

Blagojević, V.A., Lukić, V., Begović, N.N., Maričić, A.M., Minić, D.M.
Hydrogen storage in a layered flexible [Ni₂(btc)(en)₂]_n coordination
polymer

(2016) International Journal of Hydrogen Energy, 41 (47), pp. 22171-
22181.

<https://doi.org/10.1016/j.ijhydene.2016.08.203>

ABSTRACT: [Ni₂(btc)(en)₂]_n coordination polymer exhibits a layered two-dimensional structure with weak interaction between the layers. Correlation of experimental measurements, DFT calculations and molecular simulations demonstrated that its structural features, primarily the inherent flexibility of the layered polymeric structure, lead to improved hydrogen storage performance at room temperature, due to significant enhancement in isosteric heats of hydrogen adsorption. Volumetric measurements of hydrogen adsorption at room temperature show up to 0.3 wt.% hydrogen absorbed at 303 K and 2.63 bar of hydrogen pressure, with isosteric heats of adsorption of about 12.5 kJ mol⁻¹. Predicted performance at room temperature is 1.8 wt.% at 48 bar and 3.5 wt.% at 100 bar, better than both MOF-5 and NU-100, with calculated values of isosteric heats for adsorption of hydrogen in 8–13 kJ mol⁻¹ range at both 77 K and 303 K. Grand canonical Monte Carlo calculations show that this material, at 77 K, exhibits gravimetric hydrogen densities of more than 10 wt.% (up to 8.3 wt.% excess) with the corresponding volumetric density of at least 66 gL⁻¹, which is comparable to MOF-5, but achieved with considerably smaller surface area of about 2500 m² g⁻¹. This study shows that layered two-dimensional MOFs could be a step towards MOF systems with significantly higher isosteric heats of adsorption, which could provide better room temperature hydrogen storage capabilities. © 2016 Hydrogen Energy Publications LLC

Dodevski, V., Stojmenović, M., Vujković, M., Krstić, J., Krstić, S., Bajuk-Bogdanović, D., Kuzmanović, B., Kaluđerović, B., Mentus, S.
Complex insight into the charge storage behavior of active carbons obtained by carbonization of the plane tree seed
(2016) Electrochimica Acta, 222, pp. 156-171.

<https://doi.org/10.1016/j.electacta.2016.10.182>

ABSTRACT: Activated carbon was prepared using plane tree seed as a cheap and renewable raw material. The samples were prepared by carbonization under N₂ atmosphere up to 850 °C, and activation in CO₂ atmosphere at different both temperatures (750 and 850 °C) and times of activation (0.3, 1 and 2 h). The influence of activation parameters on physicochemical properties was studied by XRPD, Raman spectroscopy, FTIR, N₂ physisorption, SEM and electrochemical methods. The pore structure was correlated to the specific capacitance and the amount of hydrogen stored, in alkaline, neutral and acidic electrolyte solution. The relationship of asymmetrical shape of CV curves with the porosity of samples has served to better understand some unclear issues related to the complex mechanism of charge storage. The sample activated at 850 °C for 2 h displayed the best behavior. At a high scan rate of 300 mV s⁻¹, its capacitance, amounted to ~26.8 μF cm⁻² ~19.69 μF cm⁻² and ~25.8 μF cm⁻² in KOH, Na₂SO₄, and H₂SO₄ solutions, respectively. © 2016 Elsevier Ltd

Popa, A., Sasca, V., Bajuk-Bogdanović, D., Holclajtner-Antunović, I. Synthesis, characterization and thermal stability of cobalt salts of Keggin-type heteropolyacids supported on mesoporous silica (2016) *Journal of Thermal Analysis and Calorimetry*, 126 (3), pp. 1567-1577.

<https://doi.org/10.1007/s10973-016-5650-0>

ABSTRACT: Some heteropoly salts-mesoporous silica composites were prepared from Co salt of molybdophosphoric acid CoHPMo12O40 (CoHPM) by supporting on mesoporous silica in different concentrations (20-40 mass% CoHPM) of active phase. The structure and texture of these CoHPM/silica composites were studied by powder X-ray diffraction, Fourier transformed infra-red (FT-IR) and micro-Raman spectroscopy, nitrogen physisorption at 77 K and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS). Thermal stability was investigated by thermogravimetric analysis, differential thermal analysis and differential scanning calorimetry. FT-IR and Raman studies showed that heteropoly anions preserved their Keggin structure after impregnation on mesoporous silica support. From SEM-EDS analysis, it observed that for low loading of active phase, the average content of chemical elements (Mo, P and Co) is close to the stoichiometric values, while for higher loadings, the samples exhibit some deviation of concentration values from the stoichiometric ones. The mesoporous silica-HPA composites are thermally more stable than the parent acids, due to the strong anion-support interaction. © 2016, Akadémiai Kiadó, Budapest, Hungary.

Amić, A., Marković, Z., Marković, J.M.D., Jeremić, S., Lučić, B., Amić, D.

Free radical scavenging and COX-2 inhibition by simple colon metabolites of polyphenols: A theoretical approach (2016) *Computational Biology and Chemistry*, 65, pp. 45-53.

<https://doi.org/10.1016/j.compbiolchem.2016.09.013>

ABSTRACT: Free radical scavenging and inhibitory potency against cyclooxygenase-2 (COX-2) by two abundant colon metabolites of polyphenols, i.e., 3-hydroxyphenylacetic acid (3-HPAA) and 4-hydroxyphenylpropionic acid (4-HPPA) were theoretically studied. Different free radical scavenging mechanisms are investigated in water and pentyl ethanoate as a solvent. By considering electronic properties of scavenged free radicals, hydrogen atom transfer (HAT) and sequential proton loss electron transfer (SPLET) mechanisms are found to be thermodynamically probable and competitive processes in both media. The Gibbs free energy change for reaction of inactivation of free radicals indicates 3-HPAA and 4-HPPA as potent scavengers. Their reactivity toward free radicals was predicted to decrease as follows: hydroxyl >> alkoxyyls > phenoxyyl ≈ peroxyyls >> superoxide. Shown free radical scavenging potency of 3-HPAA and 4-HPPA along with their high μM concentration produced by microbial colon degradation of polyphenols could enable at least in situ inactivation of free radicals. Docking analysis with structural forms of 3-HPAA and 4-HPPA indicates dianionic ligands as potent inhibitors of COX-2, an inducible enzyme involved in colon carcinogenesis. Obtained results suggest that suppressing levels

of free radicals and COX-2 could be achieved by 3-HPAA and 4-HPPA indicating that these compounds may contribute to reduced risk of colon cancer development. © 2016 Elsevier Ltd

Milenković, A., Smičiklas, I., Bundaleski, N., Teodoro, O.M.N.D., Veljović, Đ., Vukelić, N.

The role of different minerals from red mud assemblage in Co(II) sorption mechanism

(2016) Colloids and Surfaces A: Physicochemical and Engineering Aspects, 508, pp. 8-20.

<https://doi.org/10.1016/j.colsurfa.2016.08.011>

ABSTRACT: A range of industrial by-products are currently under the consideration as cost-effective alternatives to conventional sorbent materials for environmental clean-up and remediation applications. Bauxite residue (red mud) has demonstrated exceptionally high potential for the immobilization of cationic pollutants. Due to heterogeneity of such material, determination of the role of individual mineral phases in the overall sorption mechanism is a challenging task. To enlighten the mechanism of Co(II) sorption by mineral assemblage of the red mud, sequential extraction analysis of Co-loaded sample was combined with the microscopic and spectroscopic studies performed by Scanning Field Emission Electron Microscope (FE-SEM), Energy Dispersive Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS). Sorbed Co(II) ions were found associated with operationally defined Fe,Mn-oxide and carbonate/acid soluble fractions. Binding of Co(II) by the red mud was achieved primarily by means of chemisorption/surface precipitation on Fe- and Ti-oxides. In coexistence with these highly selective surfaces, gibbsite and silica appeared to be low affinity sites for Co(II). Incongruent dissolution of sodalite phase was detected, indicating that its function was not to ensure sorption centers, but to increase the solution pH creating favorable environment for Co(II) binding by Fe- and Ti-oxides. The results demonstrate high stability of sorbed Co(II) and synergistic action of mineral constituents as essentially important property for red mud implementation as a purifying and remediation agent. © 2016 Elsevier B.V.

Vujković, M.J., Vidoeski, B.A., Jovanović, S.P., Bajuk-Bogdanović, D.V., Budimir, M.D., Marković, Z.M., Pavlović, V.B., Todorović-Marković, B.M., Holclajtner-Antunović, I.D.

SYNTHESIS AND CHARACTERIZATION OF ELECTROCHEMICALLY EXFOLIATED GRAPHENE-MOLYBDOPHOSPHATE HYBRID MATERIALS FOR CHARGE STORAGE DEVICES (2016) Electrochimica Acta, 217, pp. 34-46.

<https://doi.org/10.1016/j.electacta.2016.09.067>

ABSTRACT: A novel electrochemically exfoliated graphene-molybdophosphoric acid nanohybride (EG-MoPA) was prepared via a simple method. Both scanning electron (SEM) and atomic force microscopy (AFM) results show that MoPA clusters are attached to the surfaces of graphene sheets. By changing the mass ratio of EG-MoPA, the morphology of nanohybrid itself can be significantly modulated, from mostly flat graphene like structure at low amount of MoPA to very uneven, wavy surfaces when MoPA is present in higher concentration. The Raman and Fourier transform infra red (FTIR) spectra in conjunction with electrochemical results indicate that strong interaction exists between

the components of nanohybride based on charge transfer and electrostatic interaction of graphene sheets and MoPA. The electrochemical performances are improved by synergetic effect of reversible redox properties of MoPA and the double layer capacitance of a high-surface area of the obtained nanohybrides. The higher current capability of EG was achieved by anchoring the small MoPA concentration on the graphene support. The strong bonding of EG with the MoPA prevents acid to dissolve in the electrolyte upon cycling, enabling the stable capacitance behaviour of the low-doped EG sample. The capacitance for the EG doped with the high amount of MoPA was found to be much larger than for EG. However, the obtained capacitance decreases at the beginning of cycling due to the dissolution of excessive amount of surface MoPA, weakly bonded to the graphene support. © 2016 Elsevier Ltd

Pašti, I.A., Janošević Ležaić, A., Ćirić-Marjanović, G., Mirsky, V.M. Resistive gas sensors based on the composites of nanostructured carbonized polyaniline and Nafion (2016) *Journal of Solid State Electrochemistry*, 20 (11), pp. 3061-3069.

