructure INFRAMAT (part of the Bulgarian National Roadmap for Research Infrastructures) supported by Bulgarian Ministry of Education and Science under contract D01-155/28.08.2018 and D01-284/17.12.2019.

[1] N. Blumenkrantz, G. Asboe-Hansen, *Analytical Biochemistry*, **1973**, 54, 484–489.

[2] N. Blumenkrantz, G. Asboe-Hansen, *Biochemical Medicine*, **1974**, 11, 60–66.

[3] J.-F. Thibault, *Lebensmittel-Wissenschaft und Technologie*, **1979**, 12, 247–251.

[4] M.-T. Tollier, J.-P. Robin, *Annales de technologie agricole*, **1979**, 28, 1–15.

[5] <https://www.skalar.com/analyzers/automated-wet-chemistry-analyzers>

## Study of Polarizable Dielectric Fluids - Cow and Soya Milk by Dielectric Impedance Spectroscopy

E. Mladenova<sup>1</sup>, L. Dobрева<sup>2</sup>, M. Slavova<sup>1,3</sup>, G. Raikova<sup>1</sup>, O. Kostadinova<sup>1</sup>, B. Burdin<sup>1</sup>, S. Danova<sup>2</sup>

<sup>1</sup>Acad. E. Budevski Institute of Electrochemistry and Energy Systems,  
Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bl.10, 1113 Sofia, Bulgaria,

<sup>2</sup>The Stephan Angeloff Institute of Microbiology, Bulgarian Academy of Sciences,  
Acad. G. Bonchev Str. Bl. 26, 1113 Sofia, Bulgaria

<sup>3</sup>Todor Kableshkov University of Transport, 158 Geo Milev Str, 1574 Sofia, Bulgaria

e-mail: [e\\_mladenova@iees.bas.bg](mailto:e_mladenova@iees.bas.bg)

This work presents an investigation of milks (with different composition and origin) with respect to their physical behavior and electrical properties changes under application of low-frequency AC signal. The method, known as Dielectric Impedance Spectroscopy (DIS) is a valuable experimental tool for fundamental scientific research and contributes significantly to understanding the structure and microdynamics of dielectrics. Dielectric spectroscopy, depending on the frequency range used, could be apply to a wide range of systems, as gases, liquids and solid objects. For first time DIS is performed for evaluation of milk, which presents a complex colloid system composed of a polar matrix with dissolved nonpolar fluid. Different milks (plant based and animal originated) were investigated in a specially designed experimental cell, which consists of two coaxial stainless steel cylindrical electrodes with coplanar working surface. The complex permittivity measurements are presented in very illustrative  $C'/f$  plots (Fig. 1), where  $f$  is the frequency [1]. Preliminary calibration measurements of pure water were made (Fig. 1). The results presented in this paper indicates that DIS can be used as a quick test to determine the different ingredients as xylose or other sugars, as well as WS protein at different concentrations and environments if a sufficiently rich database is created.

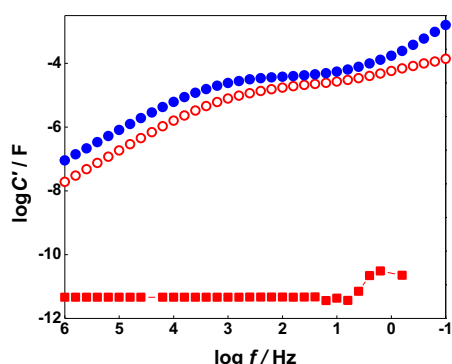


Fig. 1. Permittivity measurements: pure water (■), cow milk "LB Bulgaricum", 2% (○) and soya milk (●)

**Acknowledgments:** This work was supported by the Bulgarian Ministry of Education and Science under the National Roadmap for Scientific Infrastructure approved by DCM # 577/17.08.2018": Distributed infrastructure of centers for synthesis and characterization of new materials and conservation of archaeological and ethnographic artefacts, (Contract D01-284/17.12.2019).

[1] Z. Stoynov, D. Vladikova, E. Mladenova, *J. Solid State Electrochem.* **2013**, 17, 555–560.

## Analytical Atomic Spectroscopy in Bee Honey Analysis

E. Mladenova, I. Karadjova

Sofia University "St. Kliment Ohridski", Faculty of chemistry and pharmacy,  
1 James Bourchier Blvd., 1164 Sofia, Bulgaria  
e-mail: [elimladenova@chem.uni-sofia.bg](mailto:elimladenova@chem.uni-sofia.bg)

The bee honey is a sweet product, which is produced from the honeybees *Apis mellifera*. Honey is a natural food commodity that contains up to 200 components. Mineral content, e.g. chemical elements concentration, is important characteristic which might reflect different aspects – environmental conditions or degree of pollution of bee crossing area (air, soil, water) which is over seven squared kilometers; botanical origin (mostly for monofloral honeys) as far as biouptake of chemical elements differs for different plants and consequently in honey produced; geographical origin as far as bioavailability of soil chemical elements defines their content in plants and thus in honey. Therefore, analysis of honey for chemical elements content is important analytical task – an interesting but also challenging problem due to the high carbohydrate content in the honey matrix. The goal is determination of as more as possible chemical elements in the same time ensuring reliable and accurate results. Clearly, one instrumental method is “no method” in such a case and various combination of different methods including monelement methods like atomic absorption spectrometry and multielement methods like atomic emission inductively coupled plasma spectrometry would be fit-to-purpose. In the present study the possibilities of various atomic spectrometric methods – FAAS, ETAAS, HGAAS, ICP-OES were discussed from the point of view of necessary sample pretreatment, matrix interferences, calibration procedures, analysis cost and sample throughput. In addition, various sample pretreatment procedures (acid mineralization in an open vessel and microwave assisted digestion) were compared as well as possibilities for direct analysis of dissolved honey samples were considered. Optimal instrumental parameters based on long term experience in honey analysis were presented. Essential and toxic elements content in honeys with different geographical and botanical origin were commented.

**Acknowledgments:** This work was supported by project INFRAMAT and the Bulgarian Ministry of Education and Science under the National Research Programme "Healthy Foods for a Strong Bio-Economy and Quality of Life" approved by DCM # 577 / 17.08.2018.

## Co-Mn Mixed Oxides Supported on Hierarchical Macro-Mesoporous Silicas for CO and VOCs Oxidation

S. Todorova<sup>1</sup>, J. L. Blin<sup>2</sup>, A. Naydenov<sup>3</sup>, B. Lebeau<sup>4</sup>, D. Karashanova<sup>5</sup>, H. Kolev<sup>1</sup>,  
A. Dotzeva<sup>1</sup>, D. Filkova<sup>1</sup>, L. Vidal<sup>4</sup>, L. Michelin<sup>4</sup>, L. Josien<sup>4</sup>

<sup>1</sup>*Institute of Catalysis- BAS, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia, Bulgaria,*

<sup>2</sup>*Université de Lorraine/CNRS, L2CM, UMR7053, F-54506 Vandoeuvre-lès-Nancy cedex, France*

<sup>3</sup>*Institute of General and Inorganic Chemistry - BAS, Acad. G. Bonchev St., Bldg. 11,  
1113 Sofia, Bulgaria,*

<sup>4</sup>*Université de Haute Alsace (UHA)/CNRS, IS2M, UMR 7361, 68093 Mulhouse cedex, France,*

<sup>5</sup>*Institute of Optical Materials and Technologies "Acad. Jordan Malinowski"- BAS,  
Acad. G. Bonchev St., Bldg. 109, 1113 Sofia, Bulgaria*

*e-mail: [todorova@ic.bas.bg](mailto:todorova@ic.bas.bg)*

Air pollution has been one of European Union's main environmental policy concerns since the late 1970s ([http://ec.europa.eu/environment/index\\_en.htm](http://ec.europa.eu/environment/index_en.htm)). In 2013, the EU proposed a Clean Air Policy Package to further reduce emissions of air pollutants until 2030. There are many different techniques for VOCs removal, such adsorption, absorption, bio-filtration, thermal and catalytic combustion. The catalytic combustion is a competitive abatement technique for VOCs removal especially when the organics cannot be recycled or is present in low concentrations. There are a great number of successful commercial catalysts developed for CO and VOC oxidation. Nevertheless, still there exists a demand for development of new optimized catalysts with increased efficiency of mass and heat transfer and which do not contain any noble metals

Hierarchically porous catalysts are of recent scientific and technological interest due to their improved diffusion performances and high surface area.

This work is focused on the investigation of the structural and catalytic properties of series of mono component cobalt and manganese and bi-component Co-Mn catalysts supported on macro-mesoporous silica, which was used for the first time as a support for Co-Mn catalyst. The test reactions are CO, methane and *n*-hexane combustion.

The highest catalytic activity for Co-MM sample in CO and *n*-hexane oxidation is obtained and it is related to the predomination of Co<sup>3+</sup> species on the surface of Co<sub>3</sub>O<sub>4</sub> and the more accessible oxide particles located outside the mesopores. The encapsulation of mixed Co-Mn oxides particles in the pores of the macro-mesoporous silica is responsible for a lower catalytic activity in comparison with that of the mono-component cobalt sample. The higher catalytic activity of the bi-component catalysts supported on MMS comparing with that of samples supported on SBA-15 could be related to the fact the macro-mesoporous network favours the diffusion of the reactants toward the catalytic sites.

**Acknowledgments:** The Bulgarian authors express their gratitude for the research equipment of distributed research infrastructure INFRAMAT (part of Bulgarian National roadmap for research infrastructures) supported by Bulgarian Ministry of Education and Science under contract D01-284/17.12.2019.



## Fluoride Etching of AlZSM-5 and GaZSM-5 Zeolites

T. Todorova<sup>1</sup>, P. Shestakova<sup>2</sup>, T. Petrova<sup>1</sup>, M. Popova<sup>2</sup>, Hr. Lazarova<sup>2</sup>,  
Yu. Kalvachev<sup>1</sup>

<sup>1</sup>*Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., bl. 11,  
1113 Sofia, Bulgaria*

<sup>2</sup>*Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences,  
Acad. G. Bonchev St., bl. 9, 1113 Sofia, Bulgaria*  
e-mail: [t.todorova@ic.bas.bg](mailto:t.todorova@ic.bas.bg)

The post synthesis treatment of AlZSM-5 and GaZSM-5 zeolites by etching with buffer solution of ammonium fluoride and 0.25M HF acid was carried out. The treatment is applied in order to obtain secondary pores in crystals and to provide easier access to the catalytically active zeolite centers. Hydrothermal synthesis of these zeolites was performed from systems containing tetrapropylammonium bromide as a template. The reaction parameters of synthesis conditions for both zeolites were optimized in order to obtain pure crystalline phases. The zeolites obtained were characterized by X-ray diffraction, IR spectroscopy, scanning electron microscopy, physical adsorption-desorption of nitrogen, and solid state NMR spectroscopy. It has been found that the result materials remain with high crystallinity while new mesoporous are created in their structure. The volume due to the presence of mesopores increases by up to 67 % from the total volume, which is a drastic increase compared with the parent solids. The investigations with FTIR spectroscopy of low temperature CO adsorption and solid state NMR spectroscopy show that the treatment is slightly selective towards dissolution of heteroatom (aluminum or gallium). This phenomenon is observed for the first time for gallium-substituted zeolites. In order to study the influence of the metal atom in zeolite structure and the efficacy of the acid attack on the catalytic activity, the samples obtained were tested in reaction of m-xylene and toluene transformation <sup>[1]</sup>.

**Acknowledgments:** Equipment of INFRAMAT (Research Infrastructure from National roadmap of Bulgaria), supported by Contract D01-284/17.12.2019 with Bulgarian Ministry of Education and Science is used in the present investigations.

[1] T. Todorova, P. Shestakova, T. Petrova, M. Popova, Hr. Lazarova, Yu. Kalvachev, *J. Mater. Sci.*, **2020**, 55, 13799–13814. <https://doi.org/10.1007/s10853-020-05030-6>

## NMR Characterization of Hybrid Catalyst with Combined Lewis and Brønsted Acidity Based on Zr<sup>IV</sup> Substituted Polyoxometalate Grafted on MCM-41 Mesoporous Silica for Esterification of Renewable Levulinic Acid

P. Shestakova<sup>1</sup>, M. Popova<sup>1</sup>, H. Lazarova<sup>1</sup>, T. K. N. Luong<sup>2,3</sup>, I. Trendafilova<sup>1</sup>,  
J. Mihály<sup>4</sup>, Á. Szegedi<sup>4</sup>, T. N. Parac-Vogt<sup>2</sup>

<sup>1</sup>Institute of Organic Chemistry with Centre of Phytochemistry, BAS, 1113 Sofia, Bulgaria; <sup>2</sup>Laboratory of Bioinorganic Chemistry, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium, <sup>3</sup>Chemistry Department, College of Natural Sciences, Can Tho University, Campus II, 3/2 Street, Ninh Kieu District, Can Tho City, Vietnam; <sup>4</sup>Research Centre for Natural Sciences, Institute of Materials and Environmental Chemistry, 1117 Budapest, Magyar tudósok krt. 2, Hungary  
e-mail: [psd@orgchm.bas.bg](mailto:psd@orgchm.bas.bg)

Materials which synergistically combine Lewis and Brønsted acid properties hold potential for applications as efficient heterogeneous catalysts for preparation of biofuels and biolubricants. Herein we report new heterogeneous catalysts based on grafting the intact Lewis metal (Zr<sup>IV</sup>) substituted Keggin polyoxometalate (POM) on mesoporous silica support. A new approach for immobilization of the POM in MCM-41 silica was developed by co-condensation of Si source (TEOS) with POM in the presence of a template molecule as an alternative to the common impregnation procedure for catalyst synthesis. Catalysts' activity was studied in esterification of levulinic acid with ethanol or octanol to value-added esters. The directly synthesized hybrid catalysts outperformed significantly those obtained by impregnation exhibiting much higher catalytic activity, recyclability and resistance against leaching.

The influence of sample preparation and template removal methods on stability and integrity of the POM after its immobilization in the silica support was studied by single pulse <sup>31</sup>P and <sup>1</sup>H→<sup>31</sup>P cross-polarization NMR, while the structural transformations of the silica matrix were elucidated by <sup>29</sup>Si NMR. NMR studies revealed that the direct synthesis combined with extraction of the template under mild conditions resulted in effective immobilization of the POM, preservation of its Keggin structure and generation of high amount of active sites with Lewis and Brønsted acidity, explaining the high catalytic activity of this catalyst. The calcination method for template removal resulted in disintegration of the POM and formation of mixed oxides ZrO<sub>2</sub>/WO<sub>x</sub> and polyphosphoric acid species that remained immobilized in the silica matrix. The activity of this catalyst was comparable to that of the directly synthesized materials, due to the presence of Zr<sup>4+</sup>, phosphate (PO<sub>4</sub><sup>3-</sup>) and tungstate (WO<sub>4</sub><sup>2-</sup>) sites which have strong acidity. The post-synthesis method resulted in successful incorporation of the POM in MCM-41 silica matrix with preservation of the intact POM salt structure, however the acidity and the catalytic activity of the hybrid catalysts obtained by impregnation were lower than that of the directly synthesized materials. The directly synthesized hybrid materials exhibited also higher catalytic stability as compared to impregnated catalysts due to lack of agglomeration and leaching of the active phase under the applied reaction conditions.

