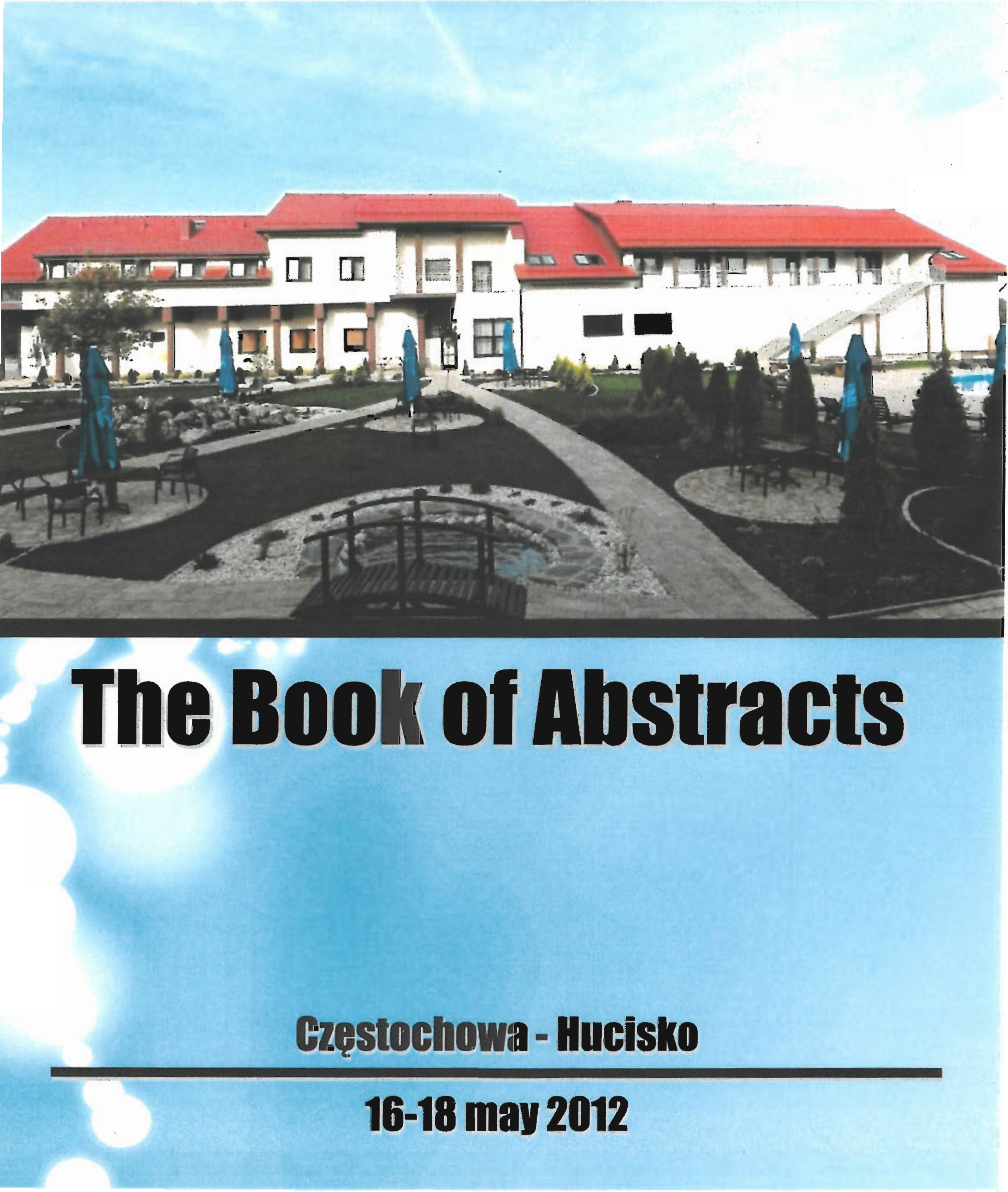
II FORUM EMR-PL



The Book of Abstracts

Częstochowa - Hucisko

16-18 may 2012

II FORUM EMR-PL

Częstochowa – Hucisko,

16-18 May 2012

UNDER THE AUSPICES OF:

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PROF. DR HAB. ENG. HENRYK DYJA, DEAN WIPMiFS PCz

WEST POMERANIAN UNIVERSITY OF TECHNOLOGY, SZCZECIN

INSTITUTE OF PHYSICS CZĘSTOCHOWA UNIVERSITY OF TECHNOLOGY

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Welcome Address

at

The Second Forum EMR-PL, Częstochowa-Hucisko, 16-18 May 2012

Professor Czesław Rudowicz

The Chairman of the Polish EMR Group

Honoured Guests, Ladies and Gentlemen:

It is a great pleasure for me, on behalf of the Council of the Polish EMR Group [PEMRG] and the Local Organising Committee, ably headed by Prof. Kazimierz Dziliński, to welcome you to the Second Forum EMR-PL organized under the auspices of the Group.

We all appreciate very much the fact that the efforts of our colleagues in Rzeszów, who had organized the First Forum EMR-PL in 2010, especially Dr Irenusz Stefaniuk, have been continued by our colleagues from Częstochowa. I am pleased that the Institute of Physics, Częstochowa University of Technology, has undertaken to host this Forum. The secluded and beautiful location in Hucisko may be especially conducive for fruitful discussions. I believe that this Forum may play an important role in enhancing the importance of the EMR and related research carried out in Poland.

Continuing with the spirit of the previous RAMIS conferences and the First Forum EMR-PL, this Forum is open to all participants involved in EMR basic research and applications. The main aims are to bring together as many EMR (EPR/ESR & FMR/AFMR) spectroscopists working in Poland as possible and to promote and facilitate collaboration among the Polish EMR community. I am confident that the scientific program of the II Forum EMR-PL will satisfy most of the participants. I am also sure the Forum will help uniting EMR spectroscopists from all over the country and provide a starting point for new collaborative links. As usual the most important part of any conference is to meet fellow researchers. So hopefully the opportunity for personal discussions provided by this meeting will be fully utilized.

I would also like to invite all participants to join us at the General Meeting of the Polish EMR Group, to be held during the Forum. A whole range of topics of interest to the whole EMR community will be discussed, among others, the venue for future Forum, the new structure of the PEMRG website, and the new composition of the PEMRG Council. It is important that the PEMRG website should represent best our community within Poland and to the outside world as well as serve as an efficient communication channel. Please note that it is crucial that all EMR centres in Poland are well represented at the PEMRG website. Hence, the role of the representatives from each centre should be strengthened. This General Meeting will be also an opportunity to select the best persons, who will coordinate efforts to secure a prosperous future for the Polish EMR community. Hence, your votes and opinions are of great importance as they may shape the future course of events. To facilitate the General Meeting, basic relevant materials have been included in the Book of Abstract.

My sincere thanks go to all members of the Local Organising Committee, especially Prof. Kazimierz Dziliński, the LOC Chairman, Prof. Ryszard Hrabański, the LOC Vice-Chairman and Dr. Konrad Gruszka, the LOC Secretary, for their dedicated work to make the II Forum EMR-PL a successful meeting. Support from the Scientific Committee in nominating the invited speakers and maintaining the high standard of this Forum is also much appreciated. I wish to express our gratitude to all sponsors for their financial support: the Dean of the Faculty of Materials Processing Technology and Applied Physics, Częstochowa University of Technology, and the Institute of Physics, the West Pomeranian University of Technology in Szczecin. Thanks are due to all speakers and participants, who by attending this meeting have helped to make this Forum a great success.

May I wish you all an enjoyable and stimulating experience at the II Forum EMR-PL.

Thank you.

Czesław Rudowicz

LECTURES

ELECTRON PARAMAGNETIC RESONANCE (EPR) STUDY OF THE THERMALLY GENERATED RADICALS IN PHOSPHORYLATED STARCH

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Modification of the starch by incorporation of phosphorus into its structure as terminal or bridging PO_4^{3-} groups changes functional properties of this biopolymer [1]. The positive consequences of the chemical modification consist on alteration of gelatinization and pasting behavior, better stability during freeze-thaw cycles and increasing content of resistant starch exhibiting anti-diabetic and anti-cancer properties. It was shown by us that, besides these improvements of the starch properties important for application in food industry, phosphorylation causes weakening of the starch structure which results in increasing tendency to thermal degradation with formation of radicals [2-4].

The number of radicals generated thermally in phosphorylated starch of various botanic origin (potato and maize) or containing different amount of amylose (Hylon VII and waxy maize) was determined by means of quantitative EPR measurements. Two types of radicals: stable and short-living ones, with unpaired electron localized at one of carbon atoms in glucose unit are generated thermally in phosphorylated starch in the temperature range commonly used for processing food. The number of short-living radicals, stabilized by a N-*tert*-Butyl-α-phenylnitrone (PBN) spin trap, is of two orders of magnitude greater than that of the stable radical species generated at the same temperature. Hydrolysis and phosphorylation strongly increase the number of stable radicals while pretreatment of the starch with high hydrostatic pressure diminishes their amount. The EPR spectra of stable radicals consist of two components, single line and another one with hyperfine structure, indicating interaction of unpaired electron with neighboring hydrogen atom. The EPR spectra of the spin trap adducts with short-living radicals contain three components differing in their dynamic properties depending on localization in zones of various degree of crystallinity. The existence of these components reflects accurately the "architecture" of the starch granules containing amorphous and semi-crystalline shells.

The obtained results proved that the EPR parameters of radicals - both stable and short-living ones - generated thermally in starch may serve as sensitive indicators of changes occurring in the starch structure upon chemical (hydrolysis, phosphorylation) and physical (heating, high pressure) treatments. The influence of botanic origin and different amylose to amylopectin ratio in the starch structure on number of radicals and their properties is also evidenced.

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HIGHER-ORDER FIELD DEPENDENT TERMS IN SPIN HAMILTONIANS FOR TRANSITION IONS – IMPLICATIONS FOR HIGH-MAGNETIC FIELD AND HIGH-FREQUENCY EMR MEASUREMENTS

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This presentation provides theoretical background of the higher-order field-dependent (HOFD) terms in the generalized spin Hamiltonians for transition ions and an overview of current status of the HOFD terms studies. Potential implications of the HOFD terms for measurements utilizing high magnetic fields, including electron magnetic resonance (EMR) techniques, will be discussed. By the HOFD terms we mean the higher-rank terms in the electronic (S) and nuclear spin (I), which are non-linear in the magnetic field (B), e.g. terms of the type: B2S2, B3S, B5S or B2I2, B3I, B5I. The HOFD terms have so far been barely explored in experimental characterization of materials containing transition-metal (3dN) and rare-earth (4fN) ions. However, in view of recent advances in high-magnetic field techniques, i.e. the high-magnetic field measurements (HMM) of magnetic properties as well as the high-magnetic field/high-frequency EMR (HMF-EMR) measurements of spectroscopic properties, studies of the HOFD terms become timely and of prime scientific significance. The high B values used in HMM and HMF-EMR make the HOFD terms with higher powers in B significant in comparison with the usual linear Zeeman term B.g.S, even if the associated parameters may be small.

The preliminary results of our feasibility study of the role of the HOFD terms in HMM and HMF-EMR characterization of magnetic, optoelectronic, and laser materials based on the transition ions will be presented. HMF-EMR offers several advantages, e.g. unprecedented spectral resolution and detection of new phenomena and spectral features, not detectable in the conventional X- or Q-band EMR. HMF-EMR techniques are especially important for the 3d4 (V+, Cr2+, Mn3+, Fe4+) and 3d6 (Mn+, Fe2+, Co3+, Ni4+) ions with the spin S = 2 ground state exhibiting very large zero field splitting. The key issues are: analysis of the mechanisms contributing to the HOFD parameters; theoretical prediction of the forms of the HOFD terms for various symmetry cases; role of the HOFD terms in the low- and high-field EMR; development of the computer simulation and fitting programs incorporating the HOFD terms; interpretation of HMF-EMR spectra including the HOFD parameters. Potential applications to various ion-host systems are envisaged, e.g., Fe2+:CdPS3, Fe2+/Fe3+:LiNbO3, In:Cr: GaAs, Mn12-acetate, and Cr2+/Cr3+:forsterite. This study may provide solid foundations for future large scale project aimed at direct applications of the HOFD terms for improving spectroscopic characterization of technologically important materials and advancement of our knowledge in the emerging area.

EPR STUDIES OF OXYGEN ACTIVATION PATHWAYS ON TRANSITION-METAL IONS

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The paramagnetic mononuclear transition metal-O_2 adducts are the key species involved in various important homo- and heterogeneous catalytic systems including enzymatic processes. Both side-on (□^{2}) and end-on (□^{1}) metal-superoxo (O_2^-) and side-on (□^{2}) metal-peroxo (O_2^{2-}) complexes have been synthesized and characterized by spectroscopic, XRD, and computational methods. Among various techniques applied for such investigations, EPR spectroscopy has been widely used due to the paramagnetic nature of the superoxo species. Yet, quantitative molecular interpretation of the corresponding EPR parameters (***g*** and $A(^{17}O)$ tensors) is not a trivial task, taking into account an intricate nature of the magnetic interactions within the metal-O_2 unit and its nearest molecular environment, as well as the constraints imposed by rather common low local symmetry of the enzymatic and zeolitic environments.

This contribution deals with the activation of O_2 on nickel(I) and copper(I) □-diketiminato biomimetic complexes and their structural analogues dispersed inside the nanopores of the ZSM-5 zeolite, which can be regarded as a heterogeneous mimetic system (zeozyme) for metal-bearing enzymes. The side-on coordination of the nickel-superoxo adduct in ZSM-5 was ascertained by detailed analysis of the EPR spectra of both $^{16}O_2$ and $^{17}O_2$ species supported by computer simulations of the spectra and relativistic DFT calculations of the EPR signatures [1]. Molecular analysis of the ***g*** and $A(^{17}O)$ tensors ($g_{xx} = 2.0635$, $g_{yy} = 2.0884$, $g_{zz} = 2.1675$, and $|A_{xx}| \sim 1.0$ mT, $|A_{yy}| = 5.67$ mT, $|A_{zz}| \sim 1.3$ mT) and quantum chemical modelling revealed an unusual electronic and magnetic structure of the observed adducts. Similar geometry and spectral parameters were obtained for the □-diketiminato-Ni(II)-superoxide. The ground state of copper(I)-based complexes was singlet, although the binding geometry was analogous to that of nickel-superoxide adduct. By means of the ETS-NOCV population analysis, three distinct orbital channels (associated with □
incongruent charge and spin density flows within the metal–O_2^- unit were identified. In particular, the
□on configuration. While for the
$3d^9$ state the □-density contour, its role was negligible for the $3d^{10}$ state. The nature of the ***g*** tensor was rationalized in terms of the contributions due to the magnetic couplings of the relevant molecular orbitals that control the ***g*** tensor anisotropy.