<https://doi.org/10.1007/s10008-016-3344-y>

ABSTRACT: Due to constant necessity to have reliable and sensitive gas sensors in many contemporary technologies, there is a permanent need for development of new sensing platforms with good sensing properties. Here, we demonstrate a novel type of resistive gas sensors based on carbonized polyaniline/Nafion composites. The sensing mechanism of such sensors is based on the sorption of gases by the composites which induce Nafion swelling and decreasing of conductivity. Chemosensitive properties can be tuned by the (i) choice of carbon materials with different conductivities, (ii) Nafion content in the composite, and (iii) thickness of the composite layer. We have shown that the sensors respond to water, acetone, ethanol, and methanol vapors. For the last two cases, we have achieved high sensitivity, fast response, wide concentration range, and good recovery. The use of simultaneous two- and four-point techniques for these sensors provides an internal control of the sensor integrity. © 2016, Springer-Verlag Berlin Heidelberg.

Salvestrini, S., Jovanović, J., Adnadjević, B. Comparison of adsorbent materials for herbicide diuron removal from water (2016) *Desalination and Water Treatment*, 57 (48-49), pp. 22868-22877.

<https://doi.org/10.1080/19443994.2016.1180484>

ABSTRACT: Diuron herbicide is a persistent and frequently detected compound in surface and groundwater. In this work, a comparative study of the performance of four types of adsorbent (two precipitated silica, zeolite Y and carbon molecular sieves (CMS)) for removing diuron from water was carried out. Precipitated silica samples were obtained by controlled precipitation of SiO₂ with sulphuric acid from water glass; zeolite Y was synthesized by a microwave-assisted hydrothermal method; CMS were synthesized by the method of controlled pyrolysis of wheat straw and chemical vapour deposition of organic matter. It was found that adsorption isotherms for precipitated silica and zeolite type Y are of linear shape, whereas the one for CMS exhibits at low

concentrations a concave shape followed by an inflection point which suggests cooperative adsorption and the formation of adsorbate multilayers. CMS adsorbent showed the highest adsorption capacity and this was likely due to its high hydrophobicity. Temperature has a negligible effect on precipitated silica and zeolite Y while it strongly affects adsorption properties of CMS. Adsorption is not thermodynamically favoured at high temperature. An unexpected decrease in the rate of adsorption was observed with increase in temperature. This is possibly related to the different adsorption behaviour of diuron conformers and aggregates. © 2016 Balaban Desalination Publications. All rights reserved.

Nakarada, D., Etinski, M., Petković, M.
Using density functional theory to study neutral and ionized stacked thymine dimers
(2016) *Journal of Physical Chemistry A*, 120 (39), pp. 7704-7713.

<https://doi.org/10.1021/acs.jpca.6b06493>

ABSTRACT: Stacking interactions in thymine dimers are studied with density functional theory. According to our calculations, six dimers of comparable stability can be prepared at low temperature, but dimerization is impossible at room temperature due to the large entropy contribution that accompanies it. Analysis of vibrational anharmonic coupling terms shows that each of the dimers exhibits distinct vibrational dynamics. Properties of electron density in the intermolecular region are used to analyze neutral stacked species and their ionized forms. Bond paths and critical points in the intermolecular region are identified, but a simple relationship between binding energy and total electron density in the intermolecular critical points could not be found due to an uneven electron distribution in the binding region. The reduced density gradient was confirmed to be a useful tool for analysis of weak stacking interactions. Those interactions also affect vertical and adiabatic ionization energies, which are computed to be slightly lower for the dimers compared to the monomer. © 2016 American Chemical Society.

Jović, A., Đorđević, A., Čebela, M., Stojković Simatović, I., Hercigonja, R., Šljukić, B.
Composite zeolite/carbonized polyaniline electrodes for p-nitrophenol sensing
(2016) *Journal of Electroanalytical Chemistry*, 778, pp. 137-147.

<https://doi.org/10.1016/j.jelechem.2016.08.025>

ABSTRACT: Electrodes based on composites of zeolites with carbonized polyaniline prepared in the presence of 5-sulfosalicylic acid are evaluated for both qualitative and quantitative determination of phenols in aqueous solutions. Zeolites used included NaX and NaY, as well as their transition metal (Mn and Cu) cation-exchanged forms, and they were all characterized using XRPD, FTIR and SEM. Cyclic voltammetry was used to study composites' electrochemical response in the presence of p-nitrophenol, phenol and 5-aminophenol in acidic, neutral and alkaline media. Linear dependence of current on p-nitrophenol concentration in acidic media was obtained in 0.1-1 mM concentration range. The comparative evaluation of the electrochemical

response of NaX/carbonized polyaniline composite and its individual components revealed significantly lower limit of detection obtained using composite electrode (1.27 μM) compared to that obtained using pure zeolite (135 μM) or pure carbonized polyaniline (94.5 μM) electrode. Composite electrode gave response to p-nitrophenol presence in neutral media as well, but it quickly disappeared with continuous scanning, while no clear response could be seen in highly alkaline media. Thus, this work demonstrates benefits of using novel composite based on zeolites and carbonized polyaniline for sensing of phenols in acidic aqueous solutions. © 2016 Elsevier B.V.

Milikić, J., Ćirić-Marjanović, G., Mentus, S., Santos, D.M.F., Sequeira, C.A.C., Šljukić, B.
Pd/c-PANI electrocatalysts for direct borohydride fuel cells
(2016) *Electrochimica Acta*, 213, pp. 298-305.

<https://doi.org/10.1016/j.electacta.2016.07.109>

ABSTRACT: Carbon-supported palladium nanoparticle electrocatalysts were prepared using two different carbon supports, commercial Vulcan® XC72 (Pd/Vul) and synthesized carbonized nanostructured polyaniline doped with 3,5-dinitrosalicylic acid (Pd/c-PANI), and using two different synthesis procedures. Morphology and Pd content for each of the four electrocatalysts were determined using transmission electron microscopy and thermogravimetric analysis, respectively. The electrocatalysts were further analyzed electrochemically using cyclic voltammetry and linear scan voltammetry with a rotating ring-disc electrode, as well as chronoamperometry, considering their activity in direct borohydride/peroxide fuel cells, i.e., for the borohydride oxidation reaction (BOR) in alkaline media as well as for the hydrogen peroxide reduction reaction (HPRR) in acidic media. The number of electrons exchanged in BOR varied between 2.4 and 4.8, while unique n value of 2 was evidenced in HPRR. Activation energies for BOR at studied materials were in the 10.3-26.2 kJ mol⁻¹ range and for HPRR in the 31.7-48.3 kJ mol⁻¹ range. © 2016 Elsevier Ltd

Stanković, B., Ostojić, B.D., Gruden, M., Popović, A., Đorđević, D.S.
Substituted naphthalenes: Stability, conformational flexibility and description of bonding based on ETS-NOCV method
(2016) *Chemical Physics Letters*, 661, pp. 136-142.

<https://doi.org/10.1016/j.cplett.2016.08.056>

ABSTRACT: For all dimethylnaphthalenes (DMNs) the transition from a planar ring conformation to a nonplanar one results in energy increase in the range 1.7-2.4 kcal/mol. There is a linear relationship between averaged rigidity constant and relative energy of DMNs. The relative stability of DMNs does not follow the aromatic stabilization based on NICS values. The ETS-NOCV analysis shows that more efficient bonding in the π -electron system is the origin of enhanced stability in laterally substituted (CH₃, Cl and NO₂) naphthalenes. The results for Caryl-CH₃ system indicate more steric repulsion in going from 2,7-DMN to 1,8-DMN following the increase of relative energies. © 2016 Elsevier B.V.

Tanić, M.N., Janković Mandić, L.J., Gajić, B.A., Daković, M.Z., Dragović, S.D., Bačić, G.G.

Natural radionuclides in soil profiles surrounding the largest coal-fired power plant in Serbia
(2016) Nuclear Technology and Radiation Protection, 31 (3), pp. 247-259.

<https://doi.org/10.2298/NTRP1603247T>

ABSTRACT: This study evaluates the influence of the largest Serbian coal-fired power plant on radionuclide concentrations in soil profiles up to 50 cm in depth. Thirty soil profiles were sampled from the plant surroundings (up to 10 km distance) and analyzed using standard methods for soil physicochemical properties and gamma ray spectrometry for specific activities of natural radionuclides (^{40}K , ^{226}Ra and ^{232}Th). Spatial and vertical distribution of radionuclides was determined and analyzed to show the relations between the specific activities in the soil and soil properties and the most influential factors of natural radionuclide variability were identified. The radiological indices for surface soil were calculated and radiological risk assessment was performed. The measured specific activities were similar to values of background levels for Serbia. The sampling depth did not show any significant influence on specific activities of natural radionuclides. The strongest predictor of specific activities of the investigated radionuclides was soil granulometry. All parameters of radiological risk assessment were below the recommended values and adopted limits. It appears that the coal-fired power plant does not have a significant impact on the spatial and vertical distribution of natural radionuclides in the area of interest, but technologically enhanced natural radioactivity as a consequence of the plant operations was identified within the first 1.5 km from the power plant. © 2016, Vinca Inst Nuclear Sci. All rights reserved.