**Acknowledgments:** Research equipment of distributed research infrastructure INFRAMAT (part of Bulgarian National Roadmap for Research Infrastructures) supported by the Bulgarian Ministry of Education and Science under contract Д01-284/17.12.2019 was used in this investigation. Financial support of the Bulgarian Hungarian Inter-Academic Exchange Agreement, and of the National Science Fond of Bulgaria, grant № КП-06-КОСТ/3/2018 is greatly acknowledged.

## Catalytic Behavior of Nanostructured Ceria Promoted Manganese in VOCs Elimination

G. Issa, M. Dimitrov, R. Ivanova, T. Tsoncheva

*Institute of Organic Chemistry with Centre of Phytochemistry- BAS,  
Ak. G. Bontchev str.9, 1113 Sofia, Bulgaria  
e-mail: [Issa@abv.bg](mailto:Issa@abv.bg)*

Volatile organic compounds (VOCs) are among the most noxious air pollutants due to their toxic nature and participation in smog formation. Among the various techniques for VOCs elimination, the catalytic combustion is the most promising and effective approach as it requires comparatively low temperatures and shows high selectivity that could lead to considerable environmental and economic benefits [1]. Nowadays, the intensive efforts are being directed toward the design and synthesis of catalytic materials based on transition metal oxides as an alternative of the noble metal catalysts as they are much cheaper and less susceptible to poisons. This study is focused on the preparation and characterization of ceria-manganese mixed oxides by different techniques and their application as catalysts for ethyl acetate total oxidation as representative VOCs. For the purpose, cerium-manganese oxides with different composition (1:2, 1:1, or 2:1 mole ratio) were prepared either by co-precipitation of the initial metal nitrates with ammonia at pH of 9 (CP technique) or by co-precipitation of the metal chlorides with ammonia in the presence of surfactant (CTAB) (HT technique). The obtained materials were characterized by nitrogen physisorption, XRD, Raman, XPS, SEM, TEM, and TPR/TG techniques. The total oxidation of ethyl acetate was studied in a flow type reactor using gas chromatograph for analyses. With the exception of pure manganese oxide, all prepared materials, exhibit high surface area and mesoporous texture. Spectral analyses indicated presence of  $MnO_x$  species which type and amount vary depending on the preparation method used. Partial substitution of manganese within the ceria fluorite lattice was also detected. TPR-TG experiments with hydrogen showed improved reducibility of all mixed oxide samples compared to the initial pure oxides due to the presence of highly dispersed  $MnO_x$  species and improved O mobility in the ceria lattice as a result of the incorporation of foreign ions in it. This provides improved catalytic activity in total oxidation of ethyl acetate than the pure oxides. Higher catalytic activity for the CP-obtained binary oxides in comparison with their HT analogues was observed. The physicochemical study indicated that it is promoted by the stabilization of more finely dispersed  $MnO_x$  species in close interaction with  $CeO_2$ .

**Acknowledgments:** The authors thank to the project КП-06-H29/2 for the financial support and bilateral project BAS-AS CR for the help with the physicochemical characterization of the samples. The authors thank to the project INFRAMAT (Research Infrastructure from National roadmap of Bulgaria), supported by Contract D01-284/17.12.2019 with Bulgarian Ministry of Education and Science for the opportunity to participate in the conference.

[1] K. Everaert, J. Baeyens, J. Hazard. Mater., 2004, 109, 113.

## Comparative Study of the Properties of Nanostructured Oxide Materials Based on Titanium Dioxide and Their Application as Catalysts for Environmental Protection

R. Ivanova, G. Issa, M. Dimitrov, T. Tsoncheva

*Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences,  
Sofia, Bulgaria*  
e-mail: [radostinaiv@abv.bg](mailto:radostinaiv@abv.bg)

The aim of the current investigation is to study in detail the effect of the second metal on the structural, textural and catalytic properties of titanium dioxide. For the purpose high surface area mesoporous ceria-titania, manganese-titania and iron-titania binary materials were synthesized using template assisted hydrothermal technique. The choice of titanium dioxide was made because of its wide technological application in photocatalysis and a number of catalytic processes, due to its good redox properties, non-toxicity and relatively low cost. A complex of different physicochemical techniques, such as nitrogen physisorption, XRD, TPR, and Raman spectroscopy, was applied for samples characterization. Total oxidation of ethyl acetate was used as a test reaction to evaluate the catalytic properties of the obtained materials with a potential application in volatile organic compounds elimination. The physicochemical characterization of the samples shows a complex interaction of the dopant ions with the titanium oxide lattice, which leads to the formation of different catalytic active sites. The changes in the textural, surface and redox properties in the binary materials could be controlled by the x/y ratio in the mixed oxides, which is in close relation to the catalytic activity and selectivity in the catalytic process. The high catalytic activity of binary materials may be due to the appearance of a synergistic effect between the individual components and/or an increase in their specific surface, especially in the case of manganese oxide dopant. In this case the formation of a solid solution is not excluded, which leads to an increase in the dispersion of binary oxides, thus improving their redox properties at lower temperatures.

**Acknowledgments:** The authors thank to the project KP-06-PM39/1/2019 for the financial support and bilateral project BAS-AS CR for the help with the physicochemical characterization of the samples. The authors thank to the project INFRAMAT (Research Infrastructure from National roadmap of Bulgaria), supported by Contract D01-284/17.12.2019 with Bulgarian Ministry of Education and Science for the opportunity to participate in the conference.

## The Electrochemical Impedance Spectroscopy as a Powerful Instrument for Corrosion Rate Determination

St. Kozhukharov<sup>1</sup>, Ch. Girginov<sup>2</sup>

<sup>1</sup>LAMAR Laboratory for Advanced Materials Research

<sup>2</sup>Department of Physical Chemistry

University of Chemical Technology and Metallurgy – Sofia, 8 Kliment Okhridsky blvd.

1756, Sofia, Bulgaria

e-mail: [stephko1980@abv.bg](mailto:stephko1980@abv.bg)

According to some recent concepts [1], the corrosion is mechanical properties deterioration and gradual geometrical shape altering of given solid state object of industrial origin, due to interactions with its surrounding environment via irreversible chemical, biological and/or physical processes, able to cause complete destruction.

Nowadays, the term “corrosion of the materials” comprises a large variety of detrimental processes which lead to lose of material integrity and mechanical properties of the corresponding products [2]. Especially, the corrosion of metals and their alloys possess generally electrochemical character. Consequently, the electrochemical analytical techniques appear as the most sensible and accurate for corrosion rate and impact determination. However, the correct measurement performance and the appropriate data interpretation need at least a basic knowledge regarding the principles and terminology related to the corrosion rate assessment.

In this sense, the present presentation is an attempt for explication of the Electrochemical Impedance Spectroscopy (EIS) method essences, the measurement technique application rules and requirements, as well as the basic principles of the data interpretation. In this sense, a special attention is turned to the composition of appropriate Model Equivalent Circuits (MECs), necessary for appropriate data extraction from the corroding samples.

**Acknowledgments:** The financial support from Bulgarian National Research Fund, under contract КП-06-H-37/16, entitled: “New environmentally friendly one- and multi-layer coatings for corrosion protection of structural materials with wide application” is highly appreciated.

[1] S. V. Kozhukharov, and Ch. A. Girginov, **Chapter 1:** Classical and Modern Methods for Corrosion Impact Rate Determination for Aluminium and Strengthened Aircraft Alloys. Fundamentals and Practical Applications. Published in: Phenomena and Theories in Corrosion Science, Methods of Prevention, András Gergely Ed. NOVA Sci. Publ. (2019), p. 3 - 150; ISBN 978-153-615253-1.

[2] S. V. Kozhukharov, **Chapter 10:** Advanced Multifunctional Corrosion Protective Coating Systems for Light-Weight Aircraft Alloys—Actual Trends and Challenges, published in: Materials Science “Thin Film Processes - Artifacts on Surface Phenomena and Technological Facets”, Jagannathan Thirumalai, Ed. IntechOpen Ltd. (2017). p. 179 - 210; ISBN 978-953-51-3068-0,

## Micelles-structured Bragg Stack of Nb<sub>2</sub>O<sub>5</sub> for Sensing applications

R.Georgiev, K.Lazarova, M.Vasileva, B. Georgieva, T. Babeva

Institute of Optical Materials and Technologies "Acad. J. Malinowski",  
Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 109, 1113 Sofia, Bulgaria.  
e-mail: [rgeorgiev@jomt.bas.bg](mailto:rgeorgiev@jomt.bas.bg)

Organic templates are commonly used for deposition of mesoporous materials through soft-templating method, that is highly utilized versatile approach due to its cost effectiveness and reproducibility. In the present study we have investigated the micellization of commercially available Pluronic PE6800 and PE6200 (PEO-b-PPO-b-PEO) in aqueous solution and their impact on porosity generation and vapors sensing properties of Nb<sub>2</sub>O<sub>5</sub> thin films. By using 1,6-diphenyl-1,3,5-hexatriene (DPH) and modified dye solubilization technique micellization conditions of the copolymer in aqueous media have been established. Using UV-VIS and photoluminescence spectroscopy Critical Micelles Concentration (CMC) at room temperature have been determined by monitoring the wavelength shift of characteristics absorption and emission peaks of DPH with concentration instead of commonly used approach of measuring DPH peaks intensity. The formation of micelles has been confirmed by TEM images recorded using staining technique for sample preparation. Besides, Dynamic Light Scattering (DLS) measurements have been conducted to determine micelle size distribution at different temperatures below the cloud point. The advantages of using micellar solution for pores generation has been demonstrated by preparation of porous thin films with polymer concentration above and below the CMC and the free volume within the films has been estimated by Bruggeman effective medium approximation. The size and shape of the pores in the films have been studied by TEM. The ability of the films to detect vapors has been tested by measuring the change of the reflectance spectra of the films prior to and after exposure to acetone vapors used as a probe molecule. In order to increase further the sensitivity, porous films have been incorporated in specially designed photonic structures, called Bragg stacks, and their application for chemical sensors with optical read-out in reflection and transmission regimes has been demonstrated and discussed.

**Acknowledgments:** Research equipment of distributed research infrastructure INFRAMAT (part of Bulgarian National roadmap for research infrastructures) supported by Bulgarian Ministry of Education and Science under contract D01-284/17.12.2019 was used in this investigation. R. Georgiev and K. Lazarova acknowledge the National Scientific Program for young scientists and postdoctoral fellows, funded by the Bulgarian Ministry of Education and Science (MES) with DCM 577/2018 and 271/2019

## Inclusion Compounds of NSAIDs with Cyclodextrins

St. Pereva<sup>1</sup>, Ts. Sarafska<sup>1</sup>, V. Nikolova<sup>1</sup>, S. Angelova<sup>2</sup>, T. Spassov<sup>1</sup>, T. Dudev<sup>1</sup>

<sup>1</sup>Sofia University, Faculty of chemistry and pharmacy, Department of applied and inorganic chemistry,

<sup>2</sup>Institute of Optical Materials and Technologies "Acad. Jordan Malinowski"

Cyclodextrins (CDs) are natural macrocyclic oligosaccharides. Thanks to their structure, they have wide applications when used as hosts in inclusion complexes with various guests (drugs, food ingredients, cosmetic compounds, etc). Natural cyclodextrins –  $\alpha$ -,  $\beta$ - and  $\gamma$ -CD have hydrophobic interior and hydrophilic exterior, thus able to accommodate a guest molecule inside their cavity. Despite having hydrophobic interior they are also non-defined hydrates – even at ambient conditions they entrap water molecules. It has been suggested that the entrapped water molecules stabilize their crystal lattice. Here we present our studies in which we were able to prove, both experimentally and using the methods of quantum chemistry (DFT), that during the complex formation the guest molecule displace (partially or completely) the water molecules from the host. As model drugs for the inclusion compounds we used ibuprofen and naproxen <sup>1 2 3</sup>

**Acknowledgments:** This work was supported by the Materials Networking Project H2020-TWINN-2015.

S.P. acknowledges the financial support received from the program "Young scientists and postdoctoral candidates" of the Bulgarian Ministry of Education and Science, MCD № 577/17.08.2018.

[1] Angelova, S.; Nikolova, V.; Pereva, S.; Spassov, T.; Dudev, T.,  $\alpha$ -Cyclodextrin: How Effectively Can Its Hydrophobic Cavity Be Hydrated?, *The Journal of Physical Chemistry B*, **2017**, 121 (39), 9260-9267.

[2] Pereva, S.; Sarafska, T.; Bogdanova, S.; Spassov, T., Efficiency of "cyclodextrin-ibuprofen" inclusion complex formation., *Journal of Drug Delivery Science and Technology*, **2016**, 35, 34-39.

[3] Pereva, S. N., V.; Angelova, S.; Spassov, T.; Dudev, T., Water inside  $\beta$ -cyclodextrin cavity: amount, stability and mechanism of binding., *Beilstein J. Org. Chem.*, **2019**, 15 ("Novel macrocycles – and old ones doing new tricks".), 1592–1600.

## Application for Analytical Ultracentrifugation and Dynamic Light Scattering for Study of the Specific Interaction Between Con A and a Star-shaped Glycopolymer

Z. Todorova, O. Tumurbaatar, N. Koseva

*Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Banchev Str., 1113 Sofia, Bulgaria.  
e-mail: [oyundari\\_0313@yahoo.com](mailto:oyundari_0313@yahoo.com)*

Glycopolymers are synthetic macromolecules bearing carbohydrate moieties which can mimic the structure and function of glycans. Star-shaped glycopolymers have been less investigated though possessing a combination of valuable properties. Therefore, we underwent study on the specific interaction between Concanavalin A (Con A) and a star-shaped phosphorus-containing glycopolymer (SSGP).