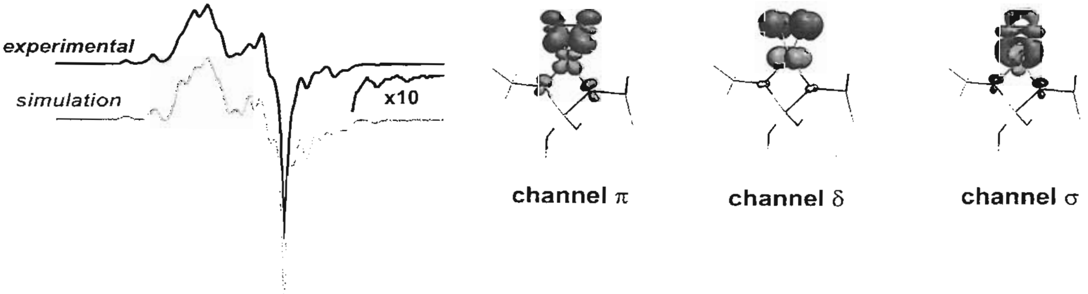

Figure 1. EPR spectrum of Ni(II)–O_2^- adduct in ZSM-5 zeolite and calculated orbital channels of charge and spin flow between O_2 and Ni(I) upon interaction

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QASI-TWO DIMENSIONAL FERROMAGNETISM IN CR2TE3 CRYSTALS

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Chromium chalcogenides are alternative, with respect to diluted magnetic semiconductors, materials for the spintronic devices production. The Cr-chalcogenides reveal hexagonal AsNi - type crystal structure . Crystals of this type have attracted considerable attention due to layered structure what determines peculiar electrical and magnetic properties of such materials (e.g. new FeAs type of high temperature superconductivity [1]). Moreover, in Cr-chalcogenides the manipulation with a number or an arrangement of Cr –vacancies as well as the substitution of metal ions lead to different classes of crystals of the Cr_{1-x} (Te, S, Se) type with a wide range of many fascinating electrical and magnetic properties. Crystals of these compounds such as $Cr_{1-x}Te$ exhibit antiferromagnetism, non-collinear spin structures or itinerant electron magnetism [2]. The substitution of Cr atoms with Ti or V creates new properties as spin-glass [3, 4].

Some chalcogenides (as Cr_{1-x} Te or Cr_{1-x} Se) exhibit metastable zinc-blende structure [5], which allows for the growth of the zinc-blende solid solution semiconductor compounds with properties of diluted magnetic semiconductors eg. CrMnTe [6], ZnCrTe [7], ZnCrSe [8]. Recently, Ko and Blamire [9] reported room-temperature ferromagnetism in CrCdTe crystals.

In present paper we investigate the $Cr_{1-x}Te$ alloy which has been prepared by melting of the powdered Cr_2Te_3 (Alfa Aesar, 99.5%) in evacuated quartz ampoule at temperature 1600 K.

The ESR spectra were recorded using the X-band (9.4 GHz) spectrometer provided with gas nitrogen cryostat (Oxford Instrument). The shape of the EPR line depends strongly on the temperature. In the vicinity of the room temperature the lines become very wide and weak or disappear completely. At lower temperatures the shape of the lines approaches the Lorentz function. The asymmetry of the lines is also visible what can be attributed to the strong exchange interactions as well as to the semimetal electrical conductivity. Above the room temperature the shape of the spectra is characteristic for paramagnetic phase. Above the room temperature lines are stable with respect to their position as well as to the width and they are relatively narrow.

The crystal structure of the $Cr_{1-x}Te$ suggests two-dimensional magnetism in the plane perpendicular to c axis. It is consistent with the temperature dependence of the g factor and the EPR lines width observed.

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ELECTRON PARAMAGNETIC RESONANCE (EPR) SPECTROSCOPY CHARACTERIZATION OF WHEAT GRAINS FROM PLANTS OF DIFFERENT WATER STRESS TOLERANCE

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Grains of wheat genotypes with different tolerance to drought-stress were investigated by electron paramagnetic resonance spectroscopy (EPR). Various types of paramagnetic centres, including transition metal ions (Mn, Fe) and different types of stable radicals were found in grains of all investigated plants. Metal ions and semiquinone radical species prevailed in outer part of grains, whereas stable carbohydrate radicals were present mainly in their inner parts. The concentrations of both types of radicals, semiquinone and carbohydrate, were significantly higher in the grains originating from more sensitive genotypes. Metal ions content exhibited the similar dependence. Detailed EPR analysis of carbohydrate radicals allowed determining various types of these species, stabilized by starch and/or soluble carbohydrates. The results of EPR analyses were compared with data on carbohydrate content in grains obtained by biochemical analyses. The latter confirmed that soluble sugars and starch were present mostly in insides of grains. Moreover, the higher amount of sucrose together with lower content of starch was characteristic for grains of plants selected as stress tolerant, what was in line with the nature of carbohydrate radicals recorded for these genotypes. The differences in the character and amount of carbohydrate radicals present in the grains of wheat with various tolerance towards stress could be helpful in the search of biomarkers of the drought-stress resistance of wheat genotypes.

HYPERFINE SUBLEVEL CORRELATION SPECTROSCOPY – A POWERFULL TOOL FOR INVESTIGATION OF SURFACE PARAMAGNETIC CENTERS

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For surface transition-metal ion (TMI) and molecular complexes hyperfine (hf) interactions between paramagnetic ions and surrounding ligands carry important information about the structure of the complex and the distribution of electron spin density. The dipolar hf interactions can be regarded as a measure of the distance between the metal centers and ligands therefore, in many cases, they contain unique information about the coordination geometry of the investigated paramagnetic species. This interaction is often approximated by a classical magnetic dipole-dipole interaction. The degree of overlap between the TMI and ligand orbitals can be derived from the distribution of the spin density related to the hyperfine constants. Unfortunately, hf interactions between the TMI and the distant ligands (or surface functional groups) are often very weak and contribute only to inhomogeneous broadening of the classic CW-EPR signal. However, these weak hf interactions can be resolved by pulse EPR techniques such as electron spin echo modulation (ESEM). This method has been proven to be a powerful tool in the investigations of disordered materials such as metal oxide surfaces and biological systems. One of the variants of ESEM experiment is a hyperfine sublevel correlation (HYSCORE) spectroscopy, a 2D experiment where correlation of the nuclear frequencies in one electron spin (m_S) manifold to nuclear frequencies in the other manifold is created by means of a mixing π pulse [1]. Application of the pulse sequence $t_{\square}$ $t_{\square}$ echo allows for measuring HYSCORE spectra capable of resolving the hyperfine couplings even below 5 MHz.

In this contribution, three examples of application of HYSCORE to study the surface complexes are shown. In spectra simulations EasySpin program [2] was used. In the case of Cu-doped nanoporous $12CaO\cdot7Al_2O_3$ (mayenite), the ^{27}Al quadruple interaction provided evidence for the incorporation of Cu^{2+} ions into mayenite framework [3]. Superhyperfine interaction of the Cu^{2+} ions with proximal ($d_{Cu-OH} = 2.4$ Å) and distal ($d_{Cu-OH} = 5.0$ Å) OH^- anions was resolved by means of ^1H HYSCORE spectra, providing an evidence for localization of extraframework OH^- ions inside the nano-cavities. In the case of nickel ions dispersed within the ZSM-5 framework, HYSCORE spectroscopy was used for studying the interaction of Ni^I/Ni^{II} with ^{13}CO and $^{14/15}NO$ adsorbates. Due to spin pairing mechanism and partial oxidation of NO, the nitrogen hf interaction of the Ni(II)-NO adduct has never been measured so far. Our results (Fig. 1) showed formation of two types of such adducts connected with topology of the zeolitic framework, with the following spin-Hamiltonian parameters: $A_{xx} = 9$ (7) MHz, $A_{yy} = 6$ (5) MHz, $A_{xx} = 14$ (9) MHz, and $e^2/qQ = 3.8$ (3.0) MHz, h = 0.0 (0,1), and small non-coincidence (10°) of hyperfine and quadruple tensors in the xz plane.

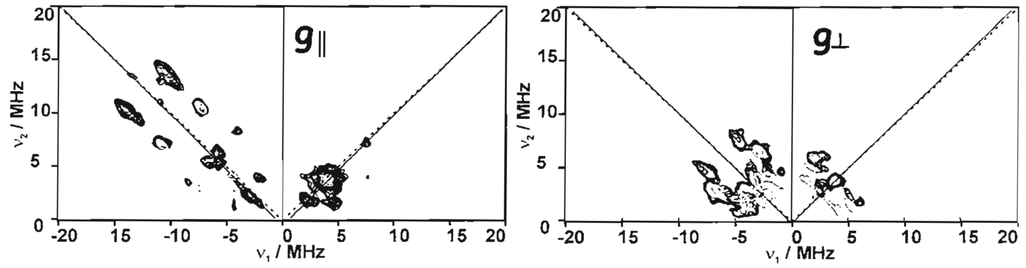

Figure 1. HYSCORE experimental and simulated spectra of Ni(II)-NO adduct in ZSM-5 zeolite

Acknowledgment: This study was supported by the grant from Ministry of Science and Higher Education of Poland under research project no. IP2011 041871.

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PLATELET ACTIVATION INDUCED BY THE GLASS SURFACE MONITORED BY SPIN PROBE METHOD.

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Alterations in the membrane organization of human blood platelets caused by the glass surface were analyzed by electron spin resonance measurements. Literature studies demonstrate that surface activation of platelets on glass is associated with elevation of cytosolic calcium, protein kinase C translocation, and talin redistribution. Surface-activated platelets respond to the action of agonists and mobilize ionized calcium [1].

The ESR spectra of the 5 doxylstearic acid labeled platelets were recorded as a function of time (t=0 when labeled platelets were placed to the glass capillary). The relative position of the maxima or minima were used to determine the outer and inner hyperfine splitting ($T_{\parallel}$ and $T_{\perp}$. The inner and outer hyperfine splitting values permit to calculate an order parameter of the membrane lipids according to the equation :

$$S = \left(\frac{T_{\parallel}-T_{\perp}}{T_{zz}-T_{xx}}\right)\left(\frac{a_N}{a_N'}\right) \qquad \text{where} \qquad a_N = \frac{1}{3}(T_{zz}+2T_{xx}); \qquad a_N' = \frac{1}{3}(T_{\parallel}+2T_{\perp})$$

Activation of platelets is accompanied by an increase of the membrane lipid rigidity from the value for resting cells around 0.62 to the maximal value 0.72 which is reached after 15 min. contacting with a glass surface. Fig. 1 illustrates the kinetics of platelets activation.

This effect seems to be indirect in nature and is mediated by altered membrane protein interactions. As it has been shown that an increased membrane lipid rigidity leads to a greater exposure of membrane proteins, including receptors, this might facilitate a formation of molecular linkages between neighboring platelets.

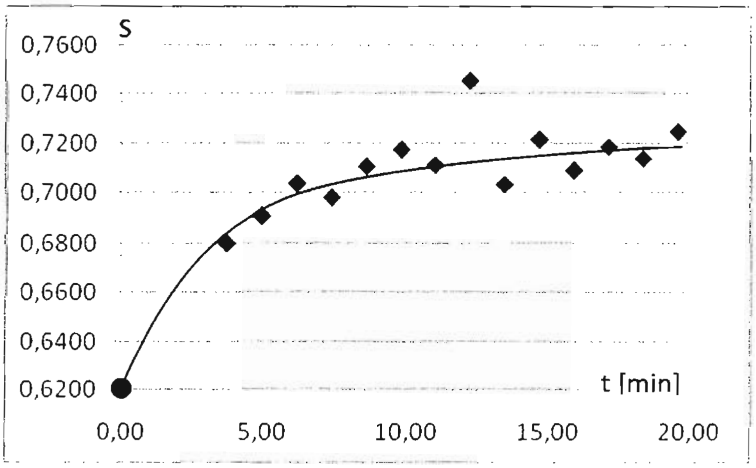

Fig.1 The changes of the membrane lipids order parameter during platelet activation on glass as a function of contact time.

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SPIN ECHOES IN EXCHANGE-COUPLED SYSTEMS

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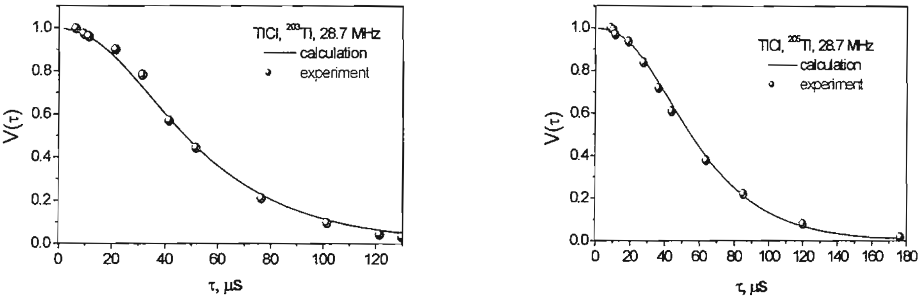
Spin echo technique is one of the most powerful methods for the investigations of the quantum dynamics of the two- and multi-level systems [1-7]. We studied Hahn echo decay in powder thallium chloride TlCl, which comprises unlike spins of two interacting ^{203}Tl and ^{205}Tl isotopes. All ^{203}Tl and ^{205}Tl NMR measurements were carried out at room temperature. The contribution of the dipole-dipole coupling of nuclear spins to the second moment of thallium resonances, calculated using Van Vleck formula [1], are 1,21 kHz^2 for ^{203}Tl and 1,69 kHz^2 for ^{205}Tl NMR, respectively, and are much smaller than the experimental measured values (16,1 kHz^2 for ^{203}Tl and 10,24 kHz^2 for ^{205}Tl NMR, respectively). Thus one concludes that the experimental second moments are predominantly determined by the indirect exchange coupling of thallium nuclei.



(a) (b)

Figure. The decay of Hahn echo signals of (a) ^{203}Tl and (b) ^{205}Tl nuclei in polycrystalline TlCl at a resonance frequency $\nu = 28.7 MHz$. The circles are the experimental data, the solid line is the result of calculation

The multi-particle character of interaction Hamiltonian for the system consisting of two type of nuclei ^{203}Tl and ^{205}Tl does not allow one to calculate explicitly the spin echo decay. Therefore, we present a simple model to calculate the Hahn echo decay of the exchange-coupled nuclear spins in solids. We assume that fluctuations of the NMR resonance frequency are connected with exchange coupling among resonant and off-resonant nuclei. Satisfactory agreement between the calculated and experimentally observed echo decay of the exchange-coupled spins of ^{203}Tl and ^{205}Tl isotopes in thallium chloride TlCl is obtained (figure).

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QUANTUM LOCALIZATION IN NANOCARBONS

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We present results of Electron Paramagnetic Resonance (EPR) of Multi-Walled Carbon Nanotubes (MWCNTs) bundles. It has been shown that with lowering of the temperature g-factor shifts from an average of $g_{\|}$ and $g_{\perp}$ to the value close to $g_{\perp}$ of graphite.

To explain observed changes the model of spin localization applied previously to different nanocarbons is used:

- electron transfer in C_{60} fullerites leads to the formation of superconducting behavior of A_3C_{60} fullerides (A stands for potassium or rubidium atoms). EPR technique has been applied to show the appearance and evolution of spins while superconductivity was demonstrated by Magnetically Modulated Microwave Absorption (MMMA) method [1],

- strong localization of spins at low temperature region within the nanographitic units (NGU) of activated carbon fibers (ACF) was described by the model which is a fusion of two approaches: Curie law behavior studied by EPR and granular metal model. NGU are linked structurally to constitute porous system. In such systems conducting properties strongly depend on potential barriers between NGU [2].

The g-shift observed for MWCNTs is a clear evidence of the localization of electrons at the single nanotubes, as diffusion (hopping) between the neighbouring ones becomes suppressed with the disappearance of thermal excitations. When localized at single nanotubes, electrons are allowed only to move perpendicularly to the nanotube what results in the presented g-factor value shift. This behaviour points at the possibility of treating the MWCNTs bundles as granular systems with potential barriers for hopping of electrons, what seems to be a common phenomenon in carbon nanostructures [2].