Vujković, M., Mentus, S.

Potentiodynamic and galvanostatic testing of $\text{NaFe}_0.95\text{V}_0.05\text{PO}_4/\text{C}$ composite in aqueous NaNO_3 solution, and the properties of aqueous $\text{Na}_1.2\text{V}_3\text{O}_8/\text{NaNO}_3/\text{NaFe}_0.95\text{V}_0.05\text{PO}_4/\text{C}$ battery
(2016) Journal of Power Sources, 325, pp. 185-193.

<https://doi.org/10.1016/j.jpowsour.2016.06.031>

ABSTRACT: The $\text{NaFe}_0.95\text{V}_0.05\text{PO}_4/\text{C}$ composite is synthesized by electrochemical ion displacement from $\text{LiFe}_0.95\text{V}_0.05\text{PO}_4/\text{C}$ composite in aqueous NaNO_3 solution. A coulombic capacity amounting to ~ 105 and ~ 82 mAh g⁻¹ at sodiation/desodiation rate of 500 and 5000 mA g⁻¹, respectively, is evidenced. For the sake of comparison the same investigations is performed with $\text{LiFe}_0.95\text{V}_0.05\text{PO}_4/\text{C}$ composite in LiNO_3 solution, and better capacity retention and rate performance is evidenced for $\text{NaFe}_0.95\text{V}_0.05\text{PO}_4/\text{C}$ one. This advancement is found to be due a higher participation of pseudocapacity in the sodiation/desodiation charge storage process. An aqueous battery composed of $\text{NaFe}_0.95\text{V}_0.05\text{PO}_4/\text{C}$ cathode, belt-like $\text{Na}_1.2\text{V}_3\text{O}_8$ anode and NaNO_3 solution as an electrolyte, tested galvanostatically, displays long-life performance with only 10% of capacity fade after 1000 charge/discharge cycles. © 2016 Elsevier B.V. All rights reserved.

Sarap, N.B., Rajačić, M.M., Đalović, I.G., Šeremešić, S.I., Đorđević, A.R., Janković, M.M., Daković, M.Z.

Distribution of natural and artificial radionuclides in chernozem soil/crop system from stationary experiments
(2016) Environmental Science and Pollution Research, 23 (17), pp. 17761-17773.

<https://doi.org/10.1007/s11356-016-6938-0>

ABSTRACT: The present paper focuses on the determination of radiological characteristics of cultivated chernozem soil and crops from long-term field experiments, taking into account the importance of distribution and transfer of radionuclides in the soil-plant system, especially in agricultural cropland. The investigation was performed on the experimental fields where maize, winter wheat, and rapeseed were cultivated. Analysis of radioactivity included determination of the gross alpha and beta activity as a screening method, as well as the activities of the following radionuclides: natural (^{210}Pb , ^{235}U , ^{238}U , ^{226}Ra , ^{232}Th , ^{40}K , ^7Be) and artificial (^{90}Sr and ^{137}Cs). The activities of natural and artificial (^{137}Cs) radionuclides were determined by gamma spectrometry, while the artificial radionuclide ^{90}Sr was determined by a radiochemical analytical method. Based on the obtained results for the specific activity of ^{40}K , ^{137}Cs , and ^{90}Sr , accumulation factors for these radionuclides were calculated in order to estimate transfer of radionuclides from soil to crops. The results of performed analyses showed that there is no increase of radioactivity that could endanger the food production through the grown crops. © 2016, Springer-Verlag Berlin Heidelberg.

Stojmenović, M., Žunić, M., Gulicovski, J., Dodevski, V., Prekajski, M., Radulović, A., Mentus, S.

Structural, morphological and electrical properties of $\text{Ce}_{1-x}\text{Ru}_x\text{O}_{2-\delta}$ ($x=0.005-0.02$) solid solutions
(2016) Ceramics International, 42 (12), pp. 14011-14020.

<https://doi.org/10.1016/j.ceramint.2016.06.007>

ABSTRACT: Nanoparticles of ceria-ruthenium oxide solid solutions with composition $\text{Ce}_{1-x}\text{Ru}_x\text{O}_{2-\delta}$ ($x=0.005-0.02$) were successfully produced by self-propagating room temperature synthesis using reaction between metal nitrates and sodium hydroxide. These compositions were characterized by X-ray powder diffraction (XRD), Raman spectroscopy, specific surface area, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The experimental measurements were complemented by calculations based on the ion-packing model. XRD analysis revealed the presence of single-phase solid solutions with CeO_2 fluorite structure (regardless of dopants concentration) and Raman spectroscopy confirmed the presence of the RuO_2 phase. Electrochemical impedance spectroscopy (EIS) measurements of sintered samples at different temperatures showed that the small ionic radius dopant reduces oxygen vacancies mobility that is responsible for the conductivity of these ceramics. © 2016 Elsevier Ltd and Techna Group S.r.l.

Ležaić, A.J., Luginbühl, S., Bajuk-Bogdanović, D., Pašti, I., Kissner, R., Rakvin, B., Walde, P., Ćirić-Marjanović, G.

Insight into the template effect of vesicles on the laccase-catalyzed oligomerization of N-phenyl-1,4-phenylenediamine from Raman spectroscopy and cyclic voltammetry measurements

(2016) Scientific Reports, 6, art. no. 30724, .

<https://doi.org/10.1038/srep30724>

ABSTRACT: We report about the first Raman spectroscopy study of a vesicle-assisted enzyme-catalyzed oligomerization reaction. The aniline dimer N-phenyl-1,4-phenylenediamine (= p-aminodiphenylamine, PADPA) was oxidized and oligomerized with *Trametes versicolor* laccase and dissolved O₂ in the presence of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) vesicles (80-100 nm diameter) as templates. The conversion of PADPA into oligomeric products, poly(PADPA), was monitored during the reaction by in situ Raman spectroscopy. The results obtained are compared with UV/vis/NIR and EPR measurements. All three complementary methods indicate that at least some of the poly(PADPA) products, formed in the presence of AOT vesicles, resemble the conductive emeraldine salt form of polyaniline (PANI-ES). The Raman measurements also show that structural units different from those of "ordinary" PANI-ES are present too. Without vesicles PANI-ES-like products are not obtained. For the first time, the as-prepared stable poly(PADPA)-AOT vesicle suspension was used directly to coat electrodes (without product isolation) for investigating redox activities of poly(PADPA) by cyclic voltammetry (CV). CV showed that poly(PADPA) produced with vesicles is redox active not only at pH 1.1-as expected for PANI-ES-but also at pH 6.0, unlike PANI-ES and poly(PADPA) synthesized without vesicles. This extended pH range of the redox activity of poly(PADPA) is important for applications. © The Author(s) 2016.

Bajuk-Bogdanović, D., Uskoković-Marković, S., Hercigonja, R., Popa, A., Holclajtner-Antunović, I.

Study of the decomposition pathway of 12-molybdophosphoric acid in aqueous solutions by micro Raman spectroscopy

(2016) Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy, 153, pp. 152-159.

<https://doi.org/10.1016/j.saa.2015.08.029>

ABSTRACT: Micro Raman spectroscopy was applied to investigate the speciation of heteropoly and isopoly molybdates in 0.05 and 0.005 M aqueous solutions of 12-molybdophosphoric acid at pH values between 1 and 6. For comparative purposes, ³¹P NMR spectroscopy was applied too. It is shown that stability of Keggin anion is influenced both by pH and concentration of solution. The Keggin structure is stable in acidic solutions (pH < 1.6) while defective Keggin structures are formed with further alkalization (up to pH 5.6). Monolacunary anion $\text{PMo}_{11}\text{O}_{39}^{7-}$ is the main component in the pH region from 1.6 to 3.4. Further removal of molybdenyl species causes the appearance of other vacant Keggin structures such as $\text{PMo}_9\text{O}_{31}(\text{OH})_3^{6-}$ and $\text{PMo}_6\text{O}_{25}^{9-}$ - at about pH 4. At pH 5.0, anion $\text{PMo}_6\text{O}_{25}^{9-}$ is the main species. In solutions with pH greater than 5.0, heteropolymolybdates disappear completely and isopolymolybdates $\text{Mo}_7\text{O}_{24}^{6-}$ and MoO_4^{2-} - are formed in higher amounts. In more diluted solution of 0.005 M, the decomposition scheme of 12-molybdophosphoric acid solution with increasing of pH takes place without observation of significant amounts of $\text{Mo}_7\text{O}_{24}^{6-}$ species. If alkalization is performed with 0.5 M instead of 5 M NaOH, there are no significant

changes in the Raman spectra of solutions. It is shown that the spectra of evaporated samples may be used for the identification of molecular species in corresponding concentrated solutions. However, Raman spectra of dry residues of more diluted solutions differ from spectra of corresponding solutions due to the reactions performed during the process of drying and cannot be used for unambiguous identification of species in solution. Acidification of 0.05 M solution of Na_2MoO_4 shows that at $\text{pH} > 5.6$, molybdate anion MoO_4^{2-} dominates, while in the pH range between 5.6 and 1, heptamolybdate anion $\text{Mo}_7\text{O}_{24}^{6-}$ is preferentially formed. © 2015 Elsevier B.V. All rights reserved.

Maksić, A., Smiljanić, M., Miljanić, S., Rakočević, Z., Štrbac, S.
Ethanol Oxidation on Rh/Pd(poly) in Alkaline Solution
(2016) *Electrochimica Acta*, 209, pp. 323-331.