Firstly, SSGP was designed and synthesized via a procedure for obtaining polyphosphoramides developed by us [1]. The product was thoroughly characterized and its behaviour in multivalent binding with Con A evaluated. To that end, analytical ultracentrifugation and dynamic light scattering techniques were applied to measure solutions of SSGP, Con A and their complexes in Tris-HCl buffer pH 7.5, containing 0.1 M NaCl, 0.5 mM CaCl<sub>2</sub> and 0.5 mM MnCl<sub>2</sub>. Sedimentation-velocity (SV) experiments were performed with a ProteomeLab XL-I (Beckman Coulter) analytical ultracentrifuge equipped with a UV-VIS detector and an optical interference system. The obtained data were processed using SEDfit [2], which produced the distribution curves of the sedimentation coefficients of the components in the solution. Up to five populations of particles with molecular masses from about 60 kDa to 840 kDa with the corresponding sedimentation coefficients ranging from 3 to 15 S were detected.

Dynamic Light Scattering (DLS) and Electroforetic Light Scattering (ELS) measurements were performed with a NanoBrook 90Plus PALS Analyzer (Brookhaven Instruments) equipped with a 35-mW solid-state laser, operating at  $\lambda = 660$  nm. At least two populations of particles with sizes  $D_{h1} \approx 10$  nm and  $D_{h2} > 150$  nm were registered.

In conclusion, the multivalent interactions between the lectin and SSGP lead to formation of associates, i.e. the star macromolecules induce protein clustering with the formation of a hydrophilic shell around the associates.

**Acknowledgments:** Research equipment of distributed research infrastructure INFRAMAT (part of Bulgarian National roadmap for research infrastructures) supported by Bulgarian Ministry of Education and Science under contract D01-284/17.12.201 was used in this investigation.

[1] Z.Todorova, N. Koseva, I. Ugrinova, K. Troev. J. Polym. Sci. A Polym. Chem., **2017**, 55 (10), 1730–1741.

[2] P. Schuck, M. S. Perugini, N. R. Gonzales, G. J. Howlett, and D. Schubert, Biophysic. J. **2002**, 82, 1096-1111.



## DNA Delivery Systems Based on Copolymers of Poly (2-Methyl-2-Oxazoline) and Polyethyleneimine

E. Haladjova<sup>1</sup>, M. Smolíček<sup>2</sup>, I. Ugrinova<sup>3</sup>, D. Momekova<sup>4</sup>, P. Shestakova<sup>5</sup>,  
Z. Kroneková<sup>2</sup>, J. Kronek<sup>2</sup>, S. Rangelov<sup>1</sup>

<sup>1</sup>*Institute of Polymers, Bulgarian Academy of Sciences, Akad. G. Bonchev St. bl. 103A,  
1113 Sofia, Bulgaria,*

<sup>2</sup>*Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia,*

<sup>3</sup>*Institute of Molecular Biology, Bulgarian Academy of Sciences, Acad. G. Bonchev St, bl. 21,  
1113 Sofia, Bulgaria,*

<sup>4</sup>*Faculty of Pharmacy, Medical University of Sofia, 2, Dunav St., Sofia 1000, Bulgaria,*

<sup>5</sup>*Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences,  
Acad. G. Bonchev St. bl. 9, 1113 Sofia, Bulgaria*

e-mail: [ehaladjova@polymer.bas.bg](mailto:ehaladjova@polymer.bas.bg)

Poly(2-methyl-2-oxazoline)-polyethyleneimine (PMeOx-co-PEI) copolymers differing by degree of polymerization (DP = 50 and 200) and PEI content (from 37 to 99 mol%) were synthesized by living cationic ring-opening polymerization of 2-methyl-2-oxazoline, followed by partial hydrolysis. Upon mixing with DNA in a wide range of N/P ratios, they formed well-defined polyplex particles of small size (typically below 100 nm) and narrow size distribution. The polyplexes demonstrated good colloidal stability and very low in vitro cytotoxicity. The copolymers exhibited buffering capacity of over 50% relative to that of the reference PEI implying effective endo-lysosomal escape of the polyplexes. Increased cellular internalization of both PCR fragments and plasmid DNA, attributable to the strongly positive  $\zeta$  potential and small size of the polyplexes, was observed. In spite of these favorable prerequisites, the transfection efficiency was low (below 20% relative to the control PEI) and was attributed to retarded swelling of the polyplex particles, endo-lysosomal rupture, and DNA release.

**Acknowledgments:** The work was supported by the bilateral cooperation project of the Slovak and Bulgarian Academies of Sciences. Research equipment of distributed research infrastructure INFRAMAT (part of Bulgarian National Roadmap for Research Infrastructures) supported by the Bulgarian Ministry of Education and Science under contracts D01-155/28.08.2018 and D01 284/17.12.2019 was used in this investigation.

## ***In situ* Irradiation NMR Spectroscopy in the Design of New Functional Materials (LED-NMR)**

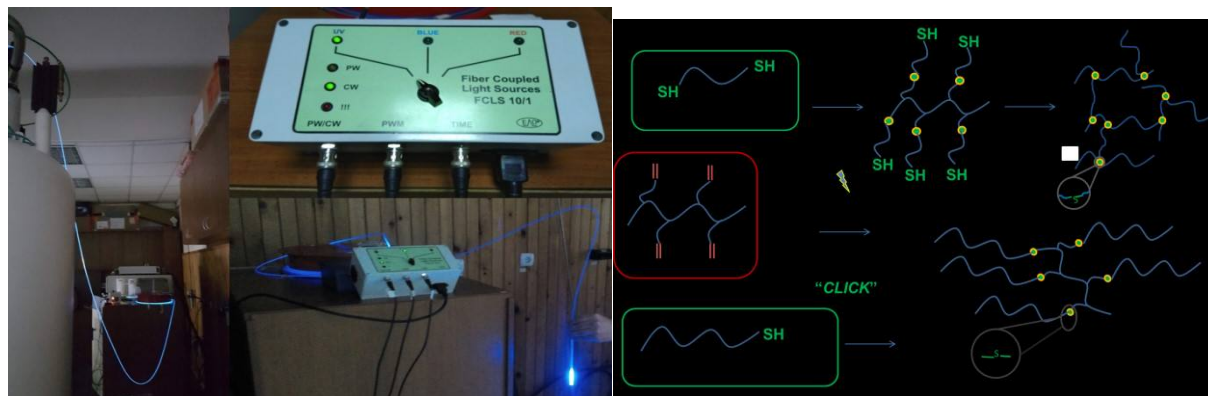
M. Dangalov<sup>1</sup>, Y. Mitrev<sup>1</sup>, N. Toncheva-Moncheva<sup>2</sup>, Ch. Novakov<sup>2</sup>, N. G. Vassilev<sup>1</sup>

<sup>1</sup>*Institute of Organic Chemistry with Center of Phytochemistry, Bulgarian Academy of Sciences, 9, Acad. G. Bonchev Str., 1113 Sofia, Bulgaria*

<sup>2</sup>*Institute of Polymers, Bulgarian Academy of Sciences, 103-A, Akad. G. Bonchev Str., 1113 Sofia, Bulgaria*

e-mail: [niki@orgchm.bas.bg](mailto:niki@orgchm.bas.bg)

*In situ* irradiation NMR spectroscopy includes illumination of the samples inside the NMR spectrometer [1]. The self-made setup was constructed with three LEDs as light sources operating at 365–470 nm, 440–460 nm or 650–670 nm coupled to an optical fiber. The setup includes a control unit connected to the IPSO computer through BNC connections. The other end of the optical fiber is inserted in a coaxial insert and illuminates the NMR sample. This setup allows application of whole variety of NMR methods to photochemical reactions. The equipment was successfully tested on photoisomerization of azobenzene [2]. The Photo-CIDNP spectroscopy was demonstrated on photo-induced reaction between benzophenone triplet and hydroquinone [3]. The synthesis of new polymeric materials was achieved *in situ* [4].



**Acknowledgments:** This work was financially supported by the Bulgarian National Science Fund (H 29/6) and by Ministry of Education and Science (INFRAMAT, D01-155).

[1] P. Nitschke, N. Lokesh, R. Gschwind, *Prog. Nucl. Magn. Reson. Spectrosc.*, **2019**, 114–115, 86–134.

[2] H. M. D. Bandara, S. C. Burdette, *Chem. Soc. Rev.*, **2012**, 41, 1809–1825.

[3] R. Amorati, I. Valgimigli, C. Viglianisi, M. Schmallegger, D. Neshchadin, G. Gescheidt, *Chem. Eur. J.*, **2017**, 23, 5299–5306.

[4] N. Toncheva-Moncheva, M. Dangalov, N. G. Vassilev, C. P. Novakov, *RSC Advances*, **2020**, 42, 25214–25222.

# **MODULE I**

# **POSTER PRESENTATIONS**

## Electrochemical Method for Studying the Process of Hydrogen Permeation into Metals During Aqueous Electrolysis. Hydrogen Permeation in Electroless Ni-P Coatings

V. Chakarova, L. Mirkova, M. Monev

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, "Acad. G. Bonchev" Str., bl. 11,  
Sofia 1113, Bulgaria*  
e-mail: [vchakarova@ipc.bas.bg](mailto:vchakarova@ipc.bas.bg)

Hydrogen permeation into metals causes very serious deleterious effect on their physical-chemical and mechanical properties due to the hydrogen embrittlement. Hydrogen penetrates the metal from many sources, e.g., corrosion, electroplating, cathodic polarization, acidic pickling. Among the experimental methods for studying the hydrogen permeation into metals, the electrochemical technique, derived by Devanathan-Stachurski is widely used to evaluate electrochemically the hydrogen permeation behaviour. It provides rapid and precise information.

In the Devanathan-Stachurski method, double symmetrical electrochemical cell is used. It is separated by a steel membrane. Hydrogen is cathodically charged on the entry side of a metallic membrane, the permeated hydrogen is fully oxidized at the exit side under a constant positive potential and the registered current is a direct measure for the hydrogen permeated into the membrane. By a computerized system, the permeation current at the exit side is recorded against time until reaching a steady state (hydrogen permeation transient). The transients give information for various important parameters as permeation efficiency, the concentration of absorbed atomic hydrogen in the metal sub-layer just below the entry surface, the diffusion coefficient and the quantity of penetrated hydrogen.

Steel/Ni or Steel/Ni-based electrodes are widely used in industrial electrolytic cells for electrochemical production of hydrogen because of their high electrocatalytic activity with respect to hydrogen evolution reaction (HER) and good corrosion resistance. However, due to the permeation of a part of hydrogen into the electrodes and interaction with the electrodeposited Ni, a change in their structure and surface properties occurs. As a result, the electrocatalytic activity of the electrodes decreases and the HER overvoltage increases. Alloying of Ni with P could be a way for delay or prevention of the deactivation process. A number of studies report better electrocatalytic properties of electroless Ni-P alloy coatings in regard to the HER in comparison to electrodeposited Ni coatings.

The Devanathan-Stachurski method is used for investigation of the hydrogen permeation into a steel membrane (25  $\mu\text{m}$ ), preliminary covered with electrodeposited Ni (Ni-el) coating or with Ni-P coating obtained by electroless deposition. Hydrogen permeation transients are recorded under a constant current of 100  $\text{mA cm}^{-2}$  in an alkaline media (1M KOH). The following conclusions are drawn based on a comparison of the permeation current measured at the same time:

- Less hydrogen penetrates into the steel/Ni-P electrode than into the steel/Ni-el electrode;
- Permeated hydrogen decreases upon increasing P content (%) in the Ni-P alloy;
- Permeated hydrogen decreases with increasing thickness of the Ni-P coating.

**Acknowledgment:** Financial support of project INFRAMAT (National Roadmap for Scientific Infrastructure) under contract D01-284/17.12.2019 of Ministry of Education and Science is gratefully acknowledged.

## Corrosion-Protective Ability of Chemically Deposited Conversion Layers on Technically Pure Aluminum, After Application of Specific Additional Treatments of the Aluminum Substrate and Formed on it Ceria Conversion Layer

R.Andreeva, E.Stoyanova, D.Stoychev

*Institute of Physical Chemistry "Acad.R. Kaischew" – BAS, Acad.G.Bonchev str.Bl. 11,  
1113 Sofia,Bulgaria  
e-mail: [randreeva@ipc.bas.bg](mailto:randreeva@ipc.bas.bg)*

The aim of this study was to determine the influence of the pre-treatment of Al1050 in alkaline (1.5M NaOH) and acidic (5M HNO<sub>3</sub>) solutions before deposition on it a conversion ceria coatings (CCOC) and inclusion of a phosphate post-treatment operation of CCOC, leading to the formation of additional immersion phosphate layer (PhL) on the surface of Al/CCOC, on the corrosion-protective behavior of the system Al/CCOC/PhL.

The formation of CCOC was realized in solution containing CeCl<sub>3</sub> and CuCl<sub>2</sub> [1]. The post-treatment of as deposited on Al substrate CCOC was realized in two types of phosphate-containing solutions: Na<sub>3</sub>PO<sub>4</sub> or NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> [2]. The polarization resistance investigations of studied samples (in 0.1M NaCl) were carried out on Gamry Interface 1000. The polarization resistance (Rp) of the coatings was calculated by Stern-Geary equation [3], which is based on the fact that higher Rp value corresponds to higher corrosion resistance.

The highest values of Rp following the 168 hour, as well as the 336 hour exposure in the corrosion medium were registered for the samples coated with CCOC and post-treated in a NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> solution. The comparison of the results of the Rp values and the concentrations of Ce<sup>3+</sup>/Ce<sup>4+</sup>, Al и P before and after exposure of the samples in corrosion medium show that the change of Rp and concentrations of the Ce<sup>4+</sup> and P on the surface are directly related. The proposed formation of the insoluble corrosion products on surface of studied systems and the accomplished synergic effects of the protective action of formatted cerium and aluminum oxides/phosphates layers determining the increase of the Rp value (with the time of exposure). It is concluded that the mixed conversion layers included stable cerium oxides and phosphates are more effective barrier of the chloride ions diffusion to the substrate surface and increase the corrosion resistance of Al1050 to the general and pitting corrosion.

**Acknowledgments:** The authors are grateful to the financial support of project INFRAMAT (National Roadmap for Scientific Infrastructure) under contract D01-284/17.12.2019 of Ministry of Education and Science is gratefully acknowledged.

- [1] R. Andreeva, E. Stoyanova, A. Tsanev, D. Stoychev, *J. Phys. Conf. Series* 700, **2016**, 012049.
- [2] D.K. Heller, W.G. Fahrenholtz, G E Fair, M.J. O'Keefe, *ECS Transactions*, **2010**, 28, 203-208.
- [3] M. Stern, A.L. Geary, *Journal of the Electrochemical Society*, **1957**, 104, 56-63.