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EPR SPECTROSCOPY OF BORATE GLASSES, DOPED WITH CHROMIUM

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Electron paramagnetic resonance (EPR) spectra of the series borate glasses with $Li_2B_4O_7$:Cr, $KLiB_4O_7$:Cr, CaB_4O_7:Cr, and $LiCaBO_3$:Cr compositions were investigated at $T = 300$ K. The investigated glasses of high optical quality were obtained in the air from corresponding polycrystalline compounds using standard glass synthesis and technological conditions developed by authors of this work. The carbonates (Li_2CO_3, K_2CO_3, and $CaCO_3$) and boric acid (H_3BO_3) of high chemical purity were used for solid-state synthesis of the polycrystalline compounds. The Cr impurity was added as Cr_2O_3 oxide in amounts 0.4 and 1.6 mol. % for $Li_2B_4O_7$:Cr and $KLiB_4O_7$:Cr compounds and 0.5 and 1.0 mol. % for CaB_4O_7:Cr and $LiCaBO_3$:Cr compounds. Synthesis of the $Li_2B_4O_7$:Cr, $KLiB_4O_7$:Cr, CaB_4O_7:Cr, and $LiCaBO_3$:Cr polycrystalline compounds were carried out using solid-state reactions with multi-step heating.

The X-band EPR spectroscopy shows that the Cr impurity is incorporated in the borate glass network as isolated Cr^{3+} centers and Cr^{3+} pairs coupled by magnetic dipolar and exchange interactions. All Cr-related EPR signals in the investigated glasses have been identify and interpreted. The EPR spectra parameters of both Cr^{3+} and $Cr^{3+} - Cr^{3+}$ centers in the glasses with $Li_2B_4O_7$:Cr, $KLiB_4O_7$:Cr, CaB_4O_7:Cr, and $LiCaBO_3$:Cr compositions were measured and analyzed.

The results of EPR spectroscopy show good correlation with results of optical spectroscopy of the investigated borate glasses. Based on the results of spectroscopic and X-ray diffraction investigations the local structure of the Cr^{3+} centers in the network of $Li_2B_4O_7$, $KLiB_4O_7$, CaB_4O_7, and $LiCaBO_3$ glasses has been proposed.

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BI- AND TETRANUCLEAR Cu(II) CARBOXYLATES. EPR AND MAGNETIC STUDIES

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Although six decades have passed since antiferromagnetic exchange and unusual Cu(II) EPR spectrum for the $[Cu(CH_3COO)_2]_2(H_2O)_2$ were discovered by Bleaney and Bowers [1], their classic foundations for the dependence of static susceptibility on isotropic exchange and for the origin of zero-field splitting of the triplet due to anisotropic exchange are still actual and provide the basis for modern experimental and theoretical studies. Diversity in the coordination modes of the carboxylic group, able to coordinate as monodentate, bidentate, monodentate-bridging and bidentate-bridging ligands, allowed to prepare a numerous copper(II) carboxylate complexes exhibiting a wide variety of the structural, magnetic and EPR properties.

This report presents our contribution to magnetochemistry and EPR spectroscopy of the Cu(II) carboxylate complexes in which both iso- and anisotropic spin-spin exchange occur.

The magnetic properties of the di- [2-4] and tetranuclear [3] Cu(II) carboxylates were analyzed in terms of different exchange pathways involving bi- [2-4] or monodentate [4, 5] carboxylic bridges. In the tetramers, the presence of one μ_4-O^{2-} or two μ_3-OH^- as well as the carboxylato bridges, gave a ferromagnetic tetrahedron, with very well resolved EPR spectra characteristic of S=2 spin state, or antiferromagnetic macrocycle, respectively [3].

In another work, Cu(II) carboxylate dimers formed the supramolecular synthons due to $\pi\cdots\pi$ stacking through 1,8-naphthalimide rings linked to the carboxylic groups in various ways, leading to diversified exchange and EPR behavior [4].

The paddle-wheel type cationic Cu(II) dimers were formed by four bidentate-bridging carboxylic groups of β-alanines, but only with Cl^- counterions, two not exactly equivalent structures were found in one unit cell and differentiated by dissimilar X-band EPR spectra corresponding to slightly different zero-field splitting parameters (D) [2].

Dinuclear Cu(II) complexes with two carboxylate ligands in a monodentate bridging mode (μ_1,μ_1) exhibited a significantly weaker antiferromagnetic exchange and much smaller zero-field splitting of the S = 1 state [4, 5] as compared to those observed for the paddle-wheel type dinuclear Cu(II) carboxylates.

X-band [2-5] and especially HF EPR [2-4] were used to study the zero-field splitting D of S=1 and 2 states due to anisotropic exchange in the di- and tetranuclear Cu(II) carboxylates of known crystal structure, allowing to determine the D^{dip} and D^{exch} contributions to D after a definitive proving that D is negative [3, 6].

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THE NEW CANCER IMAGING METHOD BY THE PROTOTYPE OF EPR SCANNER

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EPR Imaging (EPRI) has a number of biological and medical applications, among which EPRI based oxymetry is of great importance [1]. The new oxygen concentration imaging method based on direct-detected rapid scan EPR is developed and presented. The signals were recorded using sinusoidal field scan with rate 10T/s for samples of lithium phtalocyanine (LiPc). For this scan rate the magnetic field passes through the spin packet resonance in a time that is comparable relative to T_1. The EPR signal is recorded for up and down magnetic field slope. The magnetization in resonance condition for each slope directions are in dynamic equilibrium that is different for up and down slopes. This leads to difference in the signal amplitude which is T_1 – dependent and could be measured by EPR signal amplitude ratio [2]. By measuring spectra when magnetic field gradient is applied both projection of the radical density distribution and projection of the T_1 are detected. It allows to obtain projection of the oxygen concentration by using only one gradient amplitude. Additionally, decreasing of acquisition time up to hundred of milliseconds for 1D profile is possible. To apply the method the home – build imager based on rapid scan direct-detection technique was developed and constructed. The magnet mechanical rigidity support system was built from polyoxymethylene (POM), polyamide (PA6) and textolite. The main magnet is based on the Helmholtz principle with unique conical shape. The designed and made magnet system construction has the capability to pinpoint the exact space position of coils in respect to the base of magnet along the principal axes with the precision of ± 0.2mm which allows to achieve a ±10ppm magnetic field homogeneity in the 6cm×6cm×3cm region (x/y/z). The magnet generates continuously a field of max 370 G, and the gradient coils are designed to yield 10 G/cm. The preliminary test of the EPR imager was done by using 212 MHz RF and 5 kHz scan frequency.

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SPIN TRAPPING AND SCAVENGING METHODS IN BEER CHEMISTRY

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Beer is one of the world's oldest prepared beverages, possibly dating back to the early Neolithic, and is recorded in the writtenhistory of ancient Egypt and Mesopotamia [1]. This complex alcoholic beverage is made from barley (malt), hop, water and brewer's yeast, rich in nutrients (carbohydrates, amino acids, minerals, and vitamins), as well as non-nutrient components such as phenolic acids and flavonoids [2]. Beer flavor and its stability is often impaired by oxidative reactions that affect the flavor stability [3]. Some minor constituents of the beer (metal ions, sulfite, ascorbate or phenolic antioxidants) could influence oxidative properties of beer [3]. The production process also has an impact on the reaction, because mixing may introduce atmospheric oxygen, whereas a higher temperature initiate the oxidation [3].

The stability of beer flavor determine its shelf life and is the subject of the studies for many years [1-5]. During the beer oxidation short-lived radicals are formed [4. These radicals could be investigated only using spin trapping EPR techniques. The spin trapping method become the standard for breweries world-wide, especially with the phenyl-*N*-*tert*-buthylnitrone (PBN) used as the spin trap. The trap is added to a beer, which is then subjected to an accelerated oxidative stress carried out at 50-60°C in the presence of air [3].

Free radical scavenging is another method exploring EPR spectroscopy which gives more detailed data about oxidative stability of beer. Previous works [1,5] showed usefulness of DPPH scavenging in studies of ascorbate content in beer. Presented study focused on using galvinoxyl as radical to scavenge. This stable, phenolic origin radical is more selective than DPPH and is widely used in phenolic antioxidants studies in food [6].

The galvinoxyl radical was found as good indicator of antioxidant effectiveness in beer. In the reported experiments eight different beers (3 dark and 5 pale) from various from Polish and Czech breweries were studied. The efficiency of galvinoxyl radicals scavenging for all three dark beers was similar (only about 15% of the radicals remained after 1 hour) and was much higher than that for all pale beers. The properties of pale beers were much better differentiated. The best free radical scavenger from this group was Czech beer Bernard dark, 25% of radicals remained after 1 h reaction; this result placed Bernard closer to dark beers than to pale. The rest of pale beers, independently if the pasteurization was performed or not, were able to scavenge only 50% of the galvinoxyl radicals at the same time.

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MODELING EMR DATA FOR FE^{2+}(S=2) IONS IN [[2FE-2S] CLUSTER IN THE REDUCED FERREDOXIN

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Paramagnetic centers formed by transition-metal ($3d^N$) ions in various biologically important materials often exhibit orthorhombic, monoclinic, or triclinic site symmetry. For such centers intricate low symmetry aspects arise, which bear on meaningful interpretation of electron magnetic resonance (EMR) and optical spectroscopy data. Especially important class of the $3d^N$ ions consists of the non-Kramers $3d^4$ (V^+, Cr^{2+}, Mn^{3+}, Fe^{4+}) and $3d^6$ (Mn^+, Fe^{2+}, Co^{3+}, Ni^{4+}) ions exhibiting the orbital singlet ground state with the spin S = 2. Due to the very large zero field splitting (ZFS), the transitions between the spin states $|S, M_S>$ are not detectable in conventional X- or Q-band EMR. Hence, the high-magnetic field / high-frequency EMR (HMF-EMR) need to be used to observe such transitions.

The focus of this presentation is on providing an overview of the modeling techniques, which utilize structural data to enable correlation of EMR data - described by the spin Hamiltonian (SH) and optical spectroscopy data - described by the crystal field (CF) Hamiltonian. Two major techniques are (i) the microscopic spin Hamiltonian (MSH) theory that is especially useful for the $3d^4$ and $3d^6$ (S = 2) ions at tetragonal, trigonal, and orthorhombic symmetry sites [1], and (ii) the CF analysis (CFA) package [2], which includes the MSH module, and is suitable for the $3d^N$ ions at arbitrary symmetry sites in crystals. The background for model calculations of the ZFS parameters (ZFSPs) and/or crystal field parameters (CFPs) using superposition model (SPM) [2] will be also presented.

Illustrative examples of potential applications of these techniques, taken from our recent studies of the $3d^4$ and $3d^6$ (S = 2) ions in biological systems, are discussed. Preliminary microscopic modeling results for the $Fe^{2+}(3d^6)$ ions with spin S=2 in reduced rubredoxin, desulforedoxin, and related analog systems will be presented. A comparative analysis of our results with the pertinent ones obtained using various density functional theory (DFT) techniques [3,4,5] is also carried out. This analysis comprises a survey of the existing spectroscopic data including spin Hamiltonian parameters, spin-orbit coupling constants, the wavefunctions, energy levels, and mixing coefficients utilized in a given MSH technique as well as the functional basis of wavefunctions, Hamiltonian terms, and computational methods utilized in DFT calculations. Data are tabulated in a systematic way and any special conditions and/or approximation used, which bear on their reliability and compatibility, are indicated. The available results of the 'conventional' MSH techniques and those based on the DFT techniques as well as limitations inherent in these techniques are critically examined. Reinterpretation of the g-tensor principal values in reduced [2Fe-2S] cluster of iron-sulfur proteins [4,5] will be considered as a case study.

The comparative analysis enables bridging the gap between DFT and crystal-field based techniques for modeling of EMR and optical spectroscopic data. This presentation serves as a primer for experimentalists.

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EPR AND DFT STUDIES ON COMPLEXES OF O-SEMIQUINONE RADICAL ANIONS WITH DIAMAGNETIC METAL CATIONS

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Semiquinone radicals are involved in electron transfer in photosynthesis and respiration systems as well as in many biochemical processes in soils. The electron transfer can be activated through noncovalent interactions (e.g., hydrogen bonding) [1,2] as well as by metal ions acting as Lewis acids [3]. Hence, the redox quinoenzymes frequently occur in conjugation with metal cations [4].

The aim of this work was experimental (EPR) and theoretical (DFT) characterization of changes in the molecular and electronic structure of various *o*-semiquinone radicals induced by their interaction with diamagnetic metal ions (Mg^{2+}, Ca^{2+} and Pb^{2+}) in aprotic (acetonitrile) and protic (water) solvents [5-8]. The combination of EPR and DFT techniques revealed the characteristic correlations between the unpaired electron distribution (see Figure) and calculated **g** tensors for the radicals and their metal ion complexes. Furtherer theoretical studies made possible to analyze the observed **g** tensors in terms of the excited states and single atoms contributions [8].

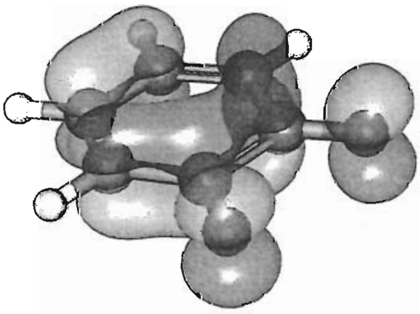

Figure: Singly occupied molecular orbital (SOMO) of the semiquinone radical derived from o-quinopne illustrating distribution of the unpaired electron.

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COMPUTER PROGRAM SPM-MC AND ITS APPLICATIONS IN EMR STUDIES OF TRANSITION IONS AT LOW SYMMETRY SITES - Fe3+ DOPED YAP CRYSTALS

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In this paper we present an extended version of the computer program SPM-MC [1] designed for modeling of the spectroscopic and structural properties of transition ions at low symmetry sites in crystals. Such modeling utilizes the relevant crystallographic data and electron magnetic resonance (EMR) data. The program SPM-MC is based on the superposition model (SPM) technique [2,3] and the Monte Carlo (MC) method. Two capabilities of the program are as follows. First capability is prediction of the structure of ML_n complexes around paramagnetic transition ions at low symmetry sites in crystals, i.e. the feasible ligands' positions distorted by an impurity, by fitting the theoretical estimates to the experimental the zero-field splitting (ZFS) parameters (ZFSPs) obtained from EMR spectra. Second capability is estimation of the ZFSPs based on the structural data and a suitable choice of the SPM parameters, i.e. the intrinsic parameters ($\bar{b}_k$) and coordination factors (t_k). The preliminary version [1] has been extended to incorporate the 4th and 6th-rank ZFS terms as well as to improve the graphical presentation of the modeling results.

The program has been thoroughly tested by applications to various types of crystal structures and ML_n complexes for which reliable input and output data exist. As a practical case study, we consider yttrium aluminum perovskite $YAlO_3$ (YAP) single crystals containing Cr^{3+} and Fe^{3+} impurity ions. For the present SPM-MC study we utilize the EMR measurements of the Cr^{3+} and Fe^{3+} ions in YAP as well as the results of the spin Hamiltonian analysis of EMR spectra reported earlier in [4]. The calculations are carried out based on the actual triclinic (C_i) site symmetry. Subsequently, the capabilities of the program SPM-MC and its potential applications are well illustrated. Major results of the SPM-MC application for Fe^{3+}:YAP ion-host system are presented here. Special focus is on two aspects. First aspect is analysis of the effect of the variation of the SPM parameters, especially the crucial intrinsic parameters ($\bar{b}_2$, $\bar{b}_4$) and coordination factors, (t_2, t_4) on the quality of fittings of experimental data and theoretical predictions. This enables to increase the reliability of the modeling results. Second aspect is analysis of the implications of low site symmetry on modeling of the spectroscopic and structural properties of the Cr^{3+} and Fe^{3+} ions in YAP.