<https://doi.org/10.1016/j.electacta.2016.05.096>

ABSTRACT: Bimetallic electrodes prepared by Rh nanoislands spontaneously deposited on polycrystalline palladium, Pd(poly), at submonolayer coverage were explored for ethanol oxidation in alkaline media. Characterization of obtained Rh/Pd(poly) nanostructures was performed ex situ by AFM imaging and by X-ray photoelectron spectroscopy. In situ characterization of the obtained electrodes and subsequent ethanol oxidation measurements were performed by cyclic voltammetry in 0.1 M KOH. Palladium surface with 50% Rh coverage exhibited the highest catalytic activity for ethanol oxidation in alkaline media. The origin of the enhanced catalysis of Rh/Pd(poly) surfaces with respect to bare Pd was explained by the electronic effect. Possible reaction pathways for ethanol oxidation were discussed taking into account the activity of obtained bimetallic electrodes for the oxidation of CO and acetaldehyde, as the most probable reaction intermediates. © 2016 Elsevier Ltd. All rights reserved.

Tosic, D., Markovic, Z., Jovanovic, S., Prekodravac, J., Budimir, M., Kepic, D., Holclajtner-Antunovic, I., Dramicanin, M., Todorovic-Markovic, B.
Rapid thermal annealing of nickel-carbon nanowires for graphene nanoribbons formation
(2016) *Synthetic Metals*, 218, pp. 43-49.

<https://doi.org/10.1016/j.synthmet.2016.04.016>

ABSTRACT: In this paper, we present a novel method for graphene nanoribbons formation using nickel nanowires as templates. Modification of electrochemical procedure for nickel nanowires synthesis was introduced by implementing graphene quantum dots as a carbon source. Thus, nickel nanowires with graphene quantum dots were prepared. These wires were exposed to rapid thermal annealing at high temperatures (500 °C, 700 °C and 800 °C). During this process carbon atoms dissolve in metal and precipitate to the nickel surface forming nickel-carbon nanowires. Atomic force microscopy, scanning electron microscopy and Raman spectroscopy were characterization methods used for analysis of changes in nickel-carbon nanowires properties depending on the different annealing temperatures. After etching nickel with nitric acid, graphene nanoribbons with average diameters of 32 nm and average

lengths of 4 μm were obtained. © 2016 Elsevier B.V. All rights reserved.

Bačić, G., Pavićević, A., Peyrot, F.

In vivo evaluation of different alterations of redox status by studying pharmacokinetics of nitroxides using magnetic resonance techniques (2016) *Redox Biology*, 8, pp. 226-242.

<https://doi.org/10.1016/j.redox.2015.10.007>

ABSTRACT: Free radicals, particularly reactive oxygen species (ROS), are involved in various pathologies, injuries related to radiation, ischemia-reperfusion or ageing. Unfortunately, it is virtually impossible to directly detect free radicals in vivo, but the redox status of the whole organism or particular organ can be studied in vivo by using magnetic resonance techniques (EPR and MRI) and paramagnetic stable free radicals - nitroxides. Here we review results obtained in vivo following the pharmacokinetics of nitroxides on experimental animals (and a few in humans) under various conditions. The focus was on conditions where the redox status has been altered by induced diseases or harmful agents, clearly demonstrating that various EPR/MRI/nitroxide combinations can reliably detect metabolically induced changes in the redox status of organs. These findings can improve our understanding of oxidative stress and provide a basis for studying the effectiveness of interventions aimed to modulate oxidative stress. Also, we anticipate that the in vivo EPR/MRI approach in studying the redox status can play a vital role in the clinical management of various pathologies in the years to come providing the development of adequate equipment and probes. © 2015 The Authors.

Xu, X., Bošnjaković-Pavlović, N., Čolović, M.B., Krstić, D.Z., Vasić, V.M., Gillet, J.-M., Wu, P., Wei, Y., Spasojević-De Biré, A.

A combined crystallographic analysis and ab initio calculations to interpret the reactivity of functionalized hexavanadates and their inhibitor potency toward Na^+/K^+ -ATPase

(2016) *Journal of Inorganic Biochemistry*, 161, pp. 27-36.

<https://doi.org/10.1016/j.jinorgbio.2016.04.029>

ABSTRACT: In vitro influence of five synthesized functionalized hexavanadates (V6) on commercial porcine cerebral cortex Na^+/K^+ -ATPase activity has been studied. Dose dependent Na^+/K^+ -ATPase inhibition was obtained for all investigated compounds. Calculated half maximal inhibitory concentration IC_{50} values, in mol/L, for Na^+/K^+ -ATPase were 7.6×10^{-5} , 1.8×10^{-5} , 2.9×10^{-5} , 5.5×10^{-5} for functionalized hexavanadates (V6) with tetrabutylammonium (TBA) [V6-CH3][TBA]₂, [V6-NO₂][TBA]₂, [V6-OH][TBA]₂ and [V6-C3][TBA]₂ respectively. [V6-OH][Na]₂ inhibited Na^+/K^+ -ATPase activity up to 30% at maximal investigated concentration 1×10^{-3} mol/L. This reactivity has been interpreted using a study of the non-covalent interactions of functionalized hexavanadate hybrids through Cambridge Structural Database (CSD) analysis. Bibliographic searching has led to 18 different structures and 99 contacts. We have observed that C-H \cdots O contacts consolidate the structures. We have also performed density functional theory (DFT) calculations and have determined electrostatic potential values at the molecular surface on a series of functionalized V6. These results

enlightened their chemical reactivity and their potential biological applications such as the inhibition of the ATPase. © 2016 Elsevier Inc.

Goronja, J., Pejić, N., Janošević Ležaić, A., Stanisavljev, D., Malenović, A.

Using a combination of experimental and mathematical method to explore critical micelle concentration of a cationic surfactant
(2016) *Journal of Chemical Education*, 93 (7), pp. 1277-1281.

<https://doi.org/10.1021/acs.jchemed.5b00913>

ABSTRACT: An undergraduate electrical conductivity measurement experiment in a physical chemistry lab and basic fitting procedures are presented that allow a characterization of micellar system of hexadecyltrimethylammonium bromide (cetyltrimethylammonium bromide, CTAB) in binary mixture of water and acetonitrile (ACN) as a cosolvent (10%, v/v) at 30.0 °C. Conductivity-concentration data were processed by inbuilt function of ORIGIN software to attain the values of critical micelle concentration by method of integration. Acquiring the data-fitting skills that are developed through the addition of a computational tool to a conventional electrical conductometry experiment has a general significance for its applications to more complex upper-level experiments with the aim to process data and perform fast calculations and graphics. © 2016 The American Chemical Society and Division of Chemical Education, Inc.

Marković, S., Tošović, J., Dimitrić Marković, J.M.

Synergic application of spectroscopic and theoretical methods to the chlorogenic acid structure elucidation
(2016) *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 164, pp. 67-75.

<https://doi.org/10.1016/j.saa.2016.03.044>

ABSTRACT: Although chlorogenic acid (5-O-caffeoylquinic acid, 5CQA) is a dietary polyphenol known for its pharmacological and nutritional properties, its structural features have not been completely elucidated. This is the first study whose aim is to contribute to clarification of the 5CQA structure by comparing the experimental and simulated IR, Raman, ¹H NMR, ¹³C NMR, and UV spectra. For this purpose, a comprehensive conformational analysis of 5CQA was performed to reveal its most stable conformations in the gas-state and solution (DMSO and methanol). The lowest-energy conformers were used to predict the spectra at two levels of theory: B3LYP-D3/and M06-2X/6-311+G(d,p) in combination with the CPCM solvation model. Both methods provide very good agreement between all experimental and simulated spectra, thus indicating correct arrangement of the atoms in the 5CQA molecule. The quinic moiety is characterized with directed hydrogen bonds, where the carboxylic hydrogen is not oriented towards the carbonyl oxygen of the carboxylic group, but towards the oxygen of the proximate hydroxyl group. In the gas-state the lowest-energy conformers are characterized with the O4H4 ... O9' hydrogen bond, whereas in the solvated state the structures with the O4H4 ... O10' hydrogen bond prevail. Knowing the fine structural details, i.e. the proper conformation of 5CQA, provides a

solid base for all further investigations related to this compound. © 2016 Elsevier B.V. All rights reserved.

Milenković, A.S., Smičiklas, I.D., Šljivić-Ivanović, M.Z., Živković, L.S., Vukelić, N.S.
Effect of experimental variables onto Co²⁺ and Sr²⁺ sorption behavior in red mud-water suspensions
(2016) Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering, 51 (8), pp. 679-690.

<https://doi.org/10.1080/10934529.2016.1159884>

ABSTRACT: The prospects of rinsed red mud (alumina production residue) utilization for liquid radioactive waste treatment have been investigated, with Co²⁺ and Sr²⁺ as model cations of radioactive elements. To evaluate the sorption effectiveness and corresponding binding mechanisms, the process was analyzed in batch conditions, by varying experimental conditions (pH, Co²⁺ and Sr²⁺ concentrations in single solutions and binary mixtures, contact time, and the concentration of competing cations and ligands common in liquid radioactive waste). Comparison of the Co²⁺ and Sr²⁺ sorption pH edges with the red mud isoelectric point has revealed that Co²⁺ removal took place at both positive and negative red mud surface, while Sr²⁺ sorption abruptly increased when the surface became negatively charged. The increase of initial cation content and pH resulted in increased equilibrium times and sorption capacity and decreased rate constants. From single metal solutions and various binary mixtures, Co²⁺ was sorbed more efficiently and selectively than Sr²⁺. While Sr²⁺ sorption was reduced by coexisting cations in the order Al³⁺ ≥ Ca²⁺ > Na⁺ ≥ Cs⁺, removal of Co²⁺ was affected by Al³⁺ species and complexing agents (EDTA and citrate). Desorption of Co²⁺ was negligible in Ca²⁺ and Sr²⁺ containing media and in solutions with initial pH 4-7. Sr²⁺ desorption was generally more pronounced, especially at low pH and in the presence of Co²⁺. Collected macroscopic data signify that Co²⁺ sorption by red mud minerals occurred via strong chemical bonds, while Sr²⁺ was retained mainly by weaker ion-exchange or electrostatic interactions. Results indicate that the rinsed red mud represent an efficient, low-cost sorbent for Co²⁺ and Sr²⁺ immobilization. © 2016 Taylor & Francis Group, LLC.