## **Corrosion Characterization of Environmentally Friendly Conversion Films on Zinc-based Protective Coatings by Electrochemical Impedance Spectroscopy**

M. Peshova, V. Bachvarov, St. Vitkova, N. Boshkov

*Institute of Physical Chemistry, Bulgarian Academy of Sciences,  
Akad. G. Bonchev Str., bl. 11, Sofia 1113, Bulgaria  
e-mail: [mpeshova@ipc.bas.bg](mailto:mpeshova@ipc.bas.bg)*

Electrochemical impedance spectroscopy (EIS) is a non-destructive method that is widely used to characterize various electrochemical systems. The values of the polarization resistance ( $R_p$ ) can be determined from the "x" axis ( $Z_{re}$ , ohms) of the EIS diagrams. The " $R_p$ " is the main parameter determining the corrosion resistance and the protective ability of metal / alloy systems - the corrosion medium. The high values of " $Z_{re}$ " ( $R_p$  respectively) determine the high protective ability of the studied coatings in a given environment and vice versa.

The aim of the present study is to obtain electrochemically the protective coatings based on zinc: zinc, ternary zinc alloys, composite zinc and composite zinc alloys with embedded carbon nanotubes (CNT), onto low-carbon steel substrates.

In order to increase their protective characteristics, the obtained coatings are further treated in an environmentally friendly solution for chemical passivation based on  $Cr^{3+}$  containing compound. This type of treatment results in the formation of an additional surface (conversion) film, that slows down the penetration of corrosion processes into the depth of the layers.

The surface morphology and chemical composition of the passivated coatings were determined by SEM and EDS analysis.

The corrosion resistance and protective ability of the coatings, respectively, without and with the presence of a conversion film, were investigated by the method of Electrochemical Impedance Spectroscopy (EIS) in a model environment causing mainly local corrosion (5%NaCl).

The results from the EIS method show an improvement in the protective properties of the coatings with conversion film in the studied model environment.

**Acknowledgments:** Financial support of project INFRAMAT (National Roadmap for Scientific Infrastructure) under contract D01-284/17.12.2019 of Ministry of Education and Science is gratefully acknowledged.

## Electroless Deposition of Pd on Carbon Substrates

R. Ivanov<sup>1</sup>, V. Tsakova<sup>1</sup>, C. Czibula<sup>2</sup>, C. Teichert<sup>2</sup>

<sup>1</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

<sup>2</sup>*Institute of Physics, Montanuniversität Leoben, A-8700 Leoben, Austria*

e-mail: [radoslav91@abv.bg](mailto:radoslav91@abv.bg)

Electroless deposition of Pd is studied on five different types of screen printed carbon electrodes, namely Carbon (C110), Mesoporous Carbon (MC), Carbon Nanofibers (CNF), Carbon Nanotubes (CNT) and Single-Walled Carbon Nanotubes (SWCNT). Before Pd deposition the substrates were studied using SEM and AFM imaging and electrochemical characterisation. The AFM measurements showed higher roughness for MC and CNF electrodes while SEM gave evidence for different surface morphologies of the five specimens. Electrochemical measurements in supporting electrolyte showed difference in the capacitive currents with lowest and highest values observed for C110 and SWCNT, respectively.

Pd deposition was carried out in the absence of reductant in the metal plating solution. Before the deposition step all carbon electrodes went through electrochemical reductive pre-treatment at negative enough potential to initiate hydrogen reduction at the electrode. It is hypothesised that molecular hydrogen entrapped during the reductive pre-treatment plays the role of reductant for the electroless deposition of Pd. The amount of deposited Pd is determined by electrochemical oxidation of the metal phase in hydrochloric acid solution. Lowest and highest amounts of electroless deposited Pd are found for C110 and SWCNT, respectively.

This investigation opens the prospect for metal modification of carbon substrates by involving hydrogen species temporarily available on the electrode surface instead of solute reductant species permanently present in the plating solution.

**Acknowledgments:** Financial support of projects INFRAMAT (National Roadmap for Scientific Infrastructure) under contract D01-284/17.12.2019 of Ministry of Education and Science and Bulgarian Science Fund under contract KP-06-Austria-5 is gratefully acknowledged.

## Effect of Gamma-irradiation on Bee Pollen Antioxidant Activity and Free Radicals Studied by EPR Spectroscopy

R. Mladenova, K. Aleksieva

*Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev str., bldg. 11,  
1113 Sofia, Bulgaria  
e-mail: [ralitsa@ic.bas.bg](mailto:ralitsa@ic.bas.bg)*

Bee pollen is a product with unique qualities, which make it irreplaceable in various fields of food industry, medicine, cosmetics and more. Bee pollen is extremely rich in several health-promoting compounds, such as enzymes, proteins, amino acids, lipids, phenolic compounds, vitamins, essential minerals and antioxidants. Many natural products need microbial control for using them as food or drug material. Disinfection of bee pollen should be performed using unheated treatment by irradiation to prevent deterioration of sugars and proteins.

The aim of the present work is to study the effect of gamma irradiation on induced free radicals, their stability and antiradical activity after sterilization of bee pollen by means of Electron Paramagnetic Resonance (EPR) spectroscopy.

The bee pollen samples were from two crops and exposed to gamma-irradiation at doses of 2, 5 and 10 kGy. O-centered free radicals induced by gamma rays can prove irradiation treatment. Their signal increased with increasing the dose used. The fading kinetic of free radicals was different for the two crops and show that identification of irradiation is possible for 5 months. The irradiation effect on radical scavenging activity of pollen extracts was investigated by using the stable free radical 1,1-diphenyl-2-picrylhydrazyl (DPPH) and the antioxidant activity was presented in Trolox Equivalents. It was found out that gamma irradiation of pollen decrease antiradical activity at 2018 crop samples irradiated with 2 kGy, while increasing at 2019 crop samples irradiated with 5 and 10 kGy was observed. Radical scavenging activity of crop 2019 is a lower than 2018.

The study show, that the signal from gamma-induced O-centered free radicals increased with the dose and could be detected for 160 days after radiation treatment. Thus the identification of cold sterilization is possible for that period. There is no linear correlation between irradiation dose and radical scavenging activity. To optimize the dose of pollen irradiation for the purpose of disinfection and prolongation of the shelf life, and increase of the antioxidant activity as well, the determination should be performed for each individual batch.

**Acknowledgments:** The authors thank the Bulgarian National Science Fund - Bulgarian Ministry of Education within the framework of Project "KP-06-N 39/12" for the financial support. Equipment of INFRAMAT (Research Infrastructure from National roadmap of Bulgaria), supported by Contract D01-284/17.12.2019 with Bulgarian Ministry of Education and Science is used in the present investigations.



## Synthesis of Chiral, Non-Racemic Aminonaphthols and Determination of Their Chiroptical Properties Using a Polarimeter

M. Tavlinova-Kirilova, M. Kamenova-Nacheva, K. Kostova, V. Dimitrov

*Institute of Organic Chemistry with Centre of Phytochemistry,  
Bulgarian Academy of Sciences, Sofia, Bulgaria  
e-mail: [maya@orgchm.bas.bg](mailto:maya@orgchm.bas.bg)*

The Mannich reaction is one of the most frequently applied multicomponent reactions in organic chemistry. In the original form of the reaction, the Mannich product is formed through the reaction of a C-H acid, formaldehyde and a secondary amine. A special alteration is the three-component modified Mannich reaction in which formaldehyde is replaced by an aromatic aldehyde, the secondary amine by different N sources, and the C-H acid by an electron-rich aromatic compound such as 1- or 2-naphthol, quinolinol or isoquinolinol is known as Betti-condensation.[1] The use of non-racemic amines in this type of condensation has opened a new area of applications of the chiral non-racemic products formed as catalysts in enantioselective transformations.[2]

We are presenting herein the synthesis of chiral aminonaphthols using different aldehydes, 6-hydroxyquinoline or 2-naphthol and chiral amines. The identity and optical purity of new synthetic substances is determined using a polarimeter.

**Acknowledgments:** *The financial support of is gratefully acknowledged. INFRAMAT is part of the National Roadmap for Scientific Infrastructure and is financially supported by the Bulgarian Ministry of Education and Science (under Contract D01-284/18.12.2019).*

[1] I. Szatmári, F. Fülöp, *Syntheses, transformations and applications of aminonaphthol derivatives prepared via modified Mannich reactions*, **2013**, 69(4), 1255-1278.

[2] M. Marinova, K. Kostova, P. Tzvetkova, M. Tavlinova-Kirilova, A. Chimov, R. Nikolova, B. Shivachev, V. Dimitrov, *Tetrahedron: Asymmetry*, **2013**, 24, 1453–1466.

## Enantioselective Addition of Et<sub>2</sub>Zn to Aldehydes - Determination of Enantiomeric Excess by High-Performance Liquid Chromatography (HPLC)

M. Kamenova-Nacheva, M. Tavlinova-Kirilova, K. Kostova, V. Dimitrov

*Institute of Organic Chemistry with Centre of Phytochemistry,  
Bulgarian Academy of Sciences, Sofia, Bulgaria  
e-mail: [anmari@orgchm.bas.bg](mailto:anmari@orgchm.bas.bg)*

During the last few years significant efforts are directed to the development of methods for asymmetric addition of organozinc reagents to aromatic and aliphatic carbonyl compounds, catalyzed by aminoalcohols or diols as chiral ligands.[1] As a result of the addition reactions enantiomerically enriched or pure secondary alcohols are formed.[2] These compounds are often used as starting reagents for the synthesis of bioactive compounds.

Herein we present the application of HPLC to determine the enantiomeric excess (ee) of secondary alcohols using chiral columns. The catalytic enantioselective addition of diethylzinc to aldehydes was applied to obtain optically active secondary alcohols. The corresponding chiral secondary alcohols were isolated as a mixture of enantiomers or pure isomers. A normal phase chiral high performance liquid chromatography analytical method has been developed to determine enantiomeric purity of samples.

**Acknowledgments:** *The financial support of INFRAMAT is gratefully acknowledged. INFRAMAT is part of the National Roadmap for Scientific Infrastructure and is financially supported by the Bulgarian Ministry of Education and Science (under Contract D01-284/18.12.2019).*

[1] V. Dimitrov, M. Kamenova-Nacheva, *Journal of the University of Chemical Technology and Metallurgy*, **2009**, 44, 317-332.

[2] M. Kamenova-Nacheva, G. M. Dobrikov, V. Dimitrov, *Tetrahedron: Asymmetry*, **2016**, 27, 852-864.

## Study of the Conformation and Thermal Stability of Bovine Serum Albumin in Complexes with Ionic Liquids Containing Naproxen Anion

P. Kardaleva<sup>1</sup>, S. Todinova<sup>2</sup>, D. Yancheva<sup>1</sup>, M. Guncheva<sup>1</sup>

<sup>1</sup>*Institute of Organic Chemistry with Centre of Phytochemistry, BAS, Acad. G. Bonchev Str. Bl. 9, 1113 Sofia, Bulgaria,*

<sup>2</sup>*Institute of Biophysics and Biomedical Engineering, BAS, Acad. G. Bonchev Str. Bl. 21, 1113 Sofia, Bulgaria*

*e-mail: [pkardaleva@orgchm.bas.bg](mailto:pkardaleva@orgchm.bas.bg)*

Ionic liquids (ILs) are salts containing asymmetric organic cations and organic or nonorganic anion. ILs based on active pharmaceutical ingredients are interesting for the pharmaceutical industry because based on their specific structure they have the potential to overcome some problems of solid-state drugs. Naproxen (NPX) is a non-steroidal drug with anti-inflammatory, antipyretic, and analgesic activities with low solubility and bioavailability. Conversion of the drug in ionic liquid formulation improves its physicochemical characteristics and possibly bioavailability. Serum albumin is the main transport protein of the drug in mammals. The focus of this study is a series of ILs containing cations esters of amino acids and NPX anion and their complex with bovine serum albumin (BSA).

We applied attenuated total reflectance Fourier deconvoluted infrared spectroscopy (ATR-FTIR) to observe the effect of the NPX-ILs on the BSA secondary structure. For all tested compounds, in the Amide I region (1600-1700 cm<sup>-1</sup>) we observed the typical bands for  $\alpha$ -helices,  $\beta$ -sheets, unordered structures and in some cases aggregates. In the presence of NPX the secondary structure of BSA is slightly unfolded, but as a whole, the structure is similar to that of the native protein in solution. In the BSA-ILs complexes we observed decreasing of  $\alpha$ -helical structures and increasing of  $\beta$ -structures and in some cases, side chains of BSA backbone are exposed to the surface and i.e. the BSA molecule becomes more open. The observed conformational changes are in agreement with the changes in the thermal stability of BSA-IL complexes monitored by differential scanning calorimetry (DSC). Three transitions slightly shifted (by 2-3°C) toward the higher temperatures were observed in the DSC curves of the BSA-IL complexes. Annealing of the DSC curves shows that for each complex the three transitions are characterized by different enthalpy, which suggests that depending on their structures, probably ILs are bound in a different pocket in BSA.

**Acknowledgments:** This work was partially supported by the Bulgarian Ministry of Education and Science under the National Research Program "Young scientist and postdoctoral Students" approved by DSM # 577/ 17.08.2018.

Research equipment of distributed research infrastructure INFRAMAT (part of Bulgarian National roadmap for research infrastructures) supported by Bulgarian Ministry of Education and Science under contract D01-284/17.12.2019 was used in this investigation.

## Quantitative NMR Spectroscopy of Sugars – Which Experiment to Choose?

Y. Mitrev, D. Gerginova, S. Simova

*Institute of Organic Chemistry with Centre of Phytochemistry, 1113 Sofia, Bulgaria.  
e-mail: yavor@orgchm.bas.bg*

NMR spectroscopy is commonly used method for investigation of the composition of various sugar-containing foods and beverages.<sup>1,2</sup> Usually, 1D proton experiments are employed, due to their high sensitivity, but at the cost of much poorer resolution, when compared to other nuclei. The resolution issues can be circumvented either by using additional post-processing techniques (e.g. spectral deconvolution) or by employing time consuming 2D experiments.

In this investigation we compare the potential of three 1D experiments –<sup>1</sup>H, <sup>13</sup>C and INEPT, for quantification of saccharides in solution. The preliminary results suggest that standard <sup>13</sup>C spectra can also be easily employed for quantitative measurements, following some general guidelines.

**Acknowledgments:** The financial support of Ministry of Education and Science (INFRAMAT project, Contracts D01-155 and D01-284) is gratefully acknowledged.

[1] F. Tang, M. Vasa, E. Hatzakis, A. Spyros, *Annual Reports on NMR Spectroscopy*, **2019**, 98, 239–306.

[2] E. Schievano, M. Tonoli, F. Rastrelli, *Analytical Chemistry*, **2017**, 89(24), 13405–13414.