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ESR PARAMATERS FOR SELECTED NI(II) COMPLEXES – APPLICATION OF QUANTUM CHEMISTRY METHODS

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ESR lineshape for high electron spin quantum numbers are determined by such parameters as g-tensor anisotropy and zero field splitting (ZFS) [1,2]. For electron spin quantum number $S \geq 1$ zero field splitting (ZFS) is a characteristic interaction. Its physical origins is due to second order effects in spin-orbit coupling. The D-value with consists of Spin-Orbit Coupling (SOC) and Spin-Spin Coupling (SSC), can be calculated using quantum chemistry calculations.

In this work we present calculations of ZFS parameters for selected Ni(II) complexes[3,4], using density functional theory (DFT)[5] as well as complete active space self consistent field (CASSCF)[6] methods. All calculations have been performed with the ORCA package[7]. The advantage of ORCA is that it allows including the SSC contribution, which is of importance for transition metal ion complexes.

ZFS parameters for aqueous solution of ($Ni(H_2O)_4F_2$)[4] and Pentacoordinate Ni(II) complexes [Ni(iPrtacn)X_2][8] (X=Cl, Br, NCS) have been obtained by applying CASSCF and DFT. The results from both methods have been compared and discussed. For the second compound ([Ni(iPrtacn)X_2]) the parameters obtained from calculations have been compared with those from experiment (Magnetization, FDMRS, HF-HFEPR) [8]. The most important conclusion from these studies is that ab initio methods give a much better agreement with the experimental values. Among the DFT methods the best agreement has been reached for hybridal functional B3P.

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PARAMAGNETIC NMR - CURRENT CHALLENGES

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Paramagnetic Nuclear Magnetic Resonance (NMR) refers to NMR spectroscopy and relaxation in molecular systems containing paramagnetic centers. In this work we focus on liquids (solutions) containing two kinds of paramagnetic molecules: nitroxide radicals and transition metal complexes. In such solutions the nuclear spin relaxation of solvent molecules is enhanced due to a strong electron spin – nuclear spin dipole-dipole coupling. This effect, referred to as paramagnetic relaxation enhancement (PRE), has been intensively studied for transition metal complexes in solutions; compared to that the features of PRE resulting from interactions with nitroxide radicals have not gained large attention. This especially concerns relaxation dispersion studies, where the nuclear relaxation is measured over a broad range of magnetic fields. The nuclear relaxation stems from intermolecular (solvent – solute) dipole-dipole interactions modulated by translational dynamics of both species involved. In consequence, from PRE dispersion studies one can determine relative translation diffusion coefficients in a variety of solutions; interesting examples are here glass-forming liquids. This requires, however, appropriate theoretical models accounting for the influence of the hyperfine interactions between the electron spin and the nitrogen spin, and the electron spin relaxation on the nuclear spin relaxation process. NMR relaxometry of paramagnetic systems has the potential to probe much faster dynamics than in the case of diamagnetic systems (pure solvents) as the presence of paramagnetic molecules leads not only to the overall relaxation enhancement, but also to a much stronger dispersion of the nuclear relaxation. We shall discuss these mechanisms in detail. Another application of paramagnetic molecules is as a source of polarization for neighboring nuclei – this is referred as to Dynamic Nuclear Polarization (DNP) [2,3]. In liquids the mechanism of DNP is mostly the Overhauser effect. By increasing the NMR signal (by taking over some electron spin polarization which is much larger than the nuclear one) one can observe internal dynamical features of large molecules. The factors determining the efficiency of DNP shall be discussed as well.

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1H RELAXATION DISPERTION IN VISCOUS SOLUTIONS OF NITROXIDE RADICALS

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This presentation is meant as a continuation of the discussion on Paramagnetic Relaxation Enhancement (PRE) caused by nitroxide radicals presented in *Paramagnetic NMR - Current Chalanges* (D. Kruk, A. Kubica, A. Korpała). ^{1}H spin-lattice relaxation dispersion curves of nitroxide radicals in several solutions (differing in viscosity) were collected in a wide range of temperatures. Two specific topics for the experimental systems shall be here thoroughly discussed:

a) 'eccentricity effects' [1]
b) isotope effects (the influence on ^{14}N/^{15}N substitution in radical molecule).

Due to strong dipole-dipole interaction between electron spins of nitroxide radicals and nuclear spins (typically protons) of solvent molecules the nuclear spin relaxation is strongly enhanced. As these interactions are of inter-molecular origin, they are modulated by relative translational dynamics of participating molecules. This picture assumes that the interacting spins are placed in the molecular centers, which is, of course, not true in reality. In consequence, the dipolar interactions are also affected by molecular tumbling (rotational diffusion). Thus, the nuclear spin relaxation dispersion reflects a combined effect of translational and rotational dynamics. Due to different time scales of both processes these contributions can be, at least to a certain extent, separated. We shall discuss in detail how the rotational dynamics affects the nuclear spin relaxation depending on the time-scale of the motion and the frequency at which the relaxation studies are performed. It is, for instance, of interest to note that while for diamagnetic systems the rotational contribution to nuclear spin relaxation dispersion is of importance in the range of higher frequencies, for paramagnetic systems it plays a considerable role in the whole range of frequencies. An example of high frequency studies showing the 'eccentricity effects' is presented in Fig. 1 [2].

Due to the hyperfine coupling between the electron spin and the nitrogen spin the relaxation rate of the solvent molecules is considerably reduced in the range of lower frequencies. When the electron spin relaxation is negligible, for ^{15}N the reduction is smaller than for ^{14}N, as shown in Fig. 2 for 343K [3]. At lower temperatures the electron relaxation becomes faster and it can compete with the translational modulations of the solvent - solute dipolar interactions. Then the relation between the relaxation rates of the solvent molecules for the cases of ^{14}N and ^{15}N inverts (i. e. the relaxation rate for the case of 14N becomes larger).

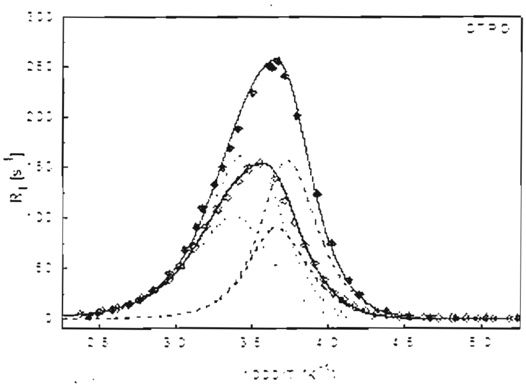

Figure 1: ^1H spin-lattice relaxation rates for 10 Mmol glycerol solution of CTPO for 15 MHz (solid diamonds) and 25MHz (open diamonds).[2]

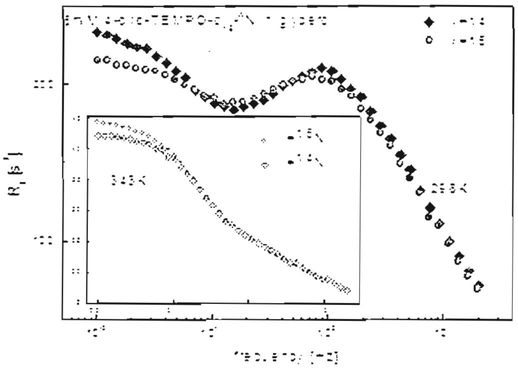

Figure 2: Experimental relaxation dispersion profiles for 10mMol glycerol solutions 4-oxo-TEMPO-d_{16}-^{15}N and 4-oxo-TEMPO-d_{16}-^{14}N at 343K and 298K.

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This work was supported by funds for science in years 2009-2012 as research project No N N202 105936 (Polish Ministry of Science and Education).

POSTERS

THE INFLUENCE OF SELECTED AMINO ACIDS ON THE DYNAMIC PROPERTIES OF THE LIPOSOME MEMBRANES: ESR STUDY

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In the present work we investigate the interaction of alanine and butyrine derivatives (Ac-Ala-NMe_2 and Ac-Abu-NMe_2) with lipid membrane formed in the liquid-crystalline phase from egg yolk lecithin (EYL liposomes) by electron spin resonance (ESR) spectroscopy using TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) or 16 DOXYL (2-ethyl-2-(15-methoxy-oxopentadecyl) -4,4-dimethyl-3-oxazolidinyloxy) spin probes. Each spin probes penetrate different regions of liposome membrane. The TEMPO probe occurs both in the hydrophobic part of the membrane and in the water environment whereas 16 DOXYL is localized in the central part of the lipid bilayer. The experiments were performed at the temperature 22 °C and the concentration of the model peptides in proportion to EYL varied from 0% to 20%.

From the ESR spectrum of TEMPO probe the spectroscopic partition parameter (F) was determined. The value of this parameter is correlated with fluidity of the hydrophilic region of lipid bilayer [1]. On the other hand, the spectrum of 16 DOXYL spin probe allows to obtain the parameter ▯(rotation correlation time of the probe) reflecting membrane fluidity of core hydrophobic region [2]. The obtained results revealed that alanine derivative up to the concentration of about 13% causes a rise in the fluidity of both the hydrophobic and hydrophilic part of liposome membrane. However, a gradual stiffening of the membrane was observed upon the addition of above 13% of dopant, with a slightly higher activity in the surface layer of the liposome membrane. Similar results were obtained for EYL liposomes doped with butyrine diamide. Ac-Abu-NMe_2 increases membrane fluidity at low concentrations (below 8%) and decreases fluidity at higher concentrations. A significantly higher dopant activity on surface structure of the membrane was observed than for its hydrophobic interior.

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THE IMPACT OF HUMIC SUBSTANCES ON THE DYNAMIC PROPERTIES OF SONIC MEMBRANES: ESR STUDY

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The impact of soil's humic substances (fraction I - Fulvic acids, fraction II - humic acids) was examined on the spectroscopic parameters of spin labels TEMPO, 5DOXYL and 16DOXYL stearic acid inside the membranes of sonic membranes of liposome , created from natural lecithin - egg yolk lecythin (EYL). TEMPO spin label involved in both: the lipid phase and water, the 5DOXYL label penetrated layer just below the polar head groups of membrane, the 16DOXYL label involved in the middle (strongly hydrophobic) parts of the lipids membrane. The study was conducted at 22 °C, when the liposome was in the liquid crystal phase. The content of humic substances in attitude to Eyl varied from 0% to 10%.

Based on the spectra of TEMPO label the spectroscopic parameter of distribution F was determined, which showed the liquidity of the hydrophilic bilayer [1]. The 16DOXYL label allow to determine of τ parameter - time of rotational correlation, which indicates membrane fluidity in the hydrophobic interior [2]. The spectra of 5DOXYL label allow to determine the order parameter T_{II}, which indicates the fluidity of intermediate layer membrane, occurring between the polar head groups and hydrocarbon chains [2]. Research shows that both fractions of humic substances slightly stiffen the membrane surface layer. In the case of the intermediate layer (5DOXYL label test) we observed a significant decline in its liquidity as a result of the impact of fraction I and a minimal increase in liquidity under the influence of fraction II. It can mean higher activity of fulvic acids with natural membranes. This information can be important for engineer substances which can control the absorption of low molecular soil humic substances and metal-organic complexes across cell membranes.

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EPR STUDY OF THE ZNO;CO THIN FILMS GROWN BY PLD METHOD

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Diluted Magnetic Semiconductors (DMS) are of interest for study mainly due to the spin-spin exchange interaction between the localized magnetic moments and the band electrons [1]. This property of DMS has potential applications in the spin-dependent semiconductor electronics [2]. Zinc-oxide have attracted intense attention in the searching for high *T* ferromagnetic DMS material, since Dietl *et al. C* [3] predicted that GaN- and ZnO-based DMSs could exhibit ferromagnetism above room temperature upon doping with transition elements. We have studied magnetic properties of zinc-oxide composite doped with various concentrations of Co ions. Samples were obtained by Pulsed Laser Deposition (PLD) method with different parameters of the laser ablation. Power of laser was changed for different samples, as well as temperature of heating.

We report on the magnetic properties of zinc-oxide (ZnO) doped with Co. Electron paramagnetic resonance (EPR) spectra have been measured and analyzed to extract information on the incorporation of the ions in the lattice.

Results of all samples were shown. Temperature dependence was analyzed and described. Magnetic anisotropy was observed. Fig 1. presents temperature dependence of EPR spectra for the sample ZnO:Co heated in 300K. We used the Curie-Weiss law to analyzed the temperature dependences of the integral intensity of EPR spectra.

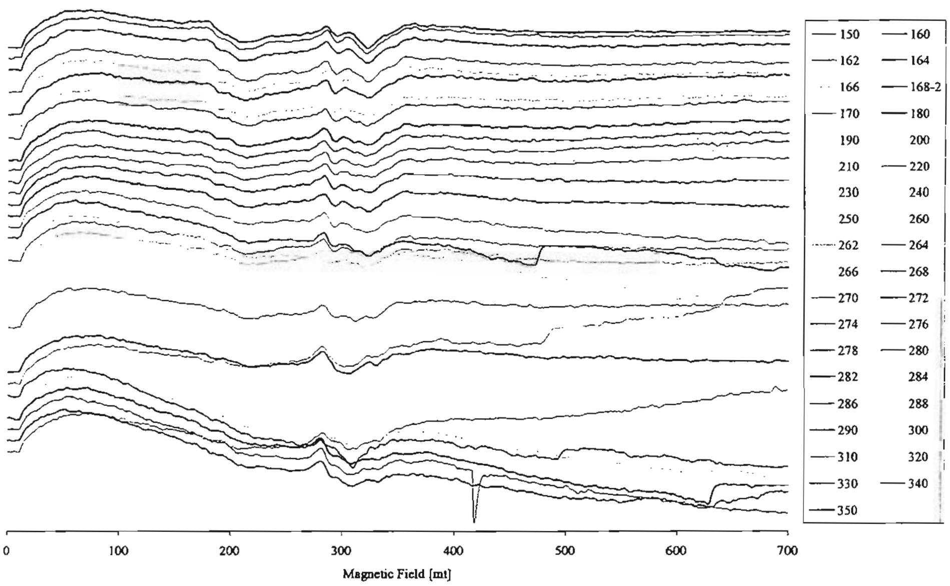

Fig 1. EPR spectra of the sample ZnO:Co in temperature range 150-350K.

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THE EPR MEASUREMENTS OF THE CERAMICS CORES USED IN AIRCRAFT INDUSTRY

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The ceramic powders are widely used in various industries, including aerospace industry. The polymer nanocomposites stiffened by ceramic nano-filling are characterized by very high hardness and resistance for abrasion in comparison with composites in micrometric scale [1].

In this work the electron paramagnetic resonance (EPR) spectra of ceramic materials (ceramic cores obtained by the high-pressure injection) with different composition have been investigated. Our aim is to find a relationship between the character of the spectrum of powders and final ceramics cores. Therefore we investigated powders which are part of materials compositions, such as the mullite, Al_2O_3 and ZrO_2. The measurements were performed at room temperature and in the temperature range from 100 K up to 350 K.

In despite of similar chemical compositions of materials differences between of EPR spectra were detected. The analysis of the line positions suggest that the lines with $g_{eff} = 4.28$, $g_{eff} = 2.00$ may be attributed to Fe^{3+} (S=5/2) ions, because they present a typical spectrum for so called disordered systems [2,3] present in a glassy hosts [4]. The line intensities decrease progressively showing the evolution of the relative line shapes and the intensities at $g = 4.3$ from isolated ions in local tetrahedral (and eventually octahedral) sites [4]. The line with g_{eff}=1.98 may be attributed to Cr^{3+} (S=3/2) ions in the slightly distorted octahedral sites [5].