Popović-Bijelić, A., Mojović, M., Stamenković, S., Jovanović, M., Selaković, V., Andjus, P., Bačić, G.
Iron-sulfur cluster damage by the superoxide radical in neural tissues of the SOD1G93A ALS rat model
(2016) Free Radical Biology and Medicine, 96, pp. 313-322.

<https://doi.org/10.1016/j.freeradbiomed.2016.04.028>

ABSTRACT: Extensive clinical investigations, in hand with biochemical and biophysical research, have associated brain iron accumulation with the pathogenesis of the amyotrophic lateral sclerosis (ALS) disease. The origin of iron is still not identified, but it is proposed that it forms redox active complexes that can participate in the Fenton reaction generating the toxic hydroxyl radical. In this paper, the state of iron in the neural tissues isolated from SOD1G93A transgenic rats was investigated using low temperature EPR spectroscopy and is

compared with that of nontransgenic (NTg) littermates. The results showed that iron in neural tissues is present as high- and low-spin, heme and non-heme iron. It appears that the SOD1G93A rat neural tissues were most likely exposed in vivo to higher amounts of reactive oxygen species when compared to the corresponding NTg tissues, as they showed increased oxidized [3Fe-4S]¹⁺ cluster content relative to [4Fe-4S]¹⁺. Also, the activity of cytochrome c oxidase (CcO) was found to be reduced in these tissues, which may be associated with the observed uncoupling of heme a₃ Fe and Cu_B in the O₂-reduction site of the enzyme. Furthermore, the SOD1G93A rat spinal cords and brainstems contained more manganese, presumably from MnSOD, than those of NTg rats. The addition of potassium superoxide to all neural tissues ex vivo, led to the [4Fe-4S]→[3Fe-4S] cluster conversion and concurrent release of Fe. These results suggest that the superoxide anion may be the cause of the observed oxidative damage to SOD1G93A rat neural tissues and that the iron-sulfur clusters may be the source of poorly liganded redox active iron implicated in ALS pathogenesis. Low temperature EPR spectroscopy appears to be a valuable tool in assessing the role of metals in neurodegenerative diseases. © 2016 Elsevier Inc.

Stojmenović, M., Vujković, M., Matović, L., Krstić, J., Dukić, A., Dodevski, V., Živković, S.M., Mentus, S.
Complex investigation of charge storage behavior of microporous carbon synthesized by zeolite template
(2016) *Microporous and Mesoporous Materials*, 228, pp. 94-106.

<https://doi.org/10.1016/j.micromeso.2016.03.029>

ABSTRACT: Microporous zeolite templated carbon (ZTC) was synthesized by impregnation method using zeolite Y (Na-form) as a template, and furfuryl alcohol as a carbon precursor. The characterization was carried out by X-ray diffractometry, Raman spectroscopy, scanning electron microscopy, nitrogen physisorption, elemental analysis and electrochemical methods. Physisorption measurements evidenced high micropore volume of obtained material (~0.43 cm³ g⁻¹). The charge storage ability in aqueous KOH, H₂SO₄ and Na₂SO₄ solutions was systematically studied by cyclic voltammetry, galvanostatic charging/discharging and complex impedance measurements. Specific coulombic capacitance, the hydrogen storage, H-ZTC bonding and relaxation time of adsorption were found to be dependent on the type of electrolyte. Neutral Na₂SO₄ aqueous solution was found to be the best for supercapacitor application, thanks to: i) the highest available voltage window ii) lowest corrosion and iii) highest capacitance amounting to 123 F g⁻¹ at 1 A g⁻¹. © 2016 Elsevier Inc. All rights reserved.

Stanisavljev, D., Bujanja, I.N., Stevanović, K.
Determination of iodate ion in the presence of hydrogen peroxide with the stopped-flow technique
(2016) *Reaction Kinetics, Mechanisms and Catalysis*, 118 (1), pp. 143-151.

<https://doi.org/10.1007/s11144-016-0977-x>

ABSTRACT: The modified titration of iodate and hydrogen peroxide with iodide in acidic medium was investigated in order to study the

possibility of separation and determination of iodate under certain conditions. The stopped-flow technique was used to kinetically distinguish titration products I 2 and I 3 - formed in both reactions. Under the given conditions, the reaction between iodate and iodide is finished considerably faster than the reaction between peroxide and iodide. For the ratio $[KIO_3]/[H_2O_2] \approx 0.08$ and acidity of $[H_2SO_4] = 1.005 \times 10^{-1} M$, the kinetic separation between both components may be achieved to within 0.3 %, in less than 3 s. The recovery value of the iodate, with the applied technique after completion of the reaction, is ≈ 98 % showing appropriately chosen reaction conditions. Our results show that when iodate-iodide and peroxide-iodide reactions occur simultaneously under certain conditions, the contribution of peroxide-iodide products may be neglected. It was shown that stopped-flow titration of iodate in specific reactions and certain iodate/peroxide ratio may be used for determination of iodate concentration within a few percent. © 2016, Akadémiai Kiadó, Budapest, Hungary.

Čupić, Ž., Ivanović-Šašić, A., Blagojević, S., Blagojević, S., Kolar-Anić, L., Anić, S.

Return map analysis of the highly nonlinear Bray-Liebhafsky reaction model

(2016) Reaction Kinetics, Mechanisms and Catalysis, 118 (1), pp. 27-38.

<https://doi.org/10.1007/s11144-016-0998-5>

ABSTRACT: By numerically simulated Bray-Liebhafsky (BL) reaction under a continuously fed well stirred tank reactor (CSTR) conditions, we discussed the attractors and Poincaré 1D maps with respect to flow rate as the control parameter. The new technique of the return maps from transient trajectories over the slow manifold is developed and applied in order to explore its multilayered structure related to dynamical states (periodic and aperiodic -chaotic oscillating modes) of the system. Kinetic relations underlying the slow manifold structure are briefly discussed. © 2016, Akadémiai Kiadó, Budapest, Hungary.

Stanković, B., Čupić, Ž., Maćešić, S., Pejić, N., Kolar-Anić, L.

Complex bifurcations in the oscillatory reaction model

(2016) Chaos, Solitons and Fractals, 87, pp. 84-91.

<https://doi.org/10.1016/j.chaos.2016.03.013>

ABSTRACT: The mixing of different types of bifurcations, i.e. supercritical Andronov-Hopf (SAH), double loop (DL) and saddle-loop (SL) bifurcations in the vicinity of their total annihilation, is examined on the highly nonlinear six-variable model for the Bray-Liebhafsky (BL) oscillatory reaction under continuously well-stirred tank reactor (CSTR) conditions. For this kind of the reaction system where the law of mass conservation is additional constraint that must be satisfied and where because of that, some simple bifurcations cannot be formed independently to the others, the considered transformations of the bifurcations are particularly important. That is why as the control parameters for bifurcation analysis, the specific flow rate (j_0), as well as the inflow hydrogen peroxide concentration ($h = [H_2O_2]_{in}$), were used. The complex bifurcations obtained from numerical simulations are compared with some experimental results. It was shown

that these complex bifurcations cannot be easily recognized in experimental investigations without knowing their evolution. © 2016 Elsevier Ltd. All rights reserved.

Damjanović, L., Mioč, U., Bajuk-Bogdanović, D., Cerović, N., Marić-Stojanović, M., Andrić, V., Holclajtner-Antunović, I.
Archaeometric Investigation of Medieval Pottery from Excavations at Novo Brdo, Serbia
(2016) *Archaeometry*, 58 (3), pp. 380-400.

<https://doi.org/10.1111/arcm.12185>

ABSTRACT: Medieval pottery from excavations at Novo Brdo, Serbia, an important mining and trading centre during the 14th and 15th centuries, was investigated by a combination of optical microscopy, inductively coupled plasma - optical emission spectrometry, Fourier transform infrared, micro-Raman and energy-dispersive X-ray fluorescence spectroscopy and X-ray powder diffraction methods in order to determine its composition and firing temperature. The samples investigated were made of medium- to coarse-grained, non-calcareous clay, by a relatively well-controlled firing procedure in an oxidizing atmosphere. The firing temperature was estimated to be 850-950°C. The similarity between the chemical composition of the investigated pottery and the local raw clay, combined with the outward appearance and the archaeological findings, indicate domestic production. The pottery is covered with the transparent lead-rich glaze. Iron and copper were used as colourants. © 2015 University of Oxford.

Maćešić, S., Čupić, Ž., Kolar-Anić, L.
Erratum to Bifurcation analysis of the reduced model of the Bray-Liebhafsky reaction (*Reac Kinet Mech Cat*, (2016), 10.1007/s11144-016-1000-2)
(2016) *Reaction Kinetics, Mechanisms and Catalysis*, 118 (1), p. 57.

<https://doi.org/10.1007/s11144-016-1015-8>

Maćešić, S., Čupić, Ž., Kolar-Anić, L.
Bifurcation analysis of the reduced model of the Bray-Liebhafsky reaction
(2016) *Reaction Kinetics, Mechanisms and Catalysis*, 118 (1), pp. 39-55.