## New Indole Arylhydrazones and Study of Their Protective Properties on Iron Induced Oxidative Damage of Biologically Important Molecules

N. Anastassova<sup>1</sup>, N. Hristova-Avakumova<sup>2</sup>, K. Radev<sup>1</sup>, D. Yancheva

<sup>1</sup>*Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences,  
Acad. G Bonchev str., bl.9, 1113 Sofia, Bulgaria,*

<sup>2</sup>*Department of Medical Physics and Biophysics, Faculty of Medicine, Medical University of Sofia,  
2 Zdrave Str., Sofia 1431, Bulgaria  
e-mail:neda@orgchm.bas.bg*

There is a compelling evidence that oxidative stress is the common underlying mechanism leading to damage of proteins, cellular dysfunction and demise that is related to serious pathological conditions, such as cancer. Under the conditions of oxidative stress the process of lipid peroxidation of polyunsaturated fatty acids is initiated and products with mutagenic and carcinogenic properties are generated. Such a product is the malondialdehyde (MDA) which undergoes a reaction with nucleosides. In our previous studies of series of benzimidazoles were denoted the most promising cytoprotectors.<sup>1</sup> Hereby we are investigating the potential of newly synthesized series of methoxy and hydroxy substituted indole hydrazones were synthesized and evaluated using biologically relevant model systems with oxidizable substrates lecithin and deoxyribose. The aim was to study their capability to influence prooxidation processes and to estimate their potential to protect lipids and DNA of induced oxidative damage. In the lecithin model system all of the investigated compound denoted stronger protection effect than the referent Melatonin. In the deoxyribose model system was displayed both prooxidant and antioxidant effects depending on the substitutions. In both system the 2,3-dihydroxy derivative demonstrated the most potent protective effect. The inhibition of the deoxyribose degradation was remarkable, higher than the referent Quercetin.

**Acknowledgments:** This work was supported by the Bulgarian Ministry of Education and Science under the National Research Programme “Young scientists and postdoctoral students,” approved by DCM # 577 / 17.08.2018.

[1] N. Anastassova, D. Yancheva, N.Hristova-Avakumova, V. Hadjimitova, T. Traykov, D. Aluani, V. Tzankova, M. Kondeva-Burdina, *Pharm. Rep.*, **2020**, 72, 846–856.

## New 2-Amino Benzimidazolyl Hydrazone Complexes: Synthesis, Spectroscopic and DFT Investigation

M. Argirova<sup>1</sup>, E. Cherneva<sup>2</sup>, D. Yancheva<sup>1</sup>

<sup>1</sup>*Institute of Organic Chemistry with Centre of Phytochemistry, Acad. G. Bonchev St., build. 9, 1113 Sofia, Bulgaria*

<sup>2</sup>*Faculty of Pharmacy, Medical University of Sofia, 2 Dunav str., 1000, Sofia, Bulgaria*  
e-mail: [margirova@orgchm.bas.bg](mailto:margirova@orgchm.bas.bg)

The benzimidazole nucleus plays an essential role in the design and synthesis of novel pharmacological agents displaying various biological activities such as antioxidant, antibacterial, anticancer, antiparasitic, analgesic, etc. [1]. On the other hand, hydrazones are organic compounds characterized by the presence of –NH–N=CH– skeleton in their molecule, and possess antimicrobial, antitubercular, anticonvulsant and antiinflammatory activities [2]. Schiff bases are of a great interest due to their capability of forming very stable complexes with metal ions via azomethine nitrogen. They are able to chelate with oxygen, nitrogen and sulfur donors and their metal complexes offered a great potential for the design of novel therapeutic medicines. A large number of Schiff base compounds have been synthesized and evaluated *in vitro* against different gram-positive and gram-negative bacteria, as well as for antiprotozoal, antioxidant and anticancer activity. Furthermore, complexes of salicylaldehyde benzoylhydrazone were shown to be a potent inhibitor of DNA synthesis and cell growth, which is an attractive task in the development of new chemotherapeutic agents [3].

Our study is focused on the design and synthesis of a novel series of complexes of Cu(II). The complexes were obtained from the benzimidazolyl ligands and copper nitrate as precursors in an ethanolic solution. Elemental analysis and spectroscopic (IR and NMR) techniques were used to establish the structures of the ligands and the complexes. The possible coordination modes, structural and vibrational characteristics were investigated by density functional theory (DFT) calculations.

**Acknowledgments:** Equipment of INFRAMAT (Research Infrastructure from National roadmap of Bulgaria), supported by Contract DO1-284/17.12.2019 with Bulgarian Ministry of Education and Science is used in part of the present investigations. The financial support of this work by the National Science Fund of Bulgaria, Contract КП-06-H39/4, is gratefully acknowledged.

[1] Y. Bansal, O. Silakari, *Bioorg. Med. Chem.*, **2012**, 20, 6208-6236

[2] R. K. Mohapatra, U. K. Mishra, *Journal of the Korean Chemical Society*, **2011**, 55, 926-931

[3] R. K. Mohapatra, P. K. Das, M. K. Pradhan, *Journal of the Iranian Chemical Society*, **2018**, 15, 2193-2227

## Are We Drinking a Real Wine? $^1\text{H}$ NMR Metabolomic Profiling of Bulgarian Wines

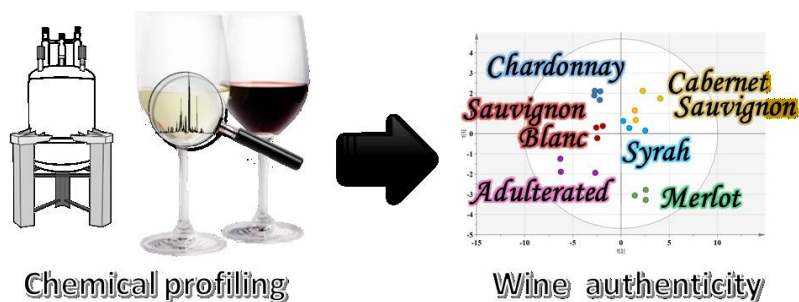
D. Gerginova, Y. Mitrev, S. Simova

Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Sofia,  
Bulgaria

e-mail: [dpg@orgchm.bas.bg](mailto:dpg@orgchm.bas.bg)

Wine is a favourite alcoholic beverage and the oldest documented medicine. In almost every culture, wine was served in ceremonies, rituals and religious festivities. Wine contains more than 10 000 compounds but unfortunately is often adulterated. NMR spectroscopy is a robust and reproducible method, often used for authentication of botanical origin and quality control of wine in European countries [1], but not yet in the region of South East Europe. Bulgarian wine is famous for its aroma, taste, vinicultural traditions and high quality, with antioxidant properties proved to be among the highest in European wines [2]. There is only scarce information about its composition and chemical profile.

Nineteen Bulgarian wines from the most widely used grape varieties: Merlot, Cabernet Sauvignon, Syrah, Sauvignon Blanc and Chardonnay and three adulterated wines were collected. The wine samples were analyzed using  $^1\text{H}$  NMR spectra. Thirty-one components (alcohols, organic and amino acids, carbohydrates, phenolic compounds and other substances) were identified and quantified. Statistically significant differences among wine samples from different botanical origin based on chemometric methods (ANOVA, PLS-DA and Nightingale's diagram) have been found. Most important for wine differentiation are the concentrations of thirteen compounds.



**Acknowledgments:** The financial support of the Bulgarian National Science Fund (UNA-17/2005, DRNF-02-13/2009) and Ministry of Education and Science - Bulgaria (INFRAMAT project, contracts D01-155 and D01-284) is gratefully acknowledged.

[1] L. Gougeon, G. da Costa, T. Richard, F. Guyon, *Food Analytical Methods*, 12, **2019**, 956–965.

[2] J. Burns, P. Gardner, J. O'Neil, et al., *Journal of Agricultural and Food Chemistry*, **2000**, 48, 220–230.

## Metabolites Isolated From Garden Snail *Helix Aspersa* With Antibacterial and Antifungal Activity Determined Through <sup>1</sup>H NMR and Mass Spectrometry

A. Dolashki <sup>1</sup>, A.Daskalova<sup>1</sup>, N. Vasilev<sup>1</sup>, S. Simova<sup>1</sup>, M. Dangelov<sup>1</sup>, L.Velkova<sup>1</sup>, V. Atanasov<sup>1</sup>, Y. Topalova<sup>2</sup>, N. Kostadinova<sup>3</sup>, E. Krumova<sup>3</sup>, M. Angelova<sup>3</sup>, T. Stoyanova<sup>1</sup>, L. Woelki<sup>1</sup>, D.Kaynarov<sup>1</sup>, P. Dolashka<sup>1</sup>

<sup>1</sup> Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bontchev str. Bl. 9, 1113 Sofia, Bulgaria,

<sup>2</sup> Sofia University "St.Kliment Ohridski", Faculty of Biology, Bulgaria,

<sup>3</sup>The Stephan Angeloff Institute of Microbiology, Bulgarian Academy of Sciences  
e-mail: [asya.daskalova@gmail.com](mailto:asya.daskalova@gmail.com)

Nowadays, researches in naturally occurring substances have shown great advances. Of specific interest are mollusc organisms which are known to produce vital proteins and peptides as part of their defense system against microbial invasion, dryness and UV rays. The mucus of garden snail *Helix aspersa* is a complex mixture of different bioactive compounds. In the present study, we focus on profiling of the low molecular weight fractions from the mucus of *H. aspersa* (Mw<1 kDa and Mw<3 kDa). Metabolic profiling based on <sup>1</sup>H Nuclear Magnetic Resonance (<sup>1</sup>H NMR) spectroscopy was applied with the aim to investigate the functional role of the metabolites in lyophilized mucus from garden snail *H. aspersa*. Twenty metabolites were unambiguously identified by <sup>1</sup>H, 1D TOCSY, 2D J-resolved, 2D COSY and 2D HSQC NMR spectra with water suppression. The obtained profiles by <sup>1</sup>H NMR show that the two fractions with low molecular weight are very similar. Metabolites with known antioxidant, antibacterial and antimicrobial activity have been detected by <sup>1</sup>H NMR and mass spectrometric analysis. The primary structure of several peptides was identified in low molecular weight fractions (Mw<1 kDa) by tandem mass spectrometry. These results revealed that the peptide fractions exhibit a predominant antibacterial activity against *B. laterosporus* and against *E. coli*; another peptide fraction <20 kDa against *P. aureofaciens*. Moreover, using *de novo* sequencing (MALDI-MS/MS analysis) we identified the primary structures of above 14 novel antimicrobial peptides in the mucus fraction with Mw 1-5 kDa. The peptides exhibited fungicidal and fungistatic activity agents *Candida membranifaciens*, *Aspergillus fumigatus* and *Aspergillus niger*.

This is the first report of low molecular weight metabolites identified in the mucus of garden snails. Knowledge of the active ingredients and their action is valuable with the scientific arguments for their potential application in cosmetics and / or pharmacology.

**Acknowledgments:** This research was funded by the Bulgarian Ministry of Education and Science through the National Scientific Program "Innovative Low-Toxic Biologically Active Means for Precision Medicine" BioActiveMed, grant number DO1-217/30.11.2018 and by the Bulgarian National Science Fund, grant number DH01-14/19.12.2016.



## Mordenite as Catalyst Support for Complete VOCs Oxidation

T. Todorova, P. Petrova, Yu. Kalvachev

*Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., bl. 11,  
1113 Sofia, Bulgaria*  
e-mail: [t.todorova@ic.bas.bg](mailto:t.todorova@ic.bas.bg)

Zeolite mordenite has been investigated as a transition metal support for the preparation of efficient catalysts in the oxidation of volatile organic compounds. The highly crystalline mordenite samples were acid treated with HF and NH<sub>4</sub>F to obtain hierarchical material with secondary porosity. The obtained supports by this method have a high active surface area, good diffusion properties and prevent the extraction of metal components during catalytic reactions. The active metal phases platinum and copper were loaded by impregnation on both mordenite materials (parent and acid treated counterparts). Monometallic Pt and Cu, and bimetallic Pt/Cu catalysts were obtained. The metal phases were fine dispersed as nanoparticles on the functional porous materials. The catalysts synthesized in this way were investigated in the reaction of complete oxidation of propane and benzene. Platinum, copper and platinum/copper were loaded and their catalytic activity was investigated and compared.

All samples are characterized by X-ray diffraction analysis, nitrogen adsorption, scanning electron microscopy (SEM), X-ray photoelectron measurements (XPS) and temperature programmed reduction (TPR). The catalytic activity of the samples obtained is investigated in the reaction of complete oxidation of propane and benzene by using of Gas Chromatography (GC).

**Acknowledgments:** This work was supported by the Bulgarian Ministry of Education and Science under the National Research Programme "Young scientists and postdoctoral students" approved by DCM № 577/17.08.2018. Equipment of INFRAMAT (Research Infrastructure from National roadmap of Bulgaria), supported by Contract D01-284/17.12.2019 with Bulgarian Ministry of Education and Science is used in the present investigations.

## Cobalt-Palladium Bimetallic System Behavior During CO Hydrogenation: Comparative Study of the Support Effect

M. Shopska, S. Todorova, I. Shtereva, H. Kolev, K. Aleksieva, G. Kadinov

Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bldg. 11, 1113 Sofia  
e-mail: [shopska@ic.bas.bg](mailto:shopska@ic.bas.bg)

Interaction between the reagents in CO hydrogenation depends on the type and quantity of active centres on the surface of catalysts. Analysing CO/H ratio of adsorbed species on the bimetallic particles new procedures of catalyst preparations could be proposed to manage catalyst activity, selectivity and operating conditions of the reaction. More complete transformation of reagents in desired products is the principal property of selective catalysts, which can be achieved by minimization of by-product determining intermediate uniformity. Optimization of the catalyst properties involves changing the factors and correcting their effect so that a higher activity be accompanied by improved selectivity. Activity and selectivity of (10%Co+0.5%Pd) system in dependence of support (TiO<sub>2</sub>(T), SiO<sub>2</sub>(S), Al<sub>2</sub>O<sub>3</sub>(A)), T<sub>red</sub>, T<sub>reac</sub> were studied. A preliminary thermal treatment in air up to 300°C was applied to decompose the deposited nitrate salts (metal sources). Catalysts and precursors were studied by number of methods: TPR, H<sub>2</sub> and CO chemisorption, EPR and XPS analysis, catalytic measurements during CO hydrogenation, *in situ* DRIFTS investigations.

Gas/ Support (mmol/g-at <sub>Me</sub> )	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
H <sub>2</sub> <sup>100°C</sup>	16.7	14.0	5.9
CO <sub>irr</sub>	20.1	20.8	26.0
CO <sub>rev</sub>	25.3	14.7	31.0
H/CO <sub>irr</sub>	2.9	2.9	0.8

Catalytic tests showed that Me/S and Me/A samples possessed high activity with close level of CO conversion. At all studied T<sub>reac</sub> the selectivity ratio CH<sub>4</sub>/CO<sub>2</sub> was higher for Me/S catalyst determined by difficult formation of CO<sub>2</sub>. Me/T sample had very low activity (CO conversion < 10%) with selectivity to CO<sub>2</sub> close to 0, but the ratio CH<sub>4</sub>/CO<sub>2</sub> increased with temperature up to 7 times and at T ≥ 325°C.