The main purpose of this work was to investigate the possible relationships between EPR spectra and the size of powder grains. We are researching character of the relationship of temperature and on this basis, we want to determine if the character is consistent with the process of Orbach.

In this paper we would like to present results for the dopants in ceramic.

Acknowledgements

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THE USE OF ELECTRON PARAMAGNETIC RESONANCE IN THE STUDY OF CONCENTRATION OF FREE RADICALS IN TISSUES SPECIMENS

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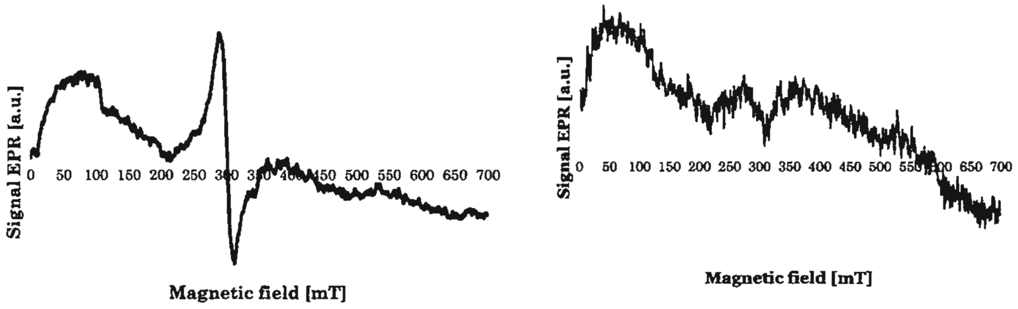
Electron Paramagnetic Spectroscopy (EPR) is the most direct and powerful method for the detection and identification of free radicals and other species with unpaired electrons. The studies on the tissue of women is one of the first studies in this area. So far studied bones of human teeth, a liver and the content of haemoglobin and the nitroxide radicals (NO) in the human body [1,2, 3]. Moreover, the EPR method is used in monitoring of oxidative stress [4].

The aim was to of the investigate the practical role of electron paramagnetic resonance in the identification of free radicals in human tissues. The samples were frozen immediately after surgery. They were stored for a short period of time. Preparation of the frozen samples was also performed in a short time. Weight for each sample was the same.



a)

b)

Fig. EPR spectra of patients: a) without omega 3 acids, b) with omega 3 acids

For the EPR measurements the standard X-band (~ 9 GHz) spectrometer, produced in Wroclaw, with digital registration of the spectra was used. The temperature measurements at 260K were done using the digital temperature control system (BRUKER ER 4131VT).
In this work we identified the spectrum and looking for correlations with omega 3 acids consumed by patients.

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BLOCH-SIEGERT SHIFT IN THE RABI OSCILLATIONS ON THE "DRESSED" ELECTRON SPIN STATES

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The Bloch-Siegert shift in the magnetic resonance arises due to the counter-rotating component of the electromagnetic field. In the common EPR experiments the Bloch-Siegert shift is usually unobservable. However, this effect becomes measurable in the EPR experiments with bichromatic fields, e. g. in the electron-electron double resonance (ELDOR) where two microwave (MW) fields with different frequencies are used [1], or in the time-resolved and continuous wave EPR using transverse MW and longitudinal radiofrequency (RF) fields [2].

We study the Rabi oscillations at the double resonance, when the RF frequency ω_{rf} is close to the Rabi frequency ω_1 in the MW field, provided the MW frequency equals the Larmor frequency of the spin system. In this case, the Rabi oscillations arise between the spin states "dressed" by the MW field [3]. When detuning $|\omega_{rf} - \omega_1|$ is comparable in magnitude to ω_{rf} and ω_1 (the dispersive regime [4]), the Bloch-Siegert effect, together with the dynamical Zeeman effect, results in the shift of the Rabi frequency in the MW field. At the resonance (ω_{rf} close to ω_1), the shift of the effective Rabi frequency in the RF field is only due to the Bloch-Siegert effect [5]. It was found that, by using the RF field with a random phase, we can simultaneously observe the absorption and the dispersion components of the Rabi oscillations between the dressed spin states. Experimental results obtained in the time-resolved EPR for E_1' centers in quartz are presented.

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ELECTRON CONFIGURATION OF IRON ION IN SIX-COORDINATED PORPHYRIN COMPLEXES

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The aromatic porphyrin ring is composed of four pyrrole rings connected by four methine bridges. Connection of the metal ion in the center of such a system gives the metalloporphyrin complex. There are many metalloporphyrins known in the nature. Chlorophyll (chlorin complex coordinated with magnesium ion) is involved in the processes of photosynthesis, the green parts of plants. Another important role of metalloporphyrins is connected with iron porphyrin complexes in the process of breathe (hemoglobin, myoglobin and some enzymes). Hemoglobin and myoglobin, which main pasts contain Fe(II) porphyrin complexes, are responsible for transportation and storage of oxygen in the body [1].

Molecular structures of metalloporphyrins can be modified in many ways. One of them is able to join one or two axial ligands directly to the iron ion. In the six-coordination structures, axial ligands can be in different positions relative to each other as well as the porphyrin ring. For example, the six-coordinate porphyrin complexes with axial ligands lying in parallel planes to each other are observed in cytochromes b_5, or cytochromes c_3, while the systems in which the axial ligands lie in perpendicular planes to each other are observed, among others, in flavocytochrome b_2. In view of recent studies, due to the orientation of axial ligands relative to each other, there are three types of such complexes, which electron configurations differ essentially: Type I – perpendicular ligands with ruffled or saddled porphyrin rings; Type II – parallel ligands with planar porphyrin rings; Type III – perpendicular ligands and planar porphyrin rings. It is well known that iron-porphyrin complexes of type I and III have the ground state of low spin iron(III) ions $(d_{xy})^2(d_{xz},d_{yz})^3$ and the type III have the ground state $(d_{xy})^1(d_{xz},d_{yz})^4$ [2]. However, it has been observed recently that, for some six-coordinated iron porphyrins spin state depends also on the phase in which they are located. For example, spin state of iron ion in the complex $[Fe(OEP)(2\text{-}MeHIm)_2]ClO_4$, in the crystalline phase, is in a high spin state, while in the liquid state it exists in thermal spin-equilibrium between low and high spin state [3].

In our study, we consider two of six-coordinated iron-porphyrin complexes: $[Fe(III)(OEP)(Im)_2]^+$ and $[Fe(III)(OEP)(3\text{-}Pic)_2]^+$. These complexes were investigated by Mössbauer, EPR and electron absorption spectroscopies. On the basis of experimental and theoretical data we have found that the complex $[Fe(III)(OEP)(Im)_2]^+$ is in the low-spin state showing the electron spin configuration $(d_{xy})^2(d_{xz},d_{yz})^3$, both in the solid state and in the liquid states. This complex can be assigned to the type II of the six-coordinated complexes. Concerning the $[Fe(III)(OEP)(3\text{-}Pic)_2]^+$ complex, on the basis of data which have been obtained so far, we can conclude that the iron ion in this complex shows the quantum-mechanically mixed spin state in the solid state.

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COMPUTATIONAL EPR SPECTROSCOPY - DFT SCHEMES FOR CALCULATION OF SPIN-HAMILTONIAN PARAMETERS

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Combination of computer simulations of the EPR spectra for real systems with relativistic quantum chemical calculations of ***g***, ***A*** and ***D*** tensors for compounds or molecular models of extended systems provides robust approach in studying details of the electronic structure and magnetism of randomly oriented paramagnetic species. Calculation of the spin-Hamiltonian parameters requires optimization of the particular calculation scheme (*ab initio* or DFT methods) for each type of the investigated systems. The agreement between calculated parameters and experimental data provides a quantitative measure of adequacy of the applied calculation approach.

In this contribution we present selected examples of paramagnetic complexes with the well defined structure such as 4-coordinated bis-□-diimine-nickel(I) complex, used for validation of DFT calculations scheme [1]. The ***g*** and ***A*** tensors were calculated by applying various approaches to the spin-orbit (SO) interaction, i.e. the zeroth-order approximation (ZORA) and the semi-relativistic Pauli Hamiltonian available in ADF [2] as well as the spin-orbit mean-field (SOMF) method available in ORCA software [3]. Moreover, various correlation-exchange potentials (local, GGA, hybrid, meta-GGA) were applied to choose the best calculation option for the investigated systems.

The ***g*** tensor components were found to be more sensitive to the correlation-exchange functional than the basis set, and the hybrid functionals are clearly preferred (Figure 1). Concerning the SO approaches, the ZORA and SOMF gave virtually the same results with minor advantage over the Pauli method. The discrepancy between calculated and experimental results depends on the spin density redistribution within a paramagnetic complex. In case of the metal-centred paramagnets the results were found to be more sensitive to the choice of the basis set, and the g_{ii} and A_{ii} values are more divergent from the experimental counterparts as compared to the ligand-centred radicals. The calculations helped also to predict a noncoincidence between the principal axes of the ***g*** and ***A*** tensors.

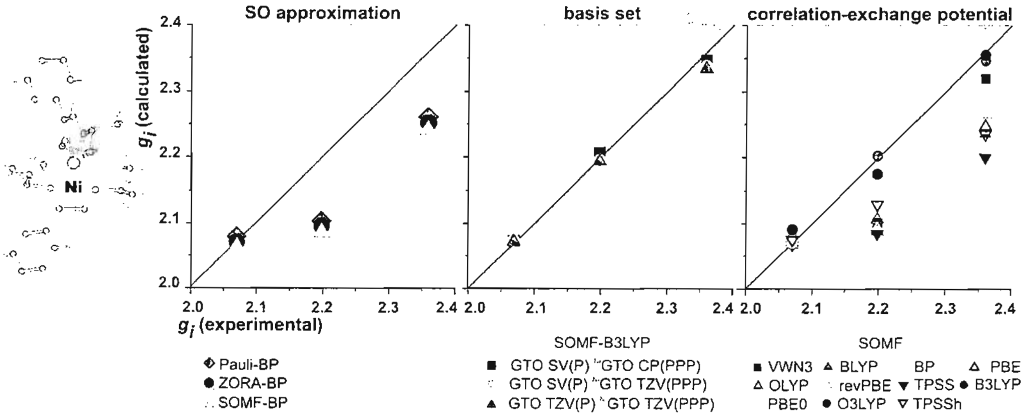

Figure 1. Influence of computational parameters on ***g*** tensor for the bis-□-diimine-nickel(I) complex

Acknowledgment: K.P. thanks for the financial support from the „Society – Environment – Technologies" project at the Jagiellonian University in the framework of the EU Social Fund. The calculations were carried out with the computer facilities of Academic Computing Centre CYFRONET-AGH under grant no. MNiSW/IBM_BC_HS21/UJ/092/2008.

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EPR/HYSCORE STUDY OF CO ADDUCTS WITH NICKEL CENTERS IN ZSM-5 MOLECULAR SIEVES

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Carbon monoxide adducts with transition-metal centers (TMI–CO) are the key species implicated in various biologically and environmentally important catalytic reactions. Since Ni-containing zeolites (ZSM-5) were found to be efficient in the selective catalytic reduction (SCR) with methane and other hydrocarbons as the reducing agents [1], one of the intermediate involved in this process is CO which forms carbonyl complexes with nickel active sites. Their structure, spectroscopic fingerprints, and reactivity in SCR conditions were elucidated using multitechnique approach involving CW and FT EPR, IR spectroscopic investigations and DFT modeling.

In the present account we show results obtained for the Ni-ZSM5 catalyst prepared by the ionic exchange techniques (in solution and solid state). Model adsorption experiments in controlled temperature showed a coexistence of the mono-, di-, tri- and tetracarbonyls of Ni(I) depending on CO pressure [2]. The characteristic CO frequencies were obtained from *in-situ* IR measurement and spin-Hamiltonian parameters were extracted by computer simulations (EPRsim32, EasySpin) of the temperature- and power-dependant EPR spectra. To get more insight into the structure of the nickel(I) polycarbonyls, ^{13}CO labeled reactant was used (Fig. 1). In the case of the tri- and tetracarbonyl species, where substantial overlap of the nickel SOMO with CO-based molecular orbitals takes place, the CW EPR measurements were able to resolve the ^{13}C hyperfine splittings. However in the case of monocarbonyl adducts, due to the Y-shaped geometry [3], the hyperfine information could only by obtained by means of the hyperfine sublevel correlation (HYSCORE). The performed experiments gave the structural information not only about local Ni(I) environment but also about the quadruple ^{27}Al interaction, and ^{13}C hyperfine splitting. Thanks to the relativistic calculations of the EPR parameters (including values of g and (^{13}C)A tensors), a successful attribution of the measured spectral fingerprints to the various carbonyl adducts was possible.

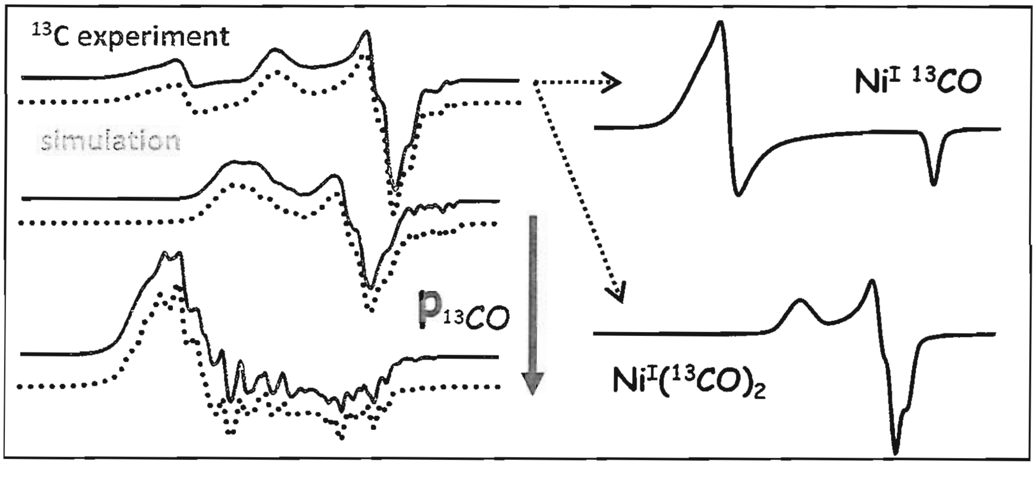

Figure 1. ^{13}CO adducts with Ni-ZSM5: pressure dependent cw-EPR spectra and simulations

Acknowledgment: T.M. thanks for the support from the International PhD studies program at the Faculty of Chemistry, Jagiellonian University, within the MPD Program of the Foundation for Polish Science co-financed by the EU Regional Development Fund.