<https://doi.org/10.1007/s11144-016-1000-2>

ABSTRACT: In this paper, an already published model of the Bray-Liebhafsky reaction was improved by removing the direct autoinhibitory step, which resulted in a new variant of the model with more realistic kinetic scheme than the earlier version. The obtained variant of the model retains all intermediate species (I-, HIO, HIO₂ and I₂) that were present in the previous model and has one reaction less. Stability analysis of the improved model was performed by stoichiometric network analysis (SNA). By this method, it was shown that improved model can simulate Andronov-Hopf and saddle-node bifurcations. In order to confirm the results of SNA, bifurcation analysis was performed with the initial concentrations of [H₂O₂]₀ as the control parameter. With selected set of rate constants and constant concentrations of external species, two Andronov-Hopf bifurcations were detected at

$[H_2O_2]_0 = 5.62 \times 10^{-2} \text{ M}$ and $[H_2O_2]_0 = 10.73 \text{ M}$, while the rate constants ought to be changed for a saddle-node to occur. Bifurcation analysis also showed that the interaction between intermediate species I-, HIO and HIO₂ has a crucial impact on the emergence of Andronov-Hopf bifurcation. © 2016, Akadémiai Kiadó, Budapest, Hungary.

Janković, B., Marinović-Cincović, M., Janković, M.
Application of the Kinetic Triplets and Geometrical Characteristics of Thermal Analysis Curves in Identifying the Main Bioactive Compounds (BC) that Govern the Thermal and Thermo-Oxidative Degradation Mechanism of Aronia melanocarpa (Black Chokeberry)
(2016) Food Biophysics, 11 (2), pp. 128-141.

<https://doi.org/10.1007/s11483-016-9424-9>

ABSTRACT: Thermal and thermo-oxidative kinetics of Aronia melanocarpa fresh samples was investigated. The current investigation was based on the application of kinetic triplets and geometrical characteristics of thermal analysis curves in identifying the main bioactive compounds that govern the thermal and thermo-oxidative degradation mechanisms. From established kinetic model in an argon atmosphere, it was found that released products arise from decomposition of phenolic compounds where autocatalysis may occur from the inevitable presence of water already in the early stages of the process through the hydrolysis reaction pathway. In the case of thermo-oxidative degradation, it was found that the main mechanistic scheme can be presented with two different forms of reaction mechanism function, such as: nth order reaction model (with $n > 1$) (in lower heating mode) and Šesták-Berggren autocatalytic model (in higher heating mode). Isoconversional analysis has been shown that neochlorogenic acid represents the governed bioactive compound which has a strong hydrogen-donating activity. Based on the mechanistic conclusions, it was established that in an air atmosphere, the cyanidin-3-glucosylrutinoside (Cy-3-GR) degradation significantly participates in overall complex mechanism. © 2016, Springer Science+Business Media New York.

Omerašević, M., Matović, L., Ružić, J., Golubović, Ž., Jovanović, U., Mentus, S., Dondur, V.
Safe trapping of cesium into pollucite structure by hot-pressing method
(2016) Journal of Nuclear Materials, 474, pp. 35-44.

<https://doi.org/10.1016/j.jnucmat.2016.03.006>

ABSTRACT: A simple one-step method with direct thermal conversion at lower temperatures for preparing a stable Cs-aluminsilicate phase, known as pollucite, is presented. Cs-exchanged form of Na, Ca-LTA type of zeolite (Cs-LTA) was pressureless sintered and hot pressed at certain temperatures in order to obtain pollucite. XRD and FTIR analysis were used to study structural changes of Cs-LTA before and after thermal treatments. Pressureless sintered sample recrystallized into pollucite phase after heat treatment at 1000 °C (3 h) (PLS1000) and hot pressed sample at 750 °C (3 h) using pressure of 35 MPa (HP750), indicating reduced temperature of 250°. SEM micrographs confirmed that HP750 has higher density than PLS1000 which leads to higher value of compressive strength. The HP750 showed better resistance to Cs leaching than the PLS1000. Based on these results one can conclude that hot

pressing is the promising method for the permanent disposal of Cs radionuclides. © 2016 Elsevier B.V. All rights reserved.

Pejić, N., Kolar-Anić, L., Maksimović, J., Janković, M., Vukojević, V., Anić, S.

Dynamic transitions in the Bray-Liebhafsky oscillating reaction. Effect of hydrogen peroxide and temperature on bifurcation (2016) *Reaction Kinetics, Mechanisms and Catalysis*, 118 (1), pp. 15-26.

<https://doi.org/10.1007/s11144-016-0984-y>

ABSTRACT: The temporal dynamics of the Bray-Liebhafsky reaction (iodate-based catalytic decomposition of hydrogen peroxide in an acidic aqueous solution) was experimentally characterized in a continuous stirred tank reactor by independently varying the temperature and the mixed inflow hydrogen peroxide concentration. When the temperature was the bifurcation parameter, the emergence/disappearance of oscillatory behavior via a supercritical Andronov-Hopf bifurcation was observed for different mixed inflow hydrogen peroxide concentrations. An increase in the mixed inflow hydrogen-peroxide concentration resulted in a shift of the bifurcation point towards higher values of temperature, but did not alter the bifurcation type. © 2016, Akadémiai Kiadó, Budapest, Hungary.

Dömötör, O., Rathgeb, A., Kuhn, P.-S., Popović-Bijelić, A., Bačić, G., Enyedy, E.A., Arion, V.B.

Investigation of the binding of cis/trans-[MCl₄(1H-indazole)(NO)]- (M = Ru, Os) complexes to human serum albumin (2016) *Journal of Inorganic Biochemistry*, 159, pp. 37-44.

<https://doi.org/10.1016/j.jinorgbio.2016.02.003>

ABSTRACT: Overall binding affinity of sodium or indazolium cis/trans-[MCl₄(1H-indazole)(NO)] (M = Ru, Os) complexes towards human serum albumin (HSA) and high molecular mass components of the blood serum was monitored by ultrafiltration. HSA was found to be mainly responsible for the binding of the studied ruthenium and osmium complexes. In other words, this protein can provide a depot for the compounds and can affect their biodistribution and transport processes. In order to elucidate the HSA binding sites tryptophan fluorescence quenching studies and displacement reactions with the established site markers warfarin and dansylglycine were performed. Conditional stability constants for the binding to sites I and II on HSA were computed showing that the studied ruthenium and osmium complexes are able to bind into both sites with moderately strong affinity (logK' = 4.4-5.1). Site I is slightly more favored over site II for all complexes. No significant differences in the HSA binding properties were found for these metal complexes demonstrating negligible influence of the type of counterion (sodium vs indazolium), the metal ion center identity (Ru vs. Os) or the position of the nitrosyl group on the binding event. Electron paramagnetic resonance spin labeling of HSA revealed that indazolium trans-[RuCl₄(1H-indazole)(NO)] and long-chain fatty acids show competitive binding to HSA. Moreover, this complex has a higher affinity for site I, but when present in excess, it is able to bind to site II as well, and displace fatty acids. © 2016 Elsevier Inc. All rights reserved.

Nišavić, M., Masnikosa, R., Butorac, A., Perica, K., Rilak, A., Korićanac, L., Hozić, A., Petković, M., Cindrić, M.
Elucidation of the binding sites of two novel Ru(II) complexes on bovine serum albumin
(2016) *Journal of Inorganic Biochemistry*, 159, pp. 89-95.

<https://doi.org/10.1016/j.jinorgbio.2016.02.034>

ABSTRACT: Hyphenated mass spectrometry (MS) techniques have attained an important position in analysis of covalent and non-covalent interactions of metal complexes with peptides and proteins. The aim of the present study was to qualitatively and quantitatively determine ruthenium binding sites on a protein using tandem mass spectrometry and allied techniques, i.e. liquid chromatography (LC) and inductively coupled plasma optical emission spectrometry (ICP-OES). For that purpose, two newly synthesized Ru(II) complexes of a meridional geometry, namely mer-[Ru(4' Cl-tpy)(en)Cl]⁺ (1) and mer-[Ru(4' Cl-tpy)(dach)Cl]⁺ (2) (where 4' Cl-tpy = 4'-chloro-2,2':6',2"-terpyridine, en = 1,2-diaminoethane and dach = 1,2-diaminocyclohexane), and bovine serum albumin were used. The binding of the complexes to the protein was investigated by means of size exclusion- and reversed phase-LC, ICP OES, matrix-assisted laser desorption ionization MS and MS/MS. Ruthenated peptide sequence and a binding target amino acid were revealed through accurate elucidation of MS/MS spectra. The results obtained in this study suggest a high binding capacity of the protein towards both complexes, with up to 5.77 ± 0.14 and 6.95 ± 0.43 mol of 1 and 2 bound per mol of protein, respectively. The proposed binding mechanism for the selected complexes includes the release of Cl ligand, its replacement with water molecule and further coordination to electron donor histidine residue. © 2016 Elsevier Inc. All rights reserved.

Maulucci, G., Bačić, G., Bridal, L., Schmidt, H.H.H.W., Tavitian, B., Viel, T., Utsumi, H., Yalçin, A.S., De Spirito, M.
Imaging Reactive Oxygen Species-Induced Modifications in Living Systems
(2016) *Antioxidants and Redox Signaling*, 24 (16), pp. 939-958.

<https://doi.org/10.1089/ars.2015.6415>

ABSTRACT: Significance: Reactive Oxygen Species (ROS) may regulate signaling, ion channels, transcription factors, and biosynthetic processes. ROS-related diseases can be due to either a shortage or an excess of ROS. Recent Advances: Since the biological activity of ROS depends on not only concentration but also spatiotemporal distribution, real-time imaging of ROS, possibly in vivo, has become a need for scientists, with potential for clinical translation. New imaging techniques as well as new contrast agents in clinically established modalities were developed in the previous decade. Critical Issues: An ideal imaging technique should determine ROS changes with high spatio-temporal resolution, detect physiologically relevant variations in ROS concentration, and provide specificity toward different redox couples. Furthermore, for in vivo applications, bioavailability of sensors, tissue penetration, and a high signal-to-noise ratio are additional requirements to be satisfied. Future Directions: None of the presented techniques fulfill all requirements for clinical translation. The obvious way forward is to incorporate anatomical and functional imaging into a common hybrid-imaging platform. © 2016 Giuseppe Maulucci et al.