It increased significantly compared to the other samples thus forming a row Me/T >> Me/S > Me/A. XPS data supposed metal particles in the pores of S and A bearing in mind that S<sub>BET</sub><sup>(S,A)</sup> > S<sub>BET</sub><sup>(T)</sup>. Samples with A and T carriers have been active in carbonate species formation of medium and significant stability. Cobalt phase and hardly reducible CoTiO<sub>3</sub> could be present in Me/T sample. EPR and XPS analyses testified SMSI effect in Me/T sample by detection of Ti<sup>3+</sup> ions in measurement at -150°C and availability of O vacancies. *In situ* DRIFTS studies found high metal dispersion and various sites for CO adsorption as well intermediates transformation with Me/S and Me/A samples. Surface was homogeneous with stable adsorption sites (large metal particles) on Me/T catalyst. Me/A and Me/T catalysts were characterized by various sites for steady CO adsorption, increased activity in CH<sub>4</sub> synthesis and accumulation of CH<sub>x</sub> intermediates at high temperatures. Carbonate-(like) species were assigned to Me/S and (Me/A) intrinsic activity in their formation.

**Acknowledgments:** This study was supported by BNSF through contract KP-06-H29-9/2018. The equipment is part of INFRAMAT, supported by the Ministry of Education and Science (contract D01-284/2019).

## Study of the Kinetics and Mechanism of Sr<sup>2+</sup> Sorption by Clinoptilolite

N. Lihareva<sup>1</sup>, L. Dimowa<sup>1</sup>, O. Petrov<sup>1</sup>, Y. Tzvetanova<sup>1</sup>, I. Piroeva<sup>2</sup>,  
S. Atanasova Vladimirova<sup>2</sup>

<sup>1</sup>*Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences,  
Acad. G. Bonchev Street, Block 107, 1113 Sofia, Bulgaria,*

<sup>2</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences,  
Acad. G. Bonchev Street, Block 11, 1113 Sofia, Bulgaria*

*e-mail: [statanasova@ipc.bas.bg](mailto:statanasova@ipc.bas.bg)*

The parameters of kinetics of Sr<sup>2+</sup> sorption by natural clinoptilolite were investigated. The overall rate constants were determined by application of pseudo-first and pseudo-second order kinetic models. The actual sorption mechanism was studied by application of both intraparticle and surface film diffusion models. The application of Rietveld structure refinement shows the preferable sites of strontium ion exchange in the clinoptilolite structure and their diffusion through cationic sites with time, as well as indicates the positions occupied by Sr<sup>2+</sup> ions at the start of the exchange process and the positions where Sr<sup>2+</sup> accumulates in subsequent ion exchange stages. The results of the study of kinetics of Sr<sup>2+</sup> sorption by natural clinoptilolite have demonstrated that the process conforms to the pseudo-second order kinetic model. The obtained equations of the model can be applied for choosing of parameters of treatment and prediction of the results of Sr<sup>2+</sup> sorption. The actual mechanism of sorption was studied by application of both intraparticle and surface film diffusion models. It was found that the division of the kinetic data in separate time intervals provides more appropriate description in accordance with the requirements of the models. It was concluded that both intraparticle and surface film diffusion influence the sorption at different stages, but it was not possible to identify clearly the mechanism, determining the rate of the sorption process. XRD structural analyses show that in the initial stage Sr<sup>2+</sup> occupies the sodium position in the large channel A. As the ion exchange process progresses, calcium cations begin to leave their positions in the smaller channel B and Sr<sup>2+</sup> cations start to accommodate there.

**Acknowledgments:** Stela Atanasova - Vladimirova acknowledges the financial support of project INFRAMAT (National Roadmap for Scientific Infrastructure) under contract D01-284/17.12.2019 of Ministry of Education and Science is gratefully acknowledged.

## Investigation of Lead (II) Removal from Aqueous Solutions Using Waste Material Based on Rice Husks

P. Vassileva<sup>1</sup>, A. Detcheva<sup>1</sup>, I. Uzunov<sup>1</sup>, S. Uzunova<sup>2</sup>, D. Voykova<sup>1</sup>

<sup>1</sup>Institute of General and Inorganic Chemistry-Bulg.Acad.Sci., 1113 Sofia, Akad.G.Bonchev Str., bl.11

<sup>2</sup>University of Chemical Technology and Metallurgy-Sofia, 8 St.Kl.Ohridski Blvd.

e-mail: [pnovachka@svr.igic.bas.bg](mailto:pnovachka@svr.igic.bas.bg)

Pollution of water with metal ions, especially with lead ions, represents an important environmental concern due to their toxicity and their further accumulation in humans throughout the food chain. Lead is one of the most dangerous metals for the human health. Although lead is prohibited in many brands, it is still used in commercial products as automotive batteries, paints, cookware, etc. It can reach water sources from various industrial activities such as mining, oil refining, metal plating and battery manufacturing. The removal of lead from wastewaters has received considerable attention in last decade. Recently, there has been significant interest in the use of agricultural by-products as sorbents for this purpose.

The present study deals with the adsorption properties of a waste material based on rice husks, as an effective sorbent with respect to Pb(II) ions from single-component solutions. The rice husks were subjected to slow pyrolysis at temperature 480°C. The material structure was characterized by the intrusion Hg-porosimetry and by BET method.

The carbon/silica ratio has been determined by thermal analysis. The morphology of the investigated material has been studied using scanning electron microscopy. The amount and composition of the fluids, dispersed on the surface of the carbonized rice husks, was determined applying extraction and gas chromatography-mass spectrometry method. Surface functionalities were determined by FTIR spectroscopy.

The adsorption properties of the biomaterial in the present study were determined by means of the batch method. Experiments were carried out by different metal ion concentrations and acidity. The concentration of Pb(II) determined by flame AAS. Equilibrium modelling data were fitted to linear Langmuir and Freundlich models. It was established that Langmuir isotherm most adequately described the adsorption processes. Kinetic of adsorption was also investigated. Pseudo-first order, pseudo-second order and intraparticle diffusion models were used to analyze kinetic data. The maximum adsorption capacity was calculated. The studied material showed good adsorption properties towards Pb(II) ions and it could be used for their effective removal from aqueous media.

**Acknowledgments:** The equipment is part of the DRI-INFRAMAT, supported by the MES (contract D01-284/2019). The study is also supported by the Bulgarian Ministry of Education and Science under the National Research Programme "Healthy Foods for a Strong Bio-Economy and Quality of Life" approved by DCM # 577 / 17.08.2018.

## Raman Spectroscopy of Water Samples

A. Kosateva, B. Tsyntsarski

*Laboratory Fuel Chemistry, Institute of Organic Chemistry with Centre of Phytochemistry,  
Bulgarian Academy of Sciences, Acad. G. Bonchev bl 9, 1113 Sofia,  
e-mail: [ani\\_popova@orgchm.bas.bg](mailto:ani_popova@orgchm.bas.bg)*

In the framework of research related to ecology and aimed at determining the dangers of pollution of water resource as a result of the activities of industrial enterprises. Raman Microscope was used to study two water samples taken from the Novi Iskar River before and after enrichment factory near town Etropole, Bulgaria. Ellatzite-Med AD is one of the largest copper mining companies in Bulgaria, dealing mainly with extraction and processing of copper porphyry gold-bearing ores from Ellatzite deposit. The samples were measured and observed on Bruker Senterra II Raman Microscope. The two samples showed difference on the microscope, but the spectra showed nothing disturbing.

**Acknowledgments:** Project BG05M2OP001-1.002-0019: „Clean technologies for sustainable environment – water, waste, energy for circular economy“, financed by the Operational programme “Science and Education for Smart Growth” 2014-2020, co-financed by the European union through the European structural and investment funds.

## Hard Anodization as an Efficient Technique for Enhancement of the Mechanical Surface Properties of Aluminum and its Alloys

Christian Girginov<sup>1</sup>, Stephan Kozhukharov<sup>2</sup>, Angel Dishliev<sup>3</sup>

<sup>1</sup>Department of Physical Chemistry, University of Chemical Technology and Metallurgy,  
8 Kilment Ohridski blvd., 1756 Sofia, Bulgaria

<sup>2</sup>Laboratory for Advanced Materials Research, University of Chemical Technology and Metallurgy,  
8 Kilment Ohridski blvd., 1756 Sofia, Bulgaria

<sup>3</sup>Department of Mathematics, University of Chemical Technology and Metallurgy,  
8 Kilment Ohridski blvd., 1756 Sofia, Bulgaria  
e-mail: [girginov@uctm.edu](mailto:girginov@uctm.edu)

Metallic products, details, constructions and facilities possess considerable susceptibility to corrosion. Besides, the corrosion processes occurring on the surfaces of metals and their alloys are predominantly electrochemical in character. Further, their heterogeneous nature is a result of the contact of the solid metallic object and corrosive components of its liquid or gaseous environment.

Thus, the most efficient and widely used approach for corrosion protection of metals is by insulating their surfaces with various types of coatings. In this sense, the hard anodization of various aluminum alloys appears an advanced method for formation of dense and mechanically durable oxide layers. On the other hand, the great industrial interest towards this type of protective coatings is predetermined by their aptitude to enhance the friction strength of the aluminum details and to be used as primers for multilayered coating systems with enhanced adhesion to the aluminum substrate.

Mainly for these reasons arises the need to summarize the basic technological aspects of the hard anodization process and their relation to the resulting improvement of the surface properties.

**Acknowledgments:** The financial support from the Bulgarian National Scientific Fund is highly appreciated (contract #КП-06-M 38/1 (2019)).

[1] A. Rajendra, B. J. Parmar, B. J. Parmar, A. K. Sharma, H. Bhojraj, M. M. Nayak, K. Rajanna *Surf. Eng.* **2005**, 21(3), 193-197; DOI: 10.1179/174329405X50000

[2] Jr, R. G. Rateick, T. C. Binkowski, B. C. Boray, *J. Mater. Sci. Lett.* **1996**, 15, 1321–1323.

[3] K. Schwirn, W. Lee, R. Hillebrand, M. Steinhart, K. Nielsch, U. Gösele, *ACS – Nano* **2008**, 2, 302–310.

[4] W. Lee, R. Ji, U. Gösele, K. Nielsch, *Nature Materials* **2006**, 5, 741–747.

## Two-Dimensional Layers of PtSe<sub>2</sub> – Synthesis and Characteristics for Opto-electronics Applications

Irnik Dionisieva<sup>1</sup>, Krastyo Buchkov<sup>1,2</sup>, Vera Marinova<sup>1</sup>, Ivalina Avramova<sup>4</sup>,  
Hristosko Dikov<sup>3</sup> and Dimitre Dimitrov<sup>1,2</sup>

<sup>1</sup> Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Sofia, Bulgaria

<sup>2</sup> Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, Bulgaria

<sup>3</sup> Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences,  
Sofia, Bulgaria

<sup>4</sup> Institute of General and Inorganic Chemistry Bulgarian Academy of Sciences, Sofia, Bulgaria  
e-mail: [irnikdionisiev@iomt.bas.bg](mailto:irnikdionisiev@iomt.bas.bg)

In this study we report the large-scale synthesis of PtSe<sub>2</sub> layers by thermally assisted selenization of pre-deposited platinum films in a horizontal quartz-tube Chemical Vapour Deposition (CVD) reactor [1, 2]. Raman spectroscopy, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) are used for characterizations. The Raman spectra of PtSe<sub>2</sub> show strong dependence on the thickness (Pt deposition time). XPS analysis was applied to examine the chemical compositions in order to assess the quality of the synthesized PtSe<sub>2</sub> films. All the studied properties reveal a great potential to obtain large area continuous layers with controlled thickness for further integration in functional heterostructures for nanoelectronic and optoelectronic devices.

**Acknowledgments:** This work is supported by the Bulgarian Ministry of Education and Science under the National Research Programme “Young scientists and postdoctoral students” approved by DCM# 577/17.08.2018. Research equipment of distributed research infrastructure INFRAMAT (part of Bulgarian National roadmap for research infrastructures) supported by Bulgarian Ministry of Education and Science under contract D01-284/17.12.2019 was used for AFM measurements.

[1] L. Pi, L. Li, K. Liu, Q. Zhang, H. Li, T. Zhai, Recent Progress on 2D Noble-Transition-Metal Dichalcogenides, *Adv. Funct. Mater.* **2019**, 29, 1904932

[2] Z. Wang, Q. Li, F. Besenbacher, M. Dong, Facile Synthesis of Single Crystal PtSe<sub>2</sub> Nanosheets for Nanoscale Electronics, *Adv. Mater.* **2016**, 28, 10224–10229

## Green and Efficient Extraction of Shikimic Acid From *Illicium Verum* with Deep Eutectic Solvents

G. Gerginov, S. Simeonov

*Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences,  
Sofia, Bulgaria, Acad. G. Bonchev str., bldg. 9, Sofia 1113  
e-mail: [svilen@orgchm.bas.bg](mailto:svilen@orgchm.bas.bg)*

Recently, Shikimic acid a compound widely abundant in the plant kingdom,[1] became the major precursor for the synthesis of antiviral Tamiflu, thus Shikimic acid is nowadays produced in multi-hundred-ton amount [2] by extraction of *Illicium verum*. However, to date, its extraction from plant material is mainly performed using classic organic solvents, which has been associated with serious environmental concerns and human risks. Furthermore, poor extraction efficiency for Shikimic acid has been commonly observed. Recently, after the pioneer work of Abbott et al. [3], a new class of ionic fluids emerged, namely deep eutectic mixtures/solvents (DES), which exhibit similar properties as the traditional ionic liquids but are in general cheaper and more environmentally benign. Most of the DESs are liquid at room temperature, consist of natural non-toxic ingredients and are characterized by their low vapour pressure thus being an appealing green alternative. Although various DESs were already applied as solvents for variety of organic reactions, yet little attention has been paid to their use as extraction solvents of natural products.

In the present study the extraction of shikimic acid from Chinese star anise (*Illicium verum*) using variety of deep eutectic solvents has been investigated. A new high performance liquid chromatography (HPLC) method for the analysis of extracts containing shikimic acid has been developed. Experiments have shown that the efficiency of the extraction with several classes of deep eutectic solvents is comparable to that of the extraction with conventional organic solvents.