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TEMPERATURE STUDY OF FMR SPECTRA OF 0.30(Fe_2O_3)/0.70(ZnO) NANOCOMPOSITE

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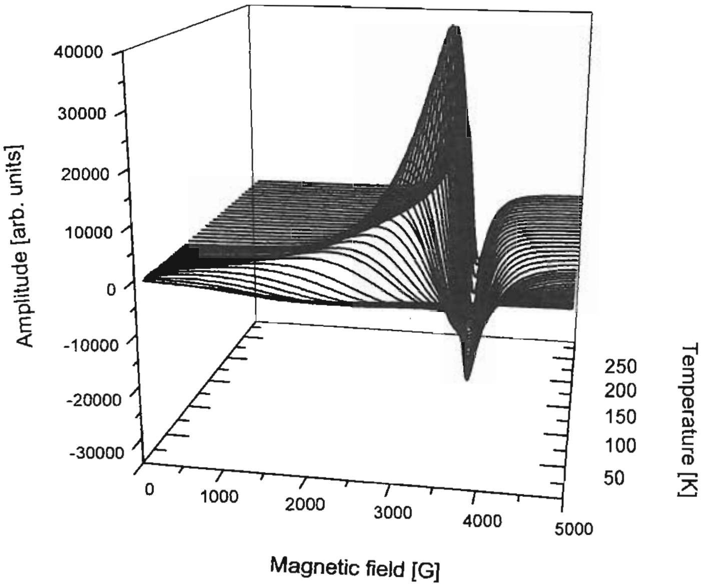
In recent years nanocrystalline materials have been studied intensively due to their manypossible applications in microelectronics and spintronics. ZnO nanocrystals doped with Fe2O3 have been synthesized by the calcination method. The obtained sample, designated as 0.3(Fe2O3)/0.7(ZnO), was characterized by means of X-ray diffraction which revealed the presence of two phases: ZnO (nanoparticles with an average size of 51 nm) and ZnFe2O4 (11 nm). Ferromagnetic resonance (FMR) study of 0.3(Fe2O3)/0.7(ZnO) nanocomposite has been carried out on Bruker E500 spectrometer in the 4 – 300 K range. The registered FMR spectra have been analyzed in terms of two component Landau – Lifszyc-type lines. Temperature dependence of the resonance field, linewidth and the integrate intensity of this compound has been determined. The results of FMR study of 0.3(Fe2O3)/0.7(ZnO) have been discussed in terms of magnetic anisotropies of underlying magnetic nanoparticles.



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TEMPERATURE DEPENDENCE OF FMR SPECTRA OF 0.1MnO/0.9ZnO NANOPARTICLES

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Nanostructures made of a wide-gap ZnO semiconductor have been studied very intensively in recent years because of their broad potential applications. Transition metal doped ZnO is of particular interest in spintronics. We have studied magnetic properties of nanosize ZnO powders doped with MnO magnetic dopand. This material was characterized by XRD that revealed the presence of ZnO and $ZnMnO_3$ phases. An average size of $ZnMnO_3$ nanoparticles was 13 nm.

Ferromagnetic resonance (FMR) study has been carried out on Bruker E 500 spectrometer in the 4-290 K temperature range. The obtained FMR spectrum was analyzed in terms of three component lines. The temperature dependence of resonance field , linewidth and integrated intensity of these component lines have been determined. Magnetic centers responsible for producing these lines have been proposed.

EPR INVESTIGATION OF UV LIGHT EFFECT ON CALCIUM CARBONATE

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Electron Paramagnetic Resonance (EPR) has found wide applications in the field of radiation dosimetry [1, 2]. This method is based on the interaction of an external magnetic field with magnetic moments of unpaired electrons in a sample, and therefore is useful to detect the free radicals.

Calcium carbonate is widely used in many branches of industry, therefore knowing its properties is essential. This study is based on investigation of calcium carbonate samples exposed to UV light. Samples of powdered calcium carbonate, each with different grain size, were exposed to UV light from Hg/Fe lamp for 1 hour and to sunlight in Sudan for 3, 7 and 9 days. Measurements, performed at room temperature using Bruker EPR spectrometer, EMX type, working at 9 GHz frequency, shown the additional light-induced signals. Their amplitude was measured regularly after the exposition. Signals of Mn^{2+} ions were used as a reference when comparing the amplitudes of the peaks. Computer resolution enhancement method was applied in order to split the signal. Further studies concerning the effect of exposition time on the amplitude of the main peak will be conducted.

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MAGNETIC RESONANCE STUDY OF CARBON ENCAPSULATED Ni NANOPARTICLES

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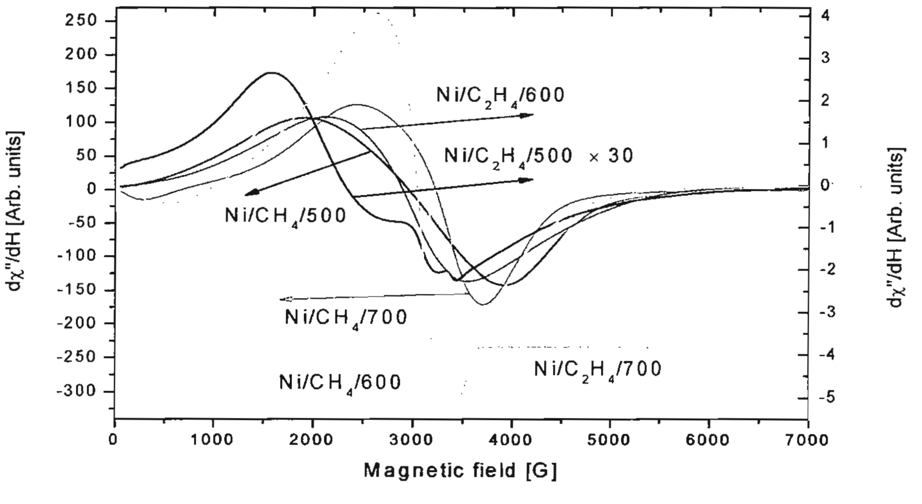
Magnetic resonance study of six samples consisting of carbon encapsulated nickel nanoparticles has been carried out at room temperature. Samples of Ni/C were prepared by carburization of nanocrystalline nickel by ethylene (C_2H_4) and methane (CH_4). The mean crystallite size of nickel nanoparticles as determined by XRD was 25 nm. Hydrocarbons decomposition on nickel nanoparticles was done at temperatures 500, 600 and 700°C [1,2]. Magnetic resonance spectra of samples designated as Ni/CH_4/500, Ni/CH_4/600, Ni/CH_4/700, Ni/C2H_4/500, Ni/C2H_4/600 and Ni/C2H_4/700 were obtained by Bruker E500 spectrometer. The integrated intensities of the resonance spectra have been correlated with the carburization conditions (temperature, type of hydrocarbon) during samples formation.



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BIOREDUCTION OF NITROXIDES IN DIFFERENT CELLS

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Nitroxide spin labels, commonly used in biomedical investigations employing EPR and NMR techniques, are metabolized in cellular systems. First, they undergo reversible, enzymatic or non-enzymatic, bioreduction to corresponding hydroxylamines. The rate of bioreduction is dependent on many factors, including mainly the structure of the nitroxide ring, the presence and type of ring substituents, charge, hydrophobicity, the type of the cell, pH, concentration of oxygen and cellular reductants, particularly ascorbic acid and glutathione.

To check the importance of ring structure on nitroxide bioreduction we evaluated the reduction rates for two five-membered nitroxides: 3-carbamoyl-2,2,5,5-tetramethylpyrroline-1-oxyl (Pirolin, PL), 3-carbamoyl-2,2,5,5-tetramethylpyrrolidine-1-oxyl (Pirolid, PL), and one six-membered: 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (Tempol, TOL) inside different cells, i.e. human red blood cells, immortalized Chinese hamster peritoneal fibroblasts (B14 cell line), and human breast adenocarcinoma MCF-7 cells. All experiments were performed under the following conditions: nitroxides were added to cells to 0,1 mM final concentration and cell suspensions with nitroxides were incubated at 37°C during the experiments. The measurements were performed on Bruker ESP 300E X-band spectrometer.

Generally, Tempol was reduced much faster in comparison to Pirolin and Pirolid independently on cells used in the study. Pirolin was reduced slower than Pirolid in erythrocytes and in B14 cells, but in MCF-7 cells PL was reduced much faster than PD. Reduction of five-membered nitroxides in B14 cells was 4 times faster for Pirolin and 6 times faster for Pirolid in comparison to reduction of these nitroxides in MCF-7 cells.

These results indicate that changes in bioreduction are strongly dependent on two factors: the nitroxide ring structure and the type of cells.

EPR STUDY OF GUANIDINIUM ZINC SULFATE CRYSTAL

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Crystal of guanidinium zinc sulfate $[C(NH_2)_3]_2Zn(SO_4)_2$, abbreviated as GZS, has been studied using three dimensional X-ray analysis [1]. The crystal are tetragonal with apace group $I\bar{4}2d$ and four formula units in unit cell. The network of zinc and sulfate ions constitutes the main feature of the structure where sulfate ions are arranged tetrahedrally around the zinc ions. The structural studies of a quite large family of hydrated complex guanidine compounds with sulfates of divalent transition metals were presented recently [2] The GZC crystal is supposed to undergo a phase transition at elevated temperatures [3]. However, DTA and DTG studies [4] did not reveal any traces of the phase transition. Recently, on the basis of the calorimetric and dielectric studies, Czapla et. al. [5] have found that the GZS crystals exhibit the second order structural phase transition at 178 K accompanied by substantial entropy changes.

The magnetic resonance methods have not been employed in studies of this system, so far. In this communication the X-band EPR measurements on manganese-doped crystals are presented. The rotation pattern of the spectra show at room temperature and above only one set of lines which is not in agreement with four Zn sites in unit cell, which can be substituted by Mn^{2+} ions. Temperature dependences of EPR spectra were studied from temperature of 400 K to liquid nitrogen temperature. A broadening of the lines was observed on lowering the temperature and the spin-Hamiltonian (SH) parameters were determined precisely at 398 K where the spectra were nicely resolved. The SH parameters were analyzed within superposition model [6] with the usage structural data.

On lowering the sample temperature up to liquid nitrogen temperature we were not able to reveal any phase transition effects due to strong lines broadening.

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PHASE TRANSITIONS IN $[(CH_3)_2]CHNH_3]_4Cd_3Cl_{10}$ CRYSTAL

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The $[(CH_3)_2]CHNH_3]_4Cd_3Cl_{10}$ crystal is an example of organic-inorganic hybrid compounds, which modification significantly affects their physico-chemical properties [1, 2]. The structural studies show that in the crystal there is a sequence of three phase transitions of orthorhombic symmetry, from the phase with Cmca space group at 355 K to the phase of space group Pbca and a temperature of 294 K to the phase P212121. At a temperature of 260 K transition to monoclinic phase is resulting in crystal twinning and cracking leading to its destruction. Therefore, no research has been undertaken in the last phase of the crystal [3, 4]. In order to determine changes in the $[(CH_3)_2]CHNH_3]_4Cd_3Cl_{10}$ crystal of doped Mn^{2+} ions which are replacing the host ions Cd^{2+} . The EPR spectra at X- band were observed in the temperature range 293-373K. Spectra of Mn^{2+} and the angular dependence of the crystal can be described by the spin Hamiltonian of orthorhombic symmetry in the form:

$$H = \beta \mathbf{SgB} + D[S_Z^2 - 1/5 \cdot S(S+1)] + E(S_X^2 - S_Y^2) + 1/6 \cdot a[S_X^4 + S_Y^4 + S_Z^4 - 1/5 \cdot S(S+1)(3S^2 + 3S - 1)] + \mathbf{SAI}$$

where $S = I = 5/2$ for Mn^{2+} ion [5].

The EPR studies were performed around the axis of a and b axis, looking for an anomaly near the phase transition temperature. For a given orientation of magnetic field we have observed the increase of intensity of the EPR lines with increasing temperature, the global splitting of the spectrum and changes of the linewidths of the side sextets. At temperatures above 333 K lines originating from the second non equivalent complex appear, which is characterized by a much larger splitting. At a temperature of 373 K we have examined the angular dependence of the position and shape of the line, which shows angular changes of the fine structure behaviuor characteristic for Mn^{2+} ions. Temperature measurements performed in the orientation of the magnetic field along the b-axis gave similar results as studies done along the a-axis. The study also showed the presence of two non equivalent complexes at temperatures higher than 333K and the disappearance of signals from the complexes exhibiting larger splitting on lowering the temperature. The observed effects may be cause due to the dynamics of molecular groups present in the environment isopropyl cations. We have also carried out the detailed studies of temperature positions and shapes of high field spectral lines. We have revealed a sharp change in the nature of spectra near transition temperature $T_C = 358$ K, which indicates that the change has the nature of the first-order phase transition. Both the intensity and width of the line of the first complex has a much higher value in comparison to the same parameters of the second complex. However, no significant changes in the positions of spectral lines originating from different complexes were observed.

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AUTOMATIC MICROPROCESSOR-CONTROLLED PRECISION GONIOMETER FOR USE IN EPR SPECTROSCOPY

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In this paper the automatic, microprocessor controlled precision goniometer is described. The great variety of spectrometers used in research causes many problems in finding suitable goniometer adapted to existing equipment. In EPR spectroscopy programmable goniometer can be used to simplify and speed-up the tedious task of measuring EPR spectra of single crystals as a function of their angular position in the magnetic field [1]. For this reason, as well as in desire to increase precision of changing rotation angle, this part of the EPR equipment was designed. The described goniometer allows to change the angle by 1.019 degree in both directions, with fixed rotation error (the value of the error is constant regardless of current position throughout the rev range). The goniometer allows to mount sample holders of different diameter and length. Because of presence of strong magnetic fields between magnet pole shoes, core, in which stepper motor is mounted was moved above the magnets.

Control of goniometer is done by using AVR family microcontroller, ATmega8, which is responsible for steering stepper motor, displaying information on LCD and communication with computer (PC) via the USB or RS232 port (what enabled to use in a larger number of applications). On the computer side a special software was written in C++ to control rotation speed, time and direction. Due to PC software, it is possible to use an automated rotation plan and also a manual control. Software on the microcontroller side was written in Bascom AVR and is responsible for simplified communication protocol handling and mainly for stepper motor operation control.

Because of the high energy use by the stepper motor and additional rotation hold-mode (which allows to suspend sample with use of some small force, eliminating any unwanted random movements) system is powered by the external power supply (separately stepper motor and control logic).

Work on the prototype is in progress and it is also planned to reduce the minimum rotation angle by application of the half-step and micro-step control techniques which will allow to the state of the art precise rotation control.

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THE TWO-CHANNEL L-BAND EPR SPECTROMETER FOR QUANTITATIVE MEASUREMENTS

J. Duchiewicz, A. Francik, A.L. Dobrucki, T. Duchiewicz, W. Stachowicz, T. Oleś, J. Błaszczyk

The article presents a new conception of the 2-channel L-band EPR spectrometer with the 2-chamber measuring cavity Loop-Gap type [1,2,3,4]. Spectrometer will be equipped with two receiving paths: one for the EPR signal with frequency of 100 kHz, coming from the sample under test, second for the EPR signal with frequency of 1 kHz, coming from the standard sample.

Thus, new spectrometer will consists of:

- L-Band microwave unit with 2-chamber measuring cavity
- Two digital EPR signal receiver units (for frequency of 100 kHz and 1 kHz)
- Hall Effect electromagnet magnetic field stabilizer
- Electromagnet with small dimensions
- Control program of the spectrometer (through the USB interface)

Due to the application of the L-Band, the described spectrometer is especially addressed to quantitative measurements of samples with considerable content of water (typical feature of the majority of the food), i.e. those poorly measurable or even not measurable in popular X-band. The proposed version of spectrometer could be useful for the distinction between low dose and high dose treated food in technological processing.. New EPR spectrometer is a competitive solution for X-band spectrometers for dosimetric measurements as offered by the Bruker company, for example.