Šljukic, B., Santos, D.M.F., Vujkovic, M., Amaral, L., Rocha, R.P., Sequeira, C.A.C., Figueiredo, J.L.
Molybdenum Carbide Nanoparticles on Carbon Nanotubes and Carbon Xerogel: Low-Cost Cathodes for Hydrogen Production by Alkaline Water Electrolysis
(2016) *ChemSusChem*, 9 (10), pp. 1200-1208.

<https://doi.org/10.1002/cssc.201501651>

ABSTRACT: Low-cost molybdenum carbide (Mo₂C) nanoparticles supported on carbon nanotubes (CNTs) and on carbon xerogel (CXG) were prepared and their activity for the hydrogen evolution reaction (HER) was evaluated in 8 m KOH aqueous electrolyte at 25-85 °C. Measurements of the HER by linear scan voltammetry allowed us to determine Tafel slopes of 71 and 74 mV dec⁻¹ at 25 °C for Mo₂C/CNT and Mo₂C/CXG, respectively. Stability tests were also performed, which showed the steady performance of the two electrocatalysts. Moreover, the HER kinetics at Mo₂C/CNT was enhanced significantly after the long-term stability tests. The specific activity of both materials was high, and a higher stability was obtained for the activated Mo₂C/CNT (40 A g⁻¹ at -0.40 V vs. the reversible hydrogen electrode). Elect for electrocatalysts: Mo₂C nanoparticles supported on carbon nanotubes (CNTs) and carbon xerogel (CXG) are prepared and their activity for the hydrogen evolution reaction is evaluated in 8 m KOH aqueous electrolyte at temperatures of 25-85 °C. Stability tests show the steady performance of the two electrocatalysts. © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Milić Komić, S., Pristov, J.B., Popović-Bijelić, A., Zakrzewska, J., Stanić, M., Kalauzi, A., Spasojević, I.
Photo-redox reactions of indole and ferric iron in water
(2016) *Applied Catalysis B: Environmental*, 185, pp. 174-180.

<https://doi.org/10.1016/j.apcatb.2015.12.018>

ABSTRACT: Iron-organic interactions are involved in a variety of environmental phenomena, including photo-redox reactions, iron cycling and bioavailability, as well as contaminant fate. In this study we examined UV-induced redox reactions of iron and indole in water. The presence of one indole in the irradiated system resulted in the presence of eight reduced ferric ions, not counting direct photolysis of Fe³⁺ complexes with OH⁻, which gives Fe²⁺ and hydroxyl radical (HO) as products. The main mechanisms that contribute to indole-related Fe³⁺ reduction i.e. Fe²⁺ accumulation are: (i) HO scavenging, which prevents oxidation of Fe²⁺ by HO; (ii) oxidation of indole and its derivatives by excited ferric iron; (iii) reduction of ferric iron by excited indole (not present under UV-A). Hydrated electrons released by UV-B-excited indole play only a minor role in the reduction of iron. Indole-derived radicals emerged as byproducts of indole/iron photo-chemistry. ¹H NMR and low-T EPR spectroscopy showed that indole forms a weak low-symmetry complex with Fe³⁺. The strongest interactions between iron and π -cloud in the indole ring are at positions 2, 3, and 7. The formation of complex promotes electron transfer from excited indole to Fe³⁺. Our findings are important for understanding the catalysis of photo-reduction of iron by heterocyclic aromatic pollutants, and for the development of protocols for indole processing in wastewaters. © 2015 Elsevier B.V.

Pašti, I.A., Marković, A., Gavrilov, N., Mentus, S.V.
Adsorption of Acetonitrile on Platinum and its Effects on Oxygen
Reduction Reaction in Acidic Aqueous Solutions—Combined Theoretical and
Experimental Study
(2016) *Electrocatalysis*, 7 (3), pp. 235-248.

<https://doi.org/10.1007/s12678-016-0301-6>

ABSTRACT: Combined theoretical and experimental study of acetonitrile (AcN) adsorption on platinum was performed and its effects on the kinetics of oxygen reduction reaction in HClO₄ and H₂SO₄ solutions were examined. Using periodic density functional theory calculations, it was shown that AcN molecule can interact with Pt surface either through the unsaturated π electron system or via lone electron pair of nitrogen atom. In both cases, adsorption energy decreases upon increasing coverage, while the modification of electronic structure of Pt surface is localized to the adsorption site. By combining the results of the DFT calculations with the results of blank cyclic voltammetry and rotating disk electrode voltammetry in O₂-saturated solutions, it was concluded that the effects of AcN on Pt surface chemistry and ORR kinetics are primarily steric in nature. Resulting measured ORR activities of polycrystalline platinum in the presence of AcN are due to the combination of (i) suppression of (bi)sulfate adsorption (in H₂SO₄ solution), (ii) suppression of surface oxidation (in both H₂SO₄ and HClO₄ solution), and (iii) site blockage by adsorbed AcN (or products of its electrochemical transformations). [Figure not available: see fulltext.] © 2016, Springer Science+Business Media New York.

Barudžija, T., Kusigerski, V., Cvjetičanin, N., Šorgić, S., Perović, M., Mitrić, M.
Structural and magnetic properties of hydrothermally synthesized β -MnO₂
and α -KxMnO₂ nanorods
(2016) *Journal of Alloys and Compounds*, 665, pp. 261-270.

<https://doi.org/10.1016/j.jallcom.2016.01.024>

ABSTRACT: Hydrothermal synthesis was applied for obtaining different manganese dioxide polymorphs whose morphology, structure and magnetic properties were thoroughly investigated. Variations in the synthesis pathways lead to the formation of tetragonal rutile-type β -MnO₂ and two tetragonal hollandite-type α -KxMnO₂ samples with different concentration of potassium cations ($x = 0.15$ and 0.18). SEM images showed nanorod shape of all specimens, while microstructure characterization done by XRD measurements revealed that crystallites have an elongated rod-like shape and, hence, it confirmed the anisotropic morphology. Magnetic ordering of β -MnO₂ is antiferromagnetic below 93 K, while both α -KxMnO₂ samples possess more complicated low-temperature behaviour of the reentrant spin-glass type: the onset of the spin-glass like state occurs at temperatures below the weak ferromagnetic ordering. © 2016 Elsevier B.V. All rights reserved.

Stoševski, I., Krstić, J., Milikić, J., Šljukić, B., Kačarević-Popović, Z., Mentus, S., Miljanić, Š.

Radiolitically synthesized nano Ag/C catalysts for oxygen reduction and borohydride oxidation reactions in alkaline media, for potential applications in fuel cells
(2016) Energy, 101, pp. 79-90.

<https://doi.org/10.1016/j.energy.2016.02.003>

ABSTRACT: Carbon-supported silver nanoparticles (Ag:NPs/C) were synthesized by gamma irradiation-induced reduction method using the poly(vinyl alcohol) or poly(vinyl alcohol)/chitosan polymer as stabilizer. Prepared samples were characterized using transmission electron microscopy and X-ray diffractometry. Subsequently, Ag:NPs/C were studied using rotating disc and rotating ring disc method as electrocatalysts for ORR (oxygen reduction reaction) and BOR (borohydride oxidation reaction) for potential application in alkaline fuel cells. The synthesis method used herein offers simple and fast approach for catalytic ink preparation, since the ink is prepared in one-step radiation process, simultaneously with Ag⁺ ions reduction. Very high and stable catalytic efficiency toward ORR via 4e⁻ path was evidenced during 4000 square pulse polarization cycles. BOR, accompanied with the simultaneous borohydride ion hydrolysis, was found to proceed at the oxidized Ag surface. © 2016 Elsevier Ltd.

Bubanja, I.N., Maćešić, S., Ivanović-Šašić, A., Čupić, Ž., Anić, S., Kolar-Anić, Lj.

Intermittent chaos in the Bray-Liebhafsky oscillator. Temperature dependence
(2016) Physical Chemistry Chemical Physics, 18 (14), pp. 9770-9778.

<https://doi.org/10.1039/c6cp00759g>

ABSTRACT: Intermittent oscillations as a chaotic mixture of large amplitude relaxation oscillations, grouped in bursts and small-amplitude sinusoidal ones or even quiescent parts between them known as gaps, were found and examined in the Bray-Liebhafsky (BL) reaction performed in CSTR under controlled temperature variations. They were obtained in a narrow temperature range from 61.0°C to 63.1°C, where 61.0°C is the critical temperature for burst emergence from the stable steady state and 63.1°C is the critical temperature for gap emergence from regular oscillations. Since intermittencies appear gradually from the regular oscillatory state, and no hysteresis was obtained with decreasing/increasing temperature in the vicinity of these two bifurcations, a linear relationship between $(\tau_B/\tau)^2$ and $(\tau_G/\tau)^2$ (where τ_B , τ_G and τ denotes duration of bursts, gaps, and whole experiment, respectively), as a function of the temperature as the control parameter, was expected and obtained. Although these intermittent oscillations are chaotic with respect to the lengths of individual gaps as well as bursts, their deterministic behavior related to temperature was additionally established. Thus, the number of bursts or gaps per unit of time (N_B/τ and N_G/τ) has the form of a normal distribution function over the temperature range in the region where intermittencies are obtained. Temperature dependence of the Lyapunov exponents was also described by a function of the normal distribution form. Hence, we established some regularities in the chaotic behavior of intermittent oscillations that are common in life but difficult for determinations. © the Owner Societies 2016.

Savovic, J., Stoiljkovic, M., Kuzmanovic, M., Momcilovic, M., Ciganovic, J., Rankovic, D., Zivkovic, S., Trtica, M.
The feasibility of TEA CO₂ laser-induced plasma for spectrochemical analysis of geological samples in simulated Martian conditions
(2016) *Spectrochimica Acta - Part B Atomic Spectroscopy*, 118, pp. 127-136.