**Acknowledgments:** The financial support of Ministry of Education and Science (INFRAMAT project, contracts D01-155/2018 and D01-284/2019) is gratefully acknowledged

[1] N. Candeias, B. Assoah, S. Simeonov, *Chem. Rev.*, **2018**, 118, 10458-10550.

[2] M. Karpf, R. Trussardi, *Angew. Chem. Int. Ed.*, **2009**, 48, 5760-5762.

[3] A. Abbott, G. Capper, D. Davies, R. Rasheed, V. Tambyrajah, *Chem. Comm.*, **2003**, 70-71.



## Atomically Deposited Nanolayers of ZnO Doped With Al: Characterizations and Applications

B. Napoleonov<sup>1,2</sup>, D. Petrova<sup>1,2</sup>, V. Marinova<sup>1</sup>, B. Blagoev<sup>3</sup>, V. Strijkova<sup>1</sup> and  
D. Dimitrov<sup>1,3</sup>

<sup>1</sup>*Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Sofia, Bulgaria*

<sup>2</sup>*South-West University "Neofit Rilski", Blagoevgrad, Bulgaria*

<sup>3</sup>*Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, Bulgaria*

e-mail: [blgv@abv.bg](mailto:blgv@abv.bg)

The integration of high uniformity, conformal and compact transparent conductive layers into next generation Indium tin oxide (ITO) - free optoelectronics including wearable and bendable structures is a huge challenge [1]. Here we demonstrate and compare transparent and conductive functionality of Aluminum-doped zinc oxide (AZO) thin films deposited on glass as well as on Polyethylene terephthalate (PET) flexible substrates by using Atomic layer deposition (ALD) technique. AZO thin films possess high optical transmittance at visible and near-infrared spectral range and electrical properties competitive to the commercial ITO layers. AZO layers deposited on flexible PET substrate demonstrate stable sheet resistance over 1000 bending cycles. Based on the performed optical and electrical characterizations several applications of ALD AZO as transparent conductive layer are shown: AZO/Glass supported Liquid Crystal (LC) display as well as AZO/PET based flexible Polymer Dispersed Liquid Crystal (PDLC) devices [2].

**Acknowledgments:** The authors gratefully acknowledge the financial support provided by Bulgarian Science Fund under the grant number КП-06-H-28/8. Research equipment of distributed research infrastructure INFRAMAT (part of Bulgarian National roadmap for research infrastructures) supported by Bulgarian Ministry of Education and Science under the contract D01-284/17.12.2019 was used for AFM measurements.

[1] K. Ellmer, Past achievements and future challenges in the development of optically transparent electrodes, *Nature Photonics*, **2012**, 6, 809–817.

[2] M. Morales-Masis, S. De Wolf, R. Woods-Robinson, J. W. Ager, C. Ballif, Transparent electrodes for efficient optoelectronics, *Adv. Electron. Mater.*, **2016**, 3, 1600529.

## Thin Nanocrystalline ZnO Films Doped With Al and Co Deposited by Electro Spray: Properties and Applications

G. Marinov<sup>1</sup>, B. Georgieva<sup>1</sup>, V. Strijkova<sup>1</sup>, N. Todorova<sup>2</sup>, T. Babeva<sup>1</sup>

<sup>1</sup>*Institute of Optical Materials and Technologies "Acad. J. Malinowski",  
Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 109, 1113 Sofia, Bulgaria.*

<sup>2</sup>*Nanofunctional and Nanocomposite Materials Laboratory,  
Institute of Nanoscience and Nanotechnology, NCSR "Demokritos", Athens, Greece  
e-mail: [gmarinov@jomt.bas.bg](mailto:gmarinov@jomt.bas.bg)*

Due to its remarkable properties such as transparency in VIS and NIR spectral ranges, low resistivity, biocompatibility and long-term stability, ZnO gains increasing scientific interest. Additionally, ZnO is inexpensive and non-toxic and finds diverse applications in optoelectronics, sensing, transparent electrodes, solar cells, etc.

In this study, a versatile fabrication method of electro spray is demonstrated for deposition of thin ZnO films doped with Aluminum, Cobalt and Al & Co. For undoped ZnO film, solutions of zinc acetate dehydrate in deionized water, ethanol and acetic acid are used, while water solutions of aluminum nitrate and cobalt acetate are used for doping (5 and 10 wt%). Substrate temperature of 300 °C, voltage of 18 kV and emitter-to-collector distance of 6 cm are used for electro spray deposition.

The film morphology and structure are studied by Scanning Electron Microscopy, Transmission Electron Microscopy and Selected Area Electron Diffraction. The crystalline status of the films is confirmed by X-ray diffraction. The surface profile and roughness are inspected by Atomic Force Microscopy and 3D optical profilometry. The optical properties are investigated through photoluminescence measurements. The dependence of the properties on the dopant type and concentration is investigated. Possible applications as photo catalyst for NO oxidation is demonstrated and discussed.

**Acknowledgments:** G. Marinov acknowledges the National Scientific Program for young scientists and postdoctoral fellows, funded by the Bulgarian Ministry of Education and Science (MES) with DCM 577/2018 and 271/2019. Research equipment of distributed research infrastructure INFRAMAT (part of Bulgarian National roadmap for research infrastructures) supported by Bulgarian Ministry of Education and Science under contract D01-284/17.12.2019 was used in this investigation.

## **MODULE II**

# **ORAL PRESENTATIONS**

## **Investigation of Manufacturing Technology of Artifacts from a Tumulus Mound near the Village of Chudomir**

P. Penkova

*National Archaeological Institute with Museum - BAS,  
2, Saborna str., Sofia 1000  
e-mail: [petyapenkova@gmail.com](mailto:petyapenkova@gmail.com)*

Investigation of Bronze Age artifacts excavated from a tumulus mound near the village of Chudomir, Structure no. 13, has been thoroughly carried out as part of the INFRAMAT Project. So far, only the research project on manufacturing technology of artifacts from the Valchitran Treasure of the same age, enlisted in the museum collection of NAIM, has been implemented in more detail. Twelve gold and one bronze objects have been fully studied. Traces of fabric adhering to the surface of the bronze item, interpreted as a razor, have been analysed. The investigation included the following research methods: observations and measurements with a digital microscope, observations and analyses using the scanning electron microscope (SEM), and ICP analyses. The accomplished research project added important details that impart information about the Bronze Age manufacturing techniques and production processes, as well as the types of tools. The results of this investigation once more clearly confirm the high level of background knowledge of the properties of metals and alloys applied by the craftsmen, as well as their skills required to operate the manufacturing techniques.

## **Analysis of Hellenistic and Celtic Tetradrachms from the Village of Terziysko, the Troyan region**

I. Hristov<sup>1</sup>, I. Prokopov<sup>2</sup>, V. Penchev<sup>3</sup>, A. Vatov<sup>3</sup>

<sup>1</sup>*National History Museum, Sofia, Vitoshko lale 16 str., Sofia, Bulgaria,*

<sup>2</sup>*South-West University "Neofit Rilski", 66 Ivan Michailov str., Blagoevgrad, Bulgaria,*

<sup>3</sup>*National History Museum, Sofia, Vitoshko lale 16 str., Sofia, Bulgaria.*

*e-mail: [a.vatov@historymuseum.org](mailto:a.vatov@historymuseum.org)*

In the early winter of 2019, a hoard of twenty-two tetradrachms from was discovered during leveling with a caterpillar machine an old road connecting the Koman hut with the Vasilyov hut in the Troyan region. The terrain is in the territory of the village of Terziysko, municipality of Troyan . Subsequently, the coins were handed over to the National Museum of History. In this article, we present the hoard and a detailed catalogue, an analysis of similar finds and interpretation of the hoard. The entire hoard of twenty-two Hellenistic and Celtic tetradrachms (silver coins) were analyzed using X-ray fluorescence spectrometry (XRF), with portable instrument Bruker S1 Titan 800 calibrated for precious metals. The tetradrachms were found to contain very high concentrations of Ag (about 93 - 97%).

### ***Acknowledgments:***

This study was supported by consortium INFRAMAT - part of the National Roadmap for Scientific Infrastructure and is financially supported by the Bulgarian Ministry of Education and Science (under Contract D01-284/18.12.2019). We acknowledge the excellent coordination of the museum administration and the storage department that allowed us to analyse this very rare hoard.

## Documentation of Underwater Archaeological Excavation through Digital Photogrammetry

P. Y. Georgiev<sup>1,3</sup>, K. Dimitrov<sup>1,2</sup>

<sup>1</sup>*Centre for Underwater Archaeology, 1 Apollonia str., Sozopol, Bulgaria*

<sup>2</sup>*National Archaeological Institute with Museum – Bulgarian Academy of Sciences,  
2 Saborna Str. Sofia, Bulgaria*

<sup>3</sup>*University of Southampton, 65A, Avenue Campus, Southampton, United Kingdom  
e-mail: [georgiev.py@gmail.com](mailto:georgiev.py@gmail.com)*

In the past decade, digital photogrammetry has established itself as a reliable and accurate method used for recording during archaeological excavations. Even more so, when the site is underwater. Here we will present a methodology that is the result of the cooperation between the Centre for Underwater Archaeology's and National Archaeological Institute with Museum on the underwater excavations at the sites at Ropotamo bay, Nesebar and Sozopol.

A rig with three mounted action cameras GoPro Hero 7 Black is used. That shoot in an angle that would provide sufficient overlap between every photograph and having photogrammetry software-generated markers on site with DGPS coordinates with scale bars for increased accuracy. Combined with postprocessing of the image's white balance, we can have a model of a 5x5 trench georeferenced and scaled with a 1.6 mm error per meter. That allows us to accurately document and in a very short time, a site that is up to 10 m deep in waters with less than 50 cm visibility.

We hope that the results achieved at the multilayered site at the bay of Ropotamo dated from the Early Bronze age to the Ottoman period; the submerged fortifications of the ancient Mesembria and the harbour accumulations from the Greek colonization of Apollonia Pontica to the Medieval ages, will present the advantages and disadvantages of using digital photogrammetry as a reliable method for recording archaeological sites.

**Acknowledgements:** We would like to express our gratitude to our friends and colleges from the University of Southampton: Prof. Jonathan Adams, Dr Rodrigo Pacheco-Ruiz, Felix Pedrotti and Dr Kotaro Yamafune from A.P.P.A.R.A.T.U.S. LLC for showing us the advantage of digital photogrammetry and helping us perfect our methodology.

## **MODULE II**

# **POSTER PRESENTATIONS**

## **Creating the e-Database *Encyclopaedia Ancient Thrace and the Thracians* Aimed at Promoting the Cultural Heritage on the Territory of the Republic of Bulgaria**

V. Fol, R. Preshlenova, R. Popova

*Institute of Balkan Studies and Prof. Alexander Fol Centre of Thracology–  
Bulgarian Academy of Sciences, 1000 Sofia, 45, Moskovska str.  
e-mail: [valeriafol@gmail.com](mailto:valeriafol@gmail.com); [valeria.fol@balkanstudies.bg](mailto:valeria.fol@balkanstudies.bg)*

The e-database *Encyclopaedia Ancient Thrace and the Thracians*, developed by the Institute for Balkan Studies with *Professor Alexander Fol* Centre of Thracology (IBSCT) of the Bulgarian Academy of Sciences, provides free access to academic information on the history, culture and language of the Thracians in a broad Southeast-European, Mediterranean and Asia Minor context. The database also presents movable and immovable archaeological artefacts with text, photographs and video. The articles are gradually translated into English to make the information useful to foreign users as well. Free access is offered to the Encyclopaedia. In addition to researchers from the Institute, the authors of the Encyclopaedia comprise scholars from similar institutes of the Bulgarian Academy of Sciences, from universities, and national, regional and municipal museums of history. The team works in cooperation with municipalities, freelance photographers and cameramen, NGOs and producer companies. The team also includes undergraduate and postgraduate students.

The bilingual e-database *Encyclopaedia Ancient Thrace and the Thracians* is an essential part of the IBSCT activities aimed at preserving the cultural heritage of Southeastern Europe, its popularisation before a broad public and its incorporation in the international research space.

The poster presentation visualises the topics developed in the e-database *Encyclopaedia Ancient Thrace and the Thracians*, the gallery, the inner links and its proposed expansion with the various technologies used for the movable and immovable archaeological artefacts, which are examined within the INFRAMAT Project.

### ***Acknowledgments:***

The Institute for Balkan Studies with Centre of Thracology expresses its gratitude for the fruitful cooperation to the management of the INFRAMAT Project, to the Brezovo Municipality, the Regional Museum of History – Sofia, the Regional Museum of History – Plovdiv, and the Thracart Culture Centre.



## Using of p\_XRF for Analysis of Archaeological Finds Made of Copper and Copper Alloys

V. Bonev<sup>1</sup>, B. Zlateva<sup>1,2</sup>, T. Stoyanov<sup>1</sup>

<sup>1</sup> *Department of Archaeology, Faculty of History,, Sofia University "St. Kl. Ohridski",  
15, Tcar Osvoboditel Blvd., Sofia 1000,*

<sup>2</sup> *Department of Analytical Chemistry, Faculty of Pharmacy and Chemistry,  
1, J. Bauchier Blvd, Sofia 1164  
e-mail: zlateva@chem.uni-sofia.bg*

The use of portable X-ray fluorescence spectrometry (XRF) equipment has been widely used in archeometric research in the last 10-15 years. XRF is a non-destructive method for elemental analysis, allowing the determination of the content of a large number of chemical elements in various types of archaeological materials. Especially in this case, when applied to the analysis of archaeological finds of copper and copper alloys (armour of the Thracian warriors - helmets, cuirasses, greaves, etc., dated in 1st millennium BC) the method is particularly suitable because of the high archaeological and the artistic value of these artifacts.

At the same time, the XRF analysis allows focusing the X-ray radiation in a very small size (spot-analysis) and allows to obtain information about the elemental content in the solder joints, for specific decoration on the surface of the helmets, as well as to detect the presence of corrosion products. In this way, on the one hand, the archeological find is preserved for exposition in the museums, while data on its chemical (elemental) composition are obtained.

An analysis of protective weapons from the collections in the museums in Northern Bulgaria (Ruse, Shumen, Silistra, Vratsa, Razgrad, Veliko Tarnovo etc.) was performed with a p-XRF Bruker S1 Titan with SSDetector (resolution of 160 eV FWHM at 6 KeV).

The obtained results were treatment with statistical methods using Statistics 10 software and on the basis of similarities / differences in the chemical composition certain characteristic features of the technology used for making the artifacts were determined, as well as some regional differences between items.

### **Acknowledgments:**

The research was carried out with the financial support of the National Scientific Fund (OPR 05/13/2018), as the p-XRF Bruker S1 Titan device was maintained with the kind support of the Inframat project (Contract DO01-155 / 28.08.2018).