The proposed EPR spectrometer is the continuation of the earlier (2008-2010) solution successfully materialized in the NCED* Development Project N R01 0018 04 "The prototype of the EPR spectrometer for dosimetric measurements and for identification of the irradiated food"

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THE ADVANCED UPGRADE OF THE BRUKER ESP-300 X-BAND EPR SPECTROMETER

J. Duchiewicz, A. Francik, A.L. Dobrucki, T. Duchiewicz, A. Sadowski, K. Gwoździński, W. Stachowicz

In the article the advanced upgrade of the Bruker EPR spectrometer model ESP-300 is described. The Bruker spectrometers of ESP-300 family were widespread in many countries in seventies of 20 century, and a few of them are still acting. This old type machine is controlled with computer operating with old type OS-9 system not available any more. Therefore, in a case of a failure it not possible to be repaired. How to "revive" such a spectrometer in a damaged condition and to make possible to control it with computer operating a modern systems e.g. Windows XP or Windows 7. The Wrocław University of Technology undertook successfully such a task, upgrading the ESP-300 spectrometer at the Institute of the Biophysics of the University in Łódź [1]. It was decided, that some original blocks of the spectrometer e.g. the magnetic field stabilizer (ER-032M) and EPR receiver (ER-023M) are not suitable for upgrading of a new spectrometer. Instead, modern units as the Hall Effect field controller [2] and the digital EPR receiver (both controlled via USB interface) [3] were installed. A separate problem is the microwave unit (ER-041M), controlled directly with built-in computer (with OS-9). Taking in account a high price of microwave parts installed in existing unit, it has been decided to construct a special, external controller (with built-in power supply), operating via USB interface. Thus, as a result of the upgrade in the reconstructed spectrometer-electromagnet, electromagnet power supply (after some modification) and measuring cavity survived. The consoles of the spectrometer were also removed as unneeded any more. A special computer program, controlling the whole spectrometer has been designed.

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ANTIOXIDANT PROPERTIES OF WINES PRODUCED AT PODKARPACIE REGION

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Sequential reduction of the triplet molecular oxygen leads to the formation reactive oxygen species (ROS), such as superoxide, hydrogen peroxide and hydroxyl radicals [1]. In the aim to enhance the defensive power of the human organism against these species many natural antioxidant products should be introduced into foodstuffs. The wine is the famous and popular drink having properties of ROS scavenging [2, 3]. In this paper we study the antioxidant activity of the selected wines produced in the south-west region of Poland, in the Subcarpathian Voivodship. We concentrate our studies on the superoxide radical anion $O_2^{\bullet -}$. We have used the EPR spectroscopy as it the best method for the radical detection. The nitrone spin trap α -(4-pyridyl-1-oxide)-N-tert-butylnitrone (POBN) has been used in the experiment (Fig 1a). The key reaction of adduct formation is shown in Fig. 1b).

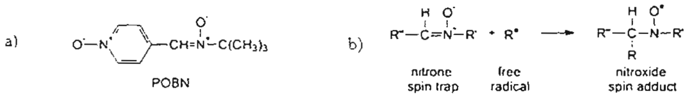

Fig 1. a) Spin trap of nitrone α -(4-pyridyl-1-oxide)-N-tert-butylnitrone (POBN), b) General scheme of spin trapping.

As a result we have recorded the EPR spectra consisting six lines forming double triplet arising from hyperfine interaction of the electron spin s =½ with proton spin I_H = ½ and nitrogen spin I_N =1.

Radicals were created in the non- Fenton reactions:

$$KOH + H_2 0 \leftrightarrow K^+ + OH^- + H_2 0 \qquad (1)$$

$$H_2O_2 + OH^- \leftrightarrow HO_2^- + H_2O \qquad (2)$$

$$H_2O_2 + HO_2^- \rightarrow O_2^{\bullet -} + {}^{\bullet}OH + H_2 0 \qquad (3)$$

Experimentally we have established that the EPR spectrum strongly depends on the concentration of the substrates in the free radical generation and trapping processes (Fig. 2).

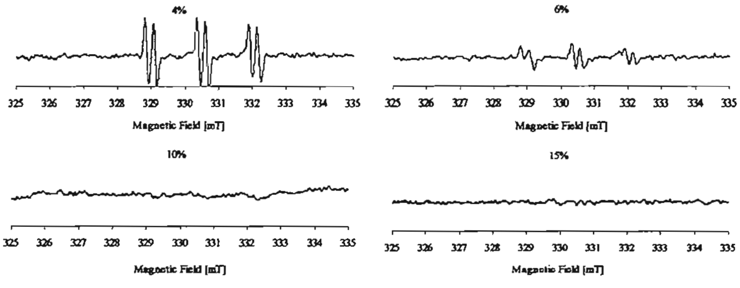

Fig. 2. Effect of concentration of the KOH solution on the EPR spectrum, with a steady 6% concentration of H_2O_2.

The radical scavenging ability of wines studied were determined from the changing in time of the intensity of the spectrum.

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RADICAL SCAVENGING GUIDED EXTRACTION OF *ARONIA MELANOCARPA* LEAVES

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Medical University of Warsaw, Faculty of Pharmacy

Aronia melanocarpa (chokeberry) is a plant from the Rosaceae family, cultivated in Poland. The berries contain a lot of antioxidants such as anthocyanins, procyanidins and tannins, phenolic acids and flavonols. The leaves are lesser known source of antioxidants. According to K. Skupień et al. [1], there are 227.9 mg phenolics per 100g of dry weight in the leaves of chokeberry. The hydroxycinnamic acids: chlorogenic, neochlorogenic, caffeic and quercetin glycosides were found. However, phytochemicals of *Aronia* leaves and their antioxidant activity should be studied in detail.

The purpose of our work is to optimize the method of extraction of antioxidants from the leaves. We used Electron Paramagnetic Resonance (EPR) spectroscopy and the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical test to determine the antioxidant capacity of the extracts. EPR has advantages over the popular UV-Vis method because the spectra of colorful and cloudy extracts can be measured. EPR spectra were recorded on Magnettech MiniScope200 X-band spectrometer. The aqueous and acetone extracts from 1g of dried chokeberry leaves were prepared. The extraction procedures were: (1) – water extract cooked and diluted with 70% MeOH, (2) - water extract, (3) - water extract without precipitate, diluted with 70 % MeOH, (4) – water extract with precipitate diluted with 70% MeOH, (5) – water extract after acid hydrolysis diluted with 70% MeOH, (6) – acetone extract without precipitate, (7) – acetone extract with precipitate. Extracts were tested for their antioxidant activity against DPPH dissolved in acetone and 96% ethanol. EPR spectra were measured after 50 minutes from mixing. The results are presented as a quantity of DPPH [mg] scavenged by an extract (Fig. 1).

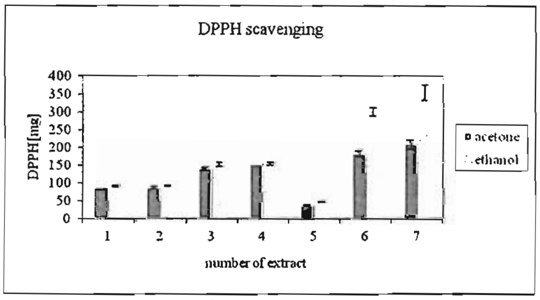

Fig. 1. The results of DPPH radical scavenging test

The 70% acetone extract (no.7) was the most active against DPPH radicals. As the next step, experiments using extraction mixtures with different proportion of water and acetone will be performed. Radical scavenging guided extraction helps to identify the fraction containing the most active free radical scavenging components of plant material [2]. Further studies will include the isolation of active compounds from extracts and their identification using NMR.

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SPIN TRAPPING STUDY OF THE OXIDATIVE STABILITY OF FLAVOURED OLIVE OILS

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Olive oil is one of the basic components of the traditional Mediterranean diet, which is thought to be responsible for decreased risk of cardiovascular diseases, obesity or type 2 diabetes [1]. However, the oxidation products of this dietary fat can have adverse effects on human health.

In search of new tastes and health promoting ingredients, home-made flavoured olive oils are gaining popularity. It is known that the flavouring with dried herbs can delay the oxidation of olive oil [2]. However, there is almost no data on the oxidative stability of olive oils prepared with fresh herbs and/or spices. In this work the influence of such flavouring on the oxidation processes of olive oil was studied with the Electron Spin Resonance technique. PBN spin trap was used and the formation of free radicals during accelerated aging at 70°C was measured according to Velasco with modifications [3]. The spectra were recorded on a Magnettech MiniScope200 X-band spectrometer at 9.3 GHz. The ESR method was combined with determining well-established oxidation status indicator, i.e. peroxide value (PV) (titration method).

Flavoured olive oils were prepared by chopping fresh herbs or spices (basil, oregano, rosemary, garlic, chili pepper), weighing the exact amount of each into a glass jar, and pouring the same volume of extra virgin olive oil. The equal-weight mixtures of basil/rosemary and garlic/chili pepper were also prepared, to investigate the potential synergistic effect of combining different flavours. All samples were stored at room temperature in the darkness. The peroxide value determination and ESR measurements were performed at 4 and 8 weeks after the oils preparation, with olive oil without additives as a control sample.

During first 4 weeks of storage all studied flavourings increased the intensity of oxidation processes to some degree, as indicated by higher peroxide value and observed spin adducts concentration. However, after 8 weeks of storage the difference between herbs and spices could be seen – herbal olive oils had slightly lower peroxide value and lower spin adducts concentration (by 20-30%) than control sample, while in case of spice flavoured oils the oxidation indexes were significantly higher than for the control sample (10-15% for PV and over 100% for radical adducts concentration). For all samples only lipid-derived spin adducts were observed.

Further studies, including the antioxidants composition and the influence of the exact preparation procedure, are needed to fully understand the influence of fresh herbs/spices flavouring on the olive oil stability.

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MICELLIZATION OF BIFUNCTIONAL N-OXIDE SURFACTANTS; EPR, DLS AND DFT STUDIES

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Surfactants are widely used in pharmaceutical, cosmetic, and biological systems. Thus, great effort has been paid to the development of new environmentally friendly surfactants with improved performance. Nonionic dicephalic *N*-oxides under present study contain one hydrophobic alkyl chain and two hydrophilic oxidized amino moieties [1]. Owing to their excellent surface and performance properties as well as less adverse environmental impact and the fact that they can be synthesized from renewable materials, such surfactants may provide a lot of opportunities in relation to household products, as well as to cosmetic and fabric industry.

The ability to form micellar aggregates is a fundamental characteristics of amphiphilic surfactants. In this study we used electron paramagnetic resonance (EPR) spectroscopy to monitor micellization behavior [2]. Two nitroxide spin probes, 5- and 16-doxylstearic acid, were proved as suitable for the studies in aqueous solutions. Different locations of the two spin probes in formed aggregates provided a great opportunity for an in-depth insight into the local microenvironmen of the micellar systems under investigation. To determine the critical micelle concentrations (CMC) the rotational correlation times were monitored as a function of surfactant concentration. In addition CMC ascertained with the use of EPR were compare to the values obtained by tensiometry methods.

The approximate size of the micellar aggregates was estimated from dynamic light scattering (DLS) method. Polydispersity index obtained for all studied compounds, suggested that the samples were monodispersive. A hydrodynamic radii, and micelles volumes were compared with parameters calculated using density functional theory (DFT). A good accordance between theory with experiment was revealed. Furthermore, aggregation numbers, which describe the number of molecules present in a micelle, were obtained from the DFT calculations.

Our results proved grate effectiveness of the spin probe method for investigation of the micelle formation and microenvironment as well as the usefulness of the DLS and DFT techniques for evaluation of the interfacial and aggregation behavior.

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SPECTROSCOPIC CHARACTERIZATION OF THE SPIN LABELED PROCAINE IN HOMOGENEOUS AND MICROHETEROGENEOUS SOLUTIONS.

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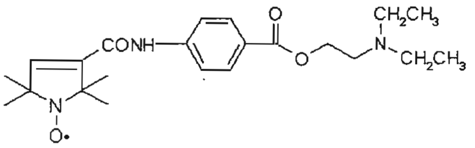
Although local anesthetics (LAs) have been used in medical treatment since the beginning of the 20th century, the mechanism of their action at the molecular level is still not fully understood. In particular, it is not unambiguously explained what role in this mechanism is played by the drug transport through the neuronal membrane to sites of sodium channels responsible for the gating properties, and whether (and how) the drug-induced change of the physical state of membrane lipids correlates with the pharmacological effect.

A powerful method to study LA interactions with lipid membranes is electron spin resonance spectroscopy (ESR) with the use of spin probes such as nitroxide derivatives of fatty acids or phospholipids, and spin labeled drugs, e.g. the nitroxide-labeled procaine (sl-PRC) of the formula given below:



This compound has been used in a few studies of model and native membranes [1–4] but the conclusions are based solely on the ESR line-shape analysis. The authors have not reported the values of ^{14}N hyperfine splitting parameters, even when the observed signals were motionally averaged triplets [2] or simulations of slow-motional spectra were performed [1, 4].

For an in-depth understanding of the sl-PRC behavior in complex membrane systems it is essential to know its spectral properties in homogeneous solutions and simple well-defined microheterogeneous systems. Therefore in the present work we examine the ESR spectra of sl-PRC in selected solvents, and in aqueous solutions of several amphiphilic self-assemblies, *viz.* micelles of sodium dodecylsulfate (SDS), vesicles of sodium bis(2-ethylhexyl)sulfosuccinate (aerosol OT), small unilamellar liposomes of synthetic lipids: 1,2-dipalmitoyl-*sn*-glycero-3-phospho-(1'-*rac*-glycerol) (DPPG, sodium salt) and 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC). We discuss the dependence of the splitting parameters (a_N and A_{zz}) and correlation times of rotational diffusion on solvent properties (polarity, H-bonding ability, viscosity), and demonstrate how the sl-PRC binding to amphiphilic aggregates is affected by their structure and charge.

Acknowledgement This work has been funded from the Polish budget for science (research project N N204537339, 2010-2013).

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EPR SPECTROSCOPY OF Cu^{2+} AND Mn^{2+} IN BORATE GLASSES

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Borate compounds in glassy and crystal phase are very interesting both from scientific point of view and wide range of possible applications including quantum and non-linear optics, radiation dosimetry and other domains. Borate glasses structure consists of randomly oriented boron oxide polyhedra (formed with boron in the center and oxygen atoms acting as a ligands), connected through sharing oxygen corners. Such structure is sometimes called 'random network'. Alkali and alkaline earth metal cations breaks some oxygen bridges between the polyhedra leaving some oxygen anions connected to only one boron atom, which leads to lowering of melting temperature of the glass. Spectroscopic properties of the glass are also dependent on introduced dopants often acting as the luminescence activators, manganese and copper are commonly studied dopants for borate compounds in this role [1,2].

Borate glasses with the $LiCaBO_3$ and CaB_4O_7 compositions doped with Cu and Mn were prepared from polycrystalline compounds: boric acid (H_3BO_3), calcium carbonate ($CaCO_3$) and additionally lithium carbonate (Li_2CO_3) for $LiCaBO_3$ glass. Doping process was performed by adding corresponding oxide: CuO or MnO_2 in amounts 0.5 and 1.0 mol. % to the raw materials. Glasses were obtained by multi step heating process of the substrates, melting product and cooling of the melt fast enough to make crystallization process unable. The obtained glasses were studied by electron paramagnetic resonance (EPR) at room temperature. The results were analyzed in comparison with corresponding data from our previous studies of the $Li_2B_4O_7$ and $KLiB_4O_7$ tetraborate glasses doped with Cu and Mn [2,3].

EPR studies shown that Cu dopant is incorporated into the glass network as Cu^{2+} ($3d^9$) paramagnetic ions. The EPR spectra of $LiCaBO_3$:Cu and CaB_4O_7:Cu are very similar and typical for other glasses. According to obtained EPR spectra parameters such as $g_{\parallel}$ and $g_{\perp}$ one can conclude that Cu^{2+} paramagnetic centers are coordinated by six O^{2-} anions with geometry of octahedron elongated along principal axis (tetragonally distorted octahedron, D_{4h} symmetry) due to Jahn-Teller effect. The ground state of unpaired electron of the Cu^{2+} cation in such case is $^2B_{1g}$ ($d_{x^2-y^2}$ orbital).