<https://doi.org/10.1016/j.sab.2016.02.020>

ABSTRACT: The present work studies the possibility of using pulsed Transversely Excited Atmospheric (TEA) carbon dioxide laser as an energy source for laser-induced breakdown spectroscopy (LIBS) analysis of rocks under simulated Martian atmospheric conditions. Irradiation of a basaltic rock sample with the laser intensity of 56 MW cm⁻², in carbon-dioxide gas at a pressure of 9 mbar, created target plasma with favorable conditions for excitation of all elements usually found in geological samples. Detection limits of minor constituents (Ba, Cr, Cu, Mn, Ni, Sr, V, and Zr) were in the 3 ppm-30 ppm range depending on the element. The precision varied between 5% and 25% for concentration levels of 1% to 10 ppm, respectively. Generally, the proposed relatively simple TEA CO₂ laser-LIBS system provides good sensitivity for geological studies under reduced CO₂ pressure. © 2016 Elsevier B.V. All rights reserved.

Ležaić, A.J., Bajuk-Bogdanović, D., Radoičić, M., Mirsky, V.M., Ciric-Marjanovic, G.
Influence of synthetic conditions on the structure and electrical properties of nanofibrous polyanilines and their nanofibrous carbonized forms
(2016) *Synthetic Metals*, 214, pp. 35-44.

<https://doi.org/10.1016/j.synthmet.2016.01.015>

ABSTRACT: Nanofibrous polyanilines (PANIs) were synthesized by several oxidative polymerization pathways that have in common the presence of excess oxidant(s) (ammonium peroxydisulfate and its mixture with hydrogen peroxide), the absence of added acid, and the absence of external template (self-assembly process). Conducting forms of the synthesized PANI nanofibers (re)doped with various acids were further used as precursors for carbonization process to obtain nanofibrous carbonaceous materials (Carb-PANIs). Morphology, molecular structure, surface properties and electrical characteristics of PANI nanofibrous precursors and their carbonized counterparts were studied by scanning electron microscopy, Raman spectroscopy, by measurements of ζ-potential and determination of isoelectric points, as well as by measurements of electrical conductivity. © 2016 Elsevier B.V. All rights reserved.

Matović, L.L., Vukelić, N.S., Jovanović, U.D., Kumrić, K.R., Krstić, J.B., Babić, B.M., Dukić, A.B.
Mechanochemically improved surface properties of activated carbon cloth for the removal of As(V) from aqueous solutions
(2016) *Arabian Journal of Chemistry*, . Article in Press.

<https://doi.org/10.1016/j.arabjc.2016.07.004>

ABSTRACT: Modified activated carbon cloth is prepared by mechanochemical modification of viscose rayon carbon cloth. The effects of different milling atmospheres, in the air and inert conditions, were investigated. Changes in kind and number of acidic and basic surface groups on the surface of activated carbon cloth, upon modification, as well as before and after the sorption of arsenic were determined. Higher number of basic groups responsible for the removal of arsenic ions was achieved by modification under inert conditions. Breakage and collapse of cylindrical fibers, decrease of particle sizes, change in the shape and consistency of the particles, as well as increase of microstructural disorder i.e. the loss of turbostratic structure occurred upon milling. pHPZC values increased from 4.46 to 5.04 and 5.77 after the air and inert milling, respectively. Adsorption followed pseudo second order kinetics with chemisorption as rate-controlling step. Langmuir isotherm best fit the equilibrium data and maximum adsorption capacity is 5.5mgg⁻¹ at a pH value close to 7.0, typical for groundwater. The mechanism of arsenic adsorption onto activated carbon cloth milled in inert atmosphere involved electrostatic and dispersive interactions between arsenic ions and carbon particles in wide pH range (from 2 to 10). © 2016 The Authors.

Petković, M., Ristić, M., Etinski, M.
Stability and Anharmonic N-H Stretching Frequencies of 1-Methylthymine Dimers: Hydrogen Bonding versus π -Stacking
(2016) Journal of Physical Chemistry A, 120 (9), pp. 1536-1544.

<https://doi.org/10.1021/acs.jpca.5b09946>

ABSTRACT: Stability of three hydrogen-bonded and six stacked 1-methylthymine (1 mT) dimers was studied with the DFT-D3 method at various temperatures. It was demonstrated that the stacked dimers are slightly less stable than the hydrogen-bonded counterparts. Existence of T-shaped dimers is addressed. Anharmonic couplings that involve N-H stretching modes of the nine species are studied. Surprisingly, we find that N-H stretching modes of the two 1 mT molecules are significantly coupled in four stacked dimers. The presented results shed light on existence of strong mode couplings between the two N-H stretching modes in stacked aromatic species. Our calculations support the proposal (J. Phys. Chem. A 2011, 115, 9429-9439) that presence of several dimers is responsible for appearance of wide and structured bands in 1 mT homodimers' jet-cooled spectra above 2900 cm⁻¹. © 2016 American Chemical Society.

Holclajtner-Antunović, I., Stojanović-Marić, M., Bajuk-Bogdanović, D., Žikić, R., Uskoković-Marković, S.
Multi-analytical study of techniques and palettes of wall paintings of the monastery of Žiča, Serbia
(2016) Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy, 156, pp. 78-88.

<https://doi.org/10.1016/j.saa.2015.11.031>

ABSTRACT: The present multi-analytical study concentrates on establishing the painting techniques and the identity of the wall painting materials used by the artists from the 13th and 14th centuries to decorate the Žiča monastery, Serbia. For this purpose, we

demonstrate that micro-Raman spectroscopy is an efficient, non-destructive method with high spatial resolution which gives molecular and crystal structural information of a wide variety of both inorganic and organic materials. It is shown that elementary composition revealed through scanning electron microscopy with energy dispersive X-ray spectroscopy and energy dispersive X-ray fluorescence spectroscopy is necessary in some cases to confirm the identity of pigments and binders identified by micro-Raman spectroscopy. It was found that a fresco technique, in combination with mainly natural earth pigments such as red ochre, yellow ochre and green earth, was used. Expensive natural pigment lapis lazuli was exclusively used for obtaining blue colour while pure vermilion was used by the artists from the first period of decorations at the beginning of the 13th century. A mixture of pigments was used for attaining different colour shades. For the gilding of saint's haloes, thin golden foil was deposited over the tin sheet. In order to get a desirable optical and aesthetical impression, the metallic leaves were deposited over the yellow ochre preparatory layer. Deposits of gypsum on wall paintings as well as traces of weddellite are degradation products formed as a result of exposing wall paintings to environmental conditions. © 2015 Elsevier B.V.

Etinski, M., Petković, M., Ristić, M.M.
A quantum-chemical study of the chlorophyll phosphorescence spectrum: Electron-vibrational coupling and coordination effects
(2016) *Chemical Physics Letters*, 647, pp. 139-144.

<https://doi.org/10.1016/j.cplett.2016.01.044>

ABSTRACT: The lowest triplet state and phosphorescence spectra of tetra-, penta- and hexacoordinated chlorophylls a, b and d were investigated by density functional theory and multimode harmonic approximation. We find good agreement between computed and experimental energies of the triplet state. Vibrational modes sensitive to coordination were identified. The simulated and experimental spectra are in reasonably good agreement. Comparing high-resolution simulated fluorescence and phosphorescence spectra we support an observation of Hartzler et al. (2014) [14] that the same vibrational modes govern lineshapes of phosphorescence and fluorescence spectra, although with different coupling strengths. © 2016 Elsevier B.V. All rights reserved.

Morina, F., Takahama, U., Mojović, M., Popović-Bijelić, A., Veljović-Jovanović, S.
Formation of stable radicals in catechin/nitrous acid systems: Participation of dinitrosocatechin
(2016) *Food Chemistry*, 194, pp. 1116-1122.

<https://doi.org/10.1016/j.foodchem.2015.08.081>

ABSTRACT: Catechins are transformed into dinitrosocatechins (diNOcats) and then oxidized to the quinones by salivary nitrite under conditions simulating the stomach. This manuscript deals with formation of stable radicals in the NO group of diNOcat during nitrite-induced oxidation of (+)-catechin and diNOcat at pH 2. We postulated two mechanisms for the stable radical formation; one is nitrous acid-induced oxidation of diNOcat in the A-ring, and the other intermolecular charge transfer from the A-ring of diNOcat and/or diNOcat quinone to the quinone moiety of the B-ring of diNOcat quinone. In addition, an unstable phenoxyl

radical, which might be transformed into quinone, was also produced, accompanying the formation of the stable radical on the NO group. Taking the above results into account, we mainly focus on the adverse effects of the radicals and quinone, which may be produced from (+)-catechin in the stomach under the conditions of high salivary nitrite concentrations. © 2015 Elsevier B.V. All rights reserved.

Janković, B.

On-line pyrolysis kinetics of swine manure solid samples collected from rearing farm: Pyrolytic behavior in dynamic heating mode (2016) *Journal of Thermal Analysis and Calorimetry*, 123 (3), pp. 2103-2120.

<https://doi.org/10.1007/s10973-015-4717-7>

ABSTRACT: The on-line dynamic pyrolysis kinetics of swine manure solid samples was investigated in this paper. It has been found that the model which includes combined Friedman's isoconversional and multi-distributed reactivity approaches can best describe the pyrolysis process. Pyrolysis kinetics of swine manure samples proceeds through two major pyrolysis zones, where in first zone exists the kinetically complex reactions related to decompositions of hemicelluloses and fat/proteins, as well as decomposition reactions related to degradation of cellulose and lignin structures. Second zone includes the reactions attached to follow-up devolatilization and carbonization processes. It was found that identified high reaction orders represent the measure of complexity and multiplicity of the mechanism. It has been found that the change in reaction order (n) values is the result of reactions that are taking place due to the instability of products, or the secondary reactions, change in apparent activation energy, and effect of varying of the pre-exponential factor values. © 2015 Akadémiai Kiadó, Budapest, Hungary.