## Application of LA-ICP-MS for Investigation of Archaeological and Geological Samples

V. Lyubomirova, R. Djingova, B. Todorov, V. Mihaylova, B. Zlateva, I. Belovezhdova

*Trace Analysis Laboratory, Faculty of Chemistry and Pharmacy, University of Sofia,  
1, J. Bourchier Blvd, 1164, Sofia, Bulgaria  
e-mail: [vlah@chem.uni-sofia.bg](mailto:vlah@chem.uni-sofia.bg)*

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), is a rapidly developing analytical technique which provides spatial resolution analysis of element composition and precise and accurate data on major, minor and trace (down to ng/g levels) elements with minimal or no sample preparation. A serious advantage in the analysis of valuable archaeological and geological samples is also the ablation of  $\mu\text{m}$ -sized sampling area which makes it non-destructive, compatible and conservation-wise analysis. Although LA-ICP-MS has been widely used, accuracy is restricted by numerous factors, including the instrumental conditions, elemental fractionation and matrix effects, strategies for quantitative calibration and the lack of sufficient matrix-matched reference materials.

According to the type of samples and the analyte elements, the analytical accuracy can be improved through the optimization of instrumental conditions, correction strategies and calibration approaches, depending on the availability of Certified Reference Materials (CRM).

The present work demonstrates the possibility for quantitative elemental analysis and elements' spatial distribution in various solid archaeological samples such as marble, bronze, glass. Using an optimized procedure for sample preparation and instrumental calibration with powdered CRMs [1], the method is also applied for rapid bulk element analysis of archaeological (pottery) [2] and geological (coals and ashes) samples.

**Acknowledgments:** The financial support of INFRAMAT (Modern research infrastructure in support of science, culture and technological development) for upgrade of the ICP-MS/LA-ICP-MS spectrometer is gratefully acknowledged. INFRAMAT is part of the National Roadmap for Scientific Infrastructure and is financially supported by the Bulgarian Ministry of Education and Science (Contract D01-155/28.08.2018 and D01-284/18.12.2019).

Analysis of geological materials (coal and ashes) are part of BG05M2OP001-1.002-0019: "Clean technologies for sustainable environment – water, waste, energy for circular economy" (Clean&Circle) 2018 – 2023, for development of a Centre of Competence, financed by the Operational programme "Science and Education for Smart Growth" 2014-2020, co-funded by the European Union through the European structural and investment funds.

[1] V. Lyubomirova, B. Todorov, R. Djingova, *C. R. Acad. Bulg. Sci.*, **2016**, 69(3), 275-282.

[2] V. Lyubomirova, Ž. Šmit, H. Fajfar, I. Kuleff, *ArchéoSciences, revue d'archéométrie*, **2017**, 41(1), 69-82.

## **Application of Gamma Spectrometry for Dating of Archaeological and Geological Samples**

B. Todorov, V. Lyubomirova, R. Djingova, V. Mihayova, B. Zlateva, I. Belovezhdova

*University of Sofia, Faculty of chemistry and pharmacy,  
1, J. Boucher, 1164 Sofia, Bulgaria  
e-mail: [b.todorov@chem.uni-sofia.bg](mailto:b.todorov@chem.uni-sofia.bg)*

The principle of radionuclides dating is based on measuring the activity of uranium and its daughter products generated by radioactive decay due to unbalanced equilibrium. Radionuclide couples  $^{230}\text{Th}/^{243}\text{U}$  and  $^{231}\text{Pa}/^{235}\text{U}$  has wide range of application for dating archeological objects (bones, teeth) and geological samples. These methods are characterized with time scale from 1 000 to 3 000 000 years dating and low cost.

**Acknowledgments:** Authors are grateful to the support of the project "INFRAMAT-1", financed by the National Science Fund, Bulgarian Ministry of Education and Science.

## A Technological Study on the Wall Paintings in the Russian Church St Nikolay in Sofia: Identification of the Binding Media by IR Spectroscopy

N. Lumov<sup>1</sup>, S. Belishki<sup>2</sup>, S. Stoyanov<sup>1</sup>, D. Yancheva<sup>1</sup>, E. Velcheva<sup>1</sup>, B. Stamboliyska<sup>1</sup>

<sup>1</sup>*Institute of Organic Chemistry with Centre of Phytochemistry, Acad. G. Bonchev St., build. 9,  
1113 Sofia, Bulgaria*

<sup>2</sup>*National Academy of Art, Faculty of Applied Arts, 73 Tzarigradsko Shose blvd,  
1113 Sofia, Bulgaria*

*e-mail: [nlumov@orgchm.bas.bg](mailto:nlumov@orgchm.bas.bg)*

The church of St Nicholas in Sofia (known as the Russian church), was decorated within several time periods - in 1912-1913 by the Russian artist Vasily Perminov and his team; in 1945-1946 by another Russian artist, Michail Maletski; in 1954 the crypt of the church was embellished with wall paintings by Nikolay Shelehov; and as a final stage the antechamber of the crypt was decorated in 1996. In order to characterize the painting techniques used by the artists in the different periods, an extended study was carried out by combined analytical methods [1]. X-ray fluorescence and micro-Raman spectroscopy have enabled identification of the main pigments encountered in the wall paintings - vermilion, hematite, ultramarine, green earths, carbon black, chrome green, titan white, barium white, and alizarin [1].

Herein we report the results from an ATR-FTIR study aiming to reveal the binding media of a series of samples originating from different parts of the church. The samples were taken from the western apse, the southern stairway, the choirs and the crypt. The analysis has shown that both oil and egg tempera techniques were used in the wall paintings. The presence of oil medium was detected by the strong IR absorption around 1740 cm<sup>-1</sup>, while egg was identified by the simultaneous presence of IR bands around 1650, 1550 and 1730 cm<sup>-1</sup>. The ATR-FTIR measurements afforded some additional information on the inorganic and organic pigments, degradation products. Thus important insights for formulating the conservation strategy were gained and the knowledge on the painting techniques and materials used by Russian artists in the ecclesiastical wall painting in Bulgaria was enriched.

**Acknowledgments:** Equipment of INFRAMAT (Research Infrastructure from National roadmap of Bulgaria), supported by Contract DO1-284/17.12.2019 with Bulgarian Ministry of Education and Science is used in part of the present investigations. This work has been financially supported by the National Science Fund of Bulgaria, Contract КП-06-ОПР 05/5.

[1] D. Yancheva, S. Belishki, N. Haralampiev, E. Velcheva, B. Stamboliyska, D. Fischer, A. Lederer, Raman Spectroscopy in the Study of the Wall Paintings in the Church of St Nicholas in Sofia (the Russian Church), In "Book of Abstracts of the 10th International Congress on the Application of Raman Spectroscopy in Art and Archaeology", 2019, pp. 130-131.

## **Application of Multispectral Imaging for the Study of the Painting *Portrait of Alexander II* by Stanislav Dospevski**

Stefan Belishki

*National Academy of Art, 1, Shipka Street, Sofia*  
e-mail: [st.belishki@nha.bg](mailto:st.belishki@nha.bg)

The *Portrait of Alexander II* by Stanislav Dospevski is one of the significant paintings in the collection of the Museum of the National Academy of Art in Sofia. In the period 2018-2020 the Department of Conservation-Restoration of the Academy conducted study of the portrait and carried out conservation-restoration treatment.

An important method, used for the preliminary examination of the portrait, was the technical photography, performed by imaging in the ultraviolet (UV), visible and near infrared (NIR) regions of the electromagnetic spectrum. The aim was to collect information on the technical features and to evaluate the condition of the painting in order to plan and implement successful treatment.

The photographs in the visible spectrum were taken in both normal and raking light, allowing study of the deformation phenomenon, cracks in the paint and gesso layers and losses of original material. Macro-photographs in visible light (VL) of recto and verso of the painting were also taken to examine the destructions and to analyse the stratigraphy of the paint layer, the decay of the gesso layer and the extent of penetration of the ink of the signature in the canvas.

The images of UV-induced visible fluorescence photography (UVF) visualised the distribution of the varnish and some patterns of the cracks, and did not show any alterations in the original structure, nor additions of new materials. No characteristic luminescence of the paint layer is observed. The reflectance photography in UV light with peak at 365 nm (UVR) mapped again the distribution of the varnish, its relief and patterns of the cracks. The thickness of the varnish was a barrier for obtaining information on the artist's pallet.

Reflected NIR photography (IRR) uncovered valuable information on the artist's technique by visualising elements of the underdrawing. This imaging technique made also clearly readable the artist's signature on the right side.

Further to the IRR, a false colour IR photography (IRFC) was taken to study the artist's pallet [fig. 3]. It revealed the use of ultramarine in area such as the blue ribbon, which was later proved by laboratory analyses. A complimentary false colour UV photography (UVFC) was taken, the results of which are yet to be interpreted.

The results of the study provided with important information on the technology of the painting and destructions of the materials, and facilitated the subsequent scientific analysis and planning of the conservation-restoration interventions.

## Case Studies of the Decorative Elements of Painted Chests from the Collection of IEFSEM-BAS

I.Mishkova, G.Baykusheva

IEFSEM-BAS, 6, Moskovska str., Sofia, Bulgaria

e-mail: [iglika.mishkova@iefem.bas.bg](mailto:iglika.mishkova@iefem.bas.bg); [gergana.baykushev@iefem.bas.b](mailto:gergana.baykushev@iefem.bas.b)

The painted chests are one of the objects of the interior architecture of the Bulgarian houses up to the Liberation, which form a specific genre in art. Some of them are shaped with a drawing typical of the Romanian city of Brasov. Others are the work of local master painters practicing the specific craft. The analysis of the written boxes is focused on two main topics - their production / use and the problems we face in terms of conservation and restoration work. This type of chests, which once played the role of wardrobes and cabinets, nowadays are often used to illustrate certain themes in ethnographic exhibitions or for decoration in modern homes. Their artistic decoration and compositions are diverse, the wood for construction and the colors used are subject to many influences. The present study seeks to answer many questions about the state of paints and methods of preservation and restoration of selected examples from the collection of the National Ethnographic Museum, studied under the INFRAMAT project.

### **Acknowledgments:**

- [1] E.Tzaneva, Bulgarian wedding chests *Museums and monuments of culture*, **1969**, vol.2  
(Е, Цанева - Български сватбени сандъци - *Музеи и паметници на културата*, **1969**, №2)
- [2] Panorama of Revival applied arts, Sofia, Bulgaria, **1998**  
(Панорама на Възрожденските приложни изкуства - София, **1998** Акад. изд. Марин Дринов)
- [3] A. Sharenkov, Technology of the pictorial materials of the Revival iconography, *Questions of conservation and restoration*. **1984**, pp. 65-75  
(А. Шаренков, Технология на живописните материали на възрожденската иконопис, *Въпроси на консервацията и реставрацията*, **1984**, 65-75 стр.)
- [4] L.Mikov, Wedding (bridal) chest - a representative work of Bulgarian Revival woodcarving, *Bulgarian Folklore Culture and Revival Art Vol. 3: Selected Studies*, **2018**, pp.205-210  
(Л. Миков, Сватбен (невестински) сандък-представителна творба на българската Възрожденска дърворезба, *Българска фолклорна култура и възрожденско изкуство Т.3: Избрани студии*, **2018**, 205-210]

## **Application of Reflectance Transformation Imaging (RTI) in the Study of Cultural Artefacts from the Fund of Architectural Complex “Balchik Palace”**

A. Vatov, T. Docheva, S. Hristova

*Central Laboratory for Conservation and Restoration  
The National Museum of History, 16 Vitoshko Lale Str. Sofia, Bulgaria  
e-mail: [svetlana.hristova033@gmail.com](mailto:svetlana.hristova033@gmail.com)*

This poster presents an RTI study – photographic method that captures a subject’s surface shape and color and enables the interactive re-lighting of the subject from any direction.

On the territory of architectural complex “Balchik Palace” in May 2020 was realized Reflectance Transformation Imaging (RTI) of stone objects and artefacts from the exposition open areas. This poster presents different examples of the information gathered. The results of the whole work provide additional information about the surface characteristics and would be very helpful to extensive public, scientists and museum specialists for future studies and examinations of these cultural objects.

**Acknowledgments:** The authors express their sincere thanks for providing objects for this study to the administration of architectural complex “Balchik palace” and the INFRAMAT consortium for the given support.

## **Solved Conservation Tasks on a Shroud, owned by Historical Museum, Pomorie**

I. Borisov, D. Kyuranova

*IEFSEM-BAS, 6, Moskovska str.*

*e-mail: [iliya.ottezgallery@yahoo.com](mailto:iliya.ottezgallery@yahoo.com)*

Enrolled in the studios of the Laboratory of Conservation and Restoration at IEFEM with Ethnographic Museum - Sofia in early 2020, the shroud, ownership of Historical Museum in Pomorie, provoked us with a series of researches. It was once part of the church inventory of the Church of the Nativity of the Blessed Virgin in Pomorie, officially consecrated in 1891.

Although unsigned, we associate the fine academic painting of the dead Jesus from the shroud with the work of the artist Nikolai Rostovtsev and a team. The shroud consists of separate elements, which are united as a common ritual object. It is made of canvas in a classic academic oil technique, to which is attached a fabric of black velvet, partially polychrome and fringed. It is painted with visibly different techniques and materials, there are many tears, as well as spots of presumed but unidentified nature. The portrait image with the dead body of Jesus is made with oil paints on a factory, primed linen canvas. Research and paints were performed jointly with researchers from the Institute of Organic Chemistry - BAS under the INFRAMAT project.

The degree of complexity in conservation activities is associated with duplication of the base, strengthening the painting and the pictorial structures of its image. The physical and mechanical properties of the secondary drapery have also changed. There are many contaminants of different nature. After their identification, the strengthening of the fabric was done in parallel with the duplication of the original canvas.

The final decision on the exposure of the shroud is dictated by the degree of its preservation as a museum object.



**INFRAMAT Coordinator:  
Institute of Physical Chemistry,  
Bulgarian Academy of Sciences  
Acad. G. Bonchev str., Bl.11, 1113 Sofia**

**Office INFRAMAT: [inframat@ipc.bas.bg](mailto:inframat@ipc.bas.bg)  
Web-site: [www.inframat.bg/en](http://www.inframat.bg/en)**

**Video presentation: [//inframat.bg/en/inframat-v-10-minuti/](http://inframat.bg/en/inframat-v-10-minuti/)**



**Distributed Infrastructure of**

***Centers for Synthesis and Characterization of New  
Materials and Restoration and Conservation of  
Archeological and Ethnographic Artefacts***

**supported by Bulgarian Ministry of Education and Science  
under contracts D01-155/2018 and D01-284/2019,  
Bulgarian National Roadmap for Research Infrastructure**