By means of EPR spectroscopy was shown that Mn dopant is incorporated into the glass network as Mn^{2+} ($3d^5$) paramagnetic ions. Obtained spectra of $LiCaBO_3$:Mn and CaB_4O_7:Mn was typical for Mn^{2+} ions in glassy state materials and can be attributed to single Mn^{2+} ions in trigonally distorted octahedral coordination of O^{2-} ions with broad distribution of crystal field parameters and pairs and small clusters of Mn^{2+} ions in the glass network.

The EPR spectra parameters of the Mn^{2+} and Cu^{2+} impurity centres in both glasses containing 0.5 and 1.0 mol.% of the MnO_2 and CuO doping oxides were determined. The obtained *g*-factor and hyperfine constant values are practically independent of the basic glass composition and concentration of Cu and Mn impurities in them. The increasing of dopant concentration leads to homogeneous broadening of EPR lines of the Mn^{2+} and Cu^{2+} centres, caused by magnetic dipolar interaction.

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NUMERICAL METHODS IN EPR EXAMINATION OF FREE RADICALS KINETIC IN GAMMA IRRADIATED ANTIBIOTICS

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Radiation sterilization technology is more actively used now that any time because of its many advantages, especially in case of antibiotics. Gamma radiation has high penetrating power, relatively low chemical reactivity and causes small temperature rise. But on the other hand radiosterilization can lead to radiolytic products appearing, in example free radicals.

12 samples of antibiotics administrated in parenteral way were used in studies. Samples were gamma irradiated by cobalt apparatus THERATRON 780E inclusive cobalt isotope ^{60}Co. Before radiosterilization, antibiotics were compressed into tablets without addition of auxiliary substances. Antibiotics were irradiated under air and the dose rate of gamma radiation was 1.2 kGy/min^{-1}. According to PN-EN552 norm the dose of radiation which was got down by every tested antibiotic amounted 25 kGy. The measurements of EPR of tested antibiotics were made by electron paramagnetic resonance spectrometer SE/X with modulation of magnetic field 100 kHz. Microwave radiation of type X of 9.3 GHz frequency was used in this case. The microwave radiation frequency was measured by MCM 101 (EPRAD). EPR spectra were recorded in forms of the first derivative absorption by 2mW microwave radiation, where we can not notice the microwave saturation. The full power of microwaves made by klystron reached 70 mW.

One- and two-exponential functions were fitted to experimental points during testing and researching of time influence of the antibiotics storage to parameters [I,A] of EPR lines. The identification of exponential model parameters K_o, K_1, K_2, τ_1 and τ_2 was executed by Gauss-Newton and Levenberg-Marguardt methods for the space of parameters searching, which scope was arbitrarily made. I (t) and A (I) patterns were fitted to one- or two-exponential functions to minimize δ error – during researching the time influence of storing of antiobiotics samples. The best theoretical matching to experimental points (estimated by following parameters K_o, K_1, K_2, τ_1 and τ_2) stated the least δ error. The pattern of made model parameters to δ error was also made in this case. I (t) and A (I) patterns were fitted to one- or two-exponential functions to minimize δ error – during researching the time influence of storing of antiobiotics samples. The best theoretical matching to experimental points (estimated by following parameters K_o, K_1, K_2, τ_1 and τ_2) stated the least δ error. Fitting of model parameters in line with mathematical function was made by Matlab.

The made researches of selected gamma irradiated antibiotics by spectroscopy of electron paramagnetic resonance showed the existance of free radicals in all samles. The free radicals in tested samples were created in irradiation antibiotics process. Experimental dependence of EPR lines intensity changes in time can be demonstrated by a one- and two- exponential functions.

Decline of the concentration is biggest during the first days after radiation. We can suppose the interactions of free radicals of medicinal substances with oxygen O_2 molecules are responsible for decreasing of concentration of free radicals in storaged antibiotics along with the time after radiation. Our study of free radicals in radiosterilized antibiotics indicates the need for characterization of medicinal substances prior to sterilization process using EPR values. We propose the concentration of free radicals and other spectroscopic parameters as useful factors to select the optimal type of sterilization for the individual drug.

The important parameters are i.a. the τ time constants and K constants of exponential functions. Time constants τ give us information about the speed of free radicals concentration decrease in radiated medicinal substances. The constants K show the free radicals concentration in irradiated madicament after long time of storage.

EFFECT OF MICROWAVE POWER ON EPR SPECTRA OF RADIOSTERILIZED AMINOGLZCOSIDE ANTIBIOTICS

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In the last years drugs sterilization by gamma-irradiation is very active investigate, because there are a lot of advantages of this method: high penetrating power (drugs can be sterilize in their final containers), low chemical reactivity, isothermal character of the gamma-rays, and radiosensitivity of microorganisms. The aim of this work was to study concentrations of paramagnetic centers, spin-spin and spin-lattice interactions in selected gamma-irradiated aminoglycoside antibiotics. Evolution of paramagnetic centers in this antibiotics during storage was examined. We compare microwave saturation of EPR spectra for different times after sample irradiation.

Samples were gamma irradiated by cobalt apparatus THERATRON 780E inclusive cobalt isotope ^{60}Co. Before radiosterilization, antibiotics were compressed into tablets without addition of auxiliary substances. The single punch eccentric tablet press Erweka EP-1 was used. Antibiotics were irradiated under air and the dose rate of gamma radiation was 1.2 kGy/min^{-1}. According to PN-EN552 norm the dose of radiation which was got down by every tested antibiotic amounted 25 kGy. The measurements of EPR of tested antibiotics were made by electron paramagnetic resonance spectrometer SE/X with modulation of magnetic field 100 kHz. Microwave radiation of type X of 9.3 GHz frequency was used in this case. The microwave radiation frequency was measured by MCM 101 (EPRAD). EPR spectra were recorded in forms of the first derivative absorption by 2mW microwave radiation, where we can not notice the microwave saturation. The full power of microwaves made by klystron reached 70 mW.

Dependence of parameters of EPR spectra – amplitudes (A) and linewidths (ΔB_{pp}) of tested samples on microwave power was stated. Researches of continuous microwave saturation of EPR lines were made in 1 day and 24 days after gamma irradiation of samples and were fitted to polynomial function of the sixth degree.

Received dependences show homogenous distribution of free radicals in all volume of irradiated antibiotics. Characteristic, for this kind of distribution of free radicals, decrease of amplitude of EPR lines for higher microwave powers and EPR lines broadening was noticed.

In was made comparison of changes of EPR spectra parameters (amplitude and linewidths) along with increase of microwave power for tested antibiotics 1 and 24 days after rrradiation. EPR lines of tested medicaments get saturated for lower microwave powers in case of samples analysed 1 day after irradiation. The changes of linewidths of EPR lines of researched antibiotics with microwave powers show similar character for analysed samples in 1 and 24 days after irradiation. The value of microwave power M (the value of microwave power corresponding to the maximum of the sixth degree polynomial function fit between EPR amplitude and the microwave power) points out the speed of spin-lattice relaxation in drug samples during their storage after gamma irradiation. For all tested antibiotics power M was similar.

EFFECT OF PHYSICAL CONDITIONS OF THERMAL STERILIZATION ON FREE RADICALS FORMATION IN FAMOTIDINE

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Free radicals were found in thermally sterilized drugs [1-4]. Free radicals concentration and properties depend on physical conditions of this process [1-4]. The aim of this work is to examine the effect of temperature and time of thermal sterilization on free radicals formation in famotidine. Famotidine is a histamine H_2-receptor antagonist that inhibits stomach acid production, and it is commonly used in the treatment of peptic ulcer disease and gastroesophageal reflux disease [5-6]. Chemical structure of the tested drug is presented in Figure 1 [5].

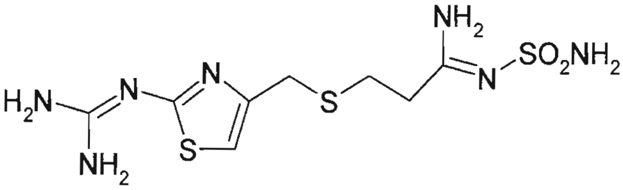

Fig. 1. Chemical structure of famotidine [5].

EPR spectra of the sterilization products were measured at room temperature by the use of RADIOPAN (Poznań) spectrometer with the system of numerical acquisition of JAGMAR Firm (Kraków). The parameters and lineshape of the EPR spectra were analysed at wide range of microwave power from 2.2 mW to 70 mW. Free radicals concentrations in the drug samples sterilized at 160 °C (120 minutes), 170 °C (60 minutes), and 180 °C (30 minutes). The tested temperatures and times of heating of the famotidine samples are the same as those in the norms of sterilization process in pharmacy [7-10]. The obtained results indicate that free radicals exist in all the tested samples, but their concentrations depend on the temperature and time of thermal treatment. The shape of the EPR spectra points out that several types of free radicals exist in the thermally sterilized famotidine. Continuous microwave saturation of the EPR lines was use to discuss the times of spin-lattice relaxation processes in the heated drug samples. It was observed that the existence of oxygen in the sample environment causes the changes in paramagnetic centers system in the thermally sterilized famotidine during storage. The changes of free radicals properties of famotidine and the others drugs [1-4] during heatin at different temperatures were compared. The application of electron paramagnetic resonance spectroscopy to optimization of sterilization processes in pharmacy was discussed.

Acknowledgements
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EPR AND DRIFT STUDIES OF THERMALLY STERILIZED SIMVASTATIN

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Sterilization process in pharmacy is preformed to kill microorganisms in drugs and as the result to rise the safety of the pharmacotherapy [1]. The popular method of drug sterilization is the thermal sterilization with hot air circulation in the drug samples [1]. The parameters of this process is determined by pharmaceutical norms [2-5]. Thermal sterilization should not produce the high amount of freer radicals in the drugs and their chemical structure should not be destroyed. Free radicals in the sterilized drugs may be studied by electron paramagnetic resonance (EPR) spectroscopy. The chemical stability of the heated drugs may be tested by the use of DRIFT spectroscopy. Free radicals and chemical structure of thermally sterilized simvastatin were examined in this work. The chemical structure of the original non-heated simvastatin is presented in Figure 1 [6]. The aim of this study is to find optimal conditions of thermal sterilization of the analysed drug.

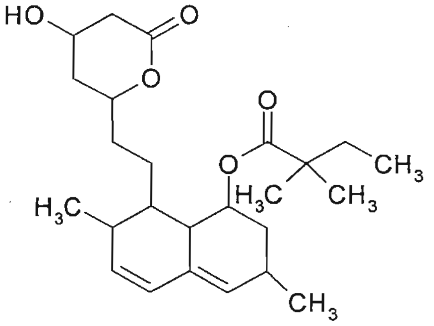

Fig. 1. Chemical structure of simvastatin [6].

Sterilization was performed at temperatures: 160 °C (120 minutes), 170 °C (60 minutes), and 180 °C (30 minutes). The electron paramagnetic resonance spectra were measured at room temperature by the use of an X-band (9.3 GHz) EPR spectrometer of RADIOPAN Firm (Poznań) and the system of numerical acquisition of JAGMAR Firm (Kraków). g-Factors, amplitudes, integral intensities, and linewidths of the EPR spectra were analysed. Free radicals concentrations were determined. The effect of microwave power on the lineshape and parameters of the EPR spectra was presented.

The Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra were recorded on a Bio-Rad FTS 165 spectrometer equipped with a Harrick Praying Mantis diffuse reflectance accessory. The spectra were recorded from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} by averaging 256 scans. Potassium bromide (KBr) was used as the diluting agent (5/95 m/m sample to KBr) and stored at 120°C before use.

The original simvastatin sample was diamagnetic. EPR spectra were obtained for the thermally sterilized simvastatin. The parameters of the EPR spectra, microwave saturation of the lines, and freer radicals concentrations in the heated samples depend on the conditions of sterilization. It was shown that EPR and DRIFT methods may be used to optimize the thermal sterilization process of simvastatin and conditions of its storage.

Acknowledgements
This study was supported by Medical University of Silesia in Katowice.

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MICROWAVE SATURATION OF EPR SPECTRUM OF CHOLIC ACID HEATED AT DIFFERRENT TEMPERATURES

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Electron paramagnetic resonance (EPR) examination of free radicals formed in cholic acid thermally sterilized according to pharmaceutical norms was performed. Chemical structure of ursodeoxycholic acidis shown in Figure 1 [1]. Heating of powdered samples was done according to Norms [2] for thermal sterilization at the following conditions (T – temperature, t – time): T = 160°C and t = 120 minutes, T = 170°C and t = 60 minutes, and T = 180°C and t = 30 minutes.

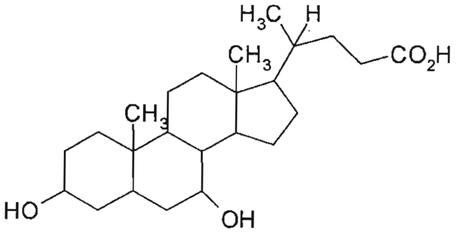

Fig. 1. Chemical structure of cholic acid [1].

EPR analysis for ursodeoxycholic acidis was done 0.5 hour, 2 and 8 days after sterilization. EPR measurements were performed for the sterilized samples at room temperature. The spectra were measured by the use of RADIOPAN (Poznań, Poland) spectrometer with microwave frequency 9.3 GHz (X-band). Microwave frequency was measured by MCM101 recorder (EPRAD, Poznań, Poland). EPR spectra were recorded as first derivative lines with magnetic modulation 100 kHz in the range of microwave power from 2.2 mW to 70 mW. The following parameters were determined: g-factor, amplitudes (A), integral intensities (I), and linewidth (ΔB_{pp}) of the EPR spectra. The shapes parameters were analysed. g-Factor was calculated from resonance condition as [3]: $g = h\nu/\mu_B B_r$, where: h – Planck constant, ν – microwave frequency, μ_B – Bohr magneton, B_r – resonance magnetic induction. Free radical concentration (N) was determined by comparison to its values for the ultramarine used as the reference.

EPR spectrum was not obtained for the non-heated sample. Asymmetrical EPR lines were measured for the studied heated drug. Properties and free radical concentration in heated ursodeoxycholic acidis during storage of this sample was studied. Free radicals appear in cholic acid after heating of the sample. The lowest free radicals concentration was obtained for the drug sterilized at temperature 160°C. Free radical concentration in heated ursodeoxycholic acidis changes with increasing storage time of the sample. Influence of microwave power on lineshape, amplitudes, integral intensities and linewidth of EPR spectra were described. Continuous microwave saturation of EPR lines point out that slow spin-lattice relaxation processes exist in the heated ursodeoxycholic acidis.

Acknowledgements This study was supported by Medical University of Silesia in Katowice.

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FREE RADICALS IN THERMALLY STERILIZED DIGOXIN AND OPTIMIZATION OF THIS PROCCESS

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Electron paramagnetic resonance (EPR) spectroscopy was used to examination of free radicals in thermally treated digoxin. Thermal treatment in hot air as sterilization process was tested. Sterilization is expected to exterminate microorganisms in drugs [1], but chemical structure and therapeutic interactions of drugs with tissues should not be modify. Conditions of thermal sterilization are described in the pharmaceutical Norms [2]. It is expected that thermal sterilization breaks chemical bonds and produce free radicals in drugs depend on temperatures. It is known a lot of our works about formation of free radicals in organic pharmaceutical substances at high temperature [3-5]. The aim of this work was to determine concentration and free radical properties of thermally sterilized digoxin. Digoxin is widely used in the treatment of various heart conditions, namely atrial fibrillation, atrial flutter and sometimes heart failure that cannot be controlled by other medication [6]. Chemical structure of digoxin is presented in Figure 1 [6].

It is not found in literature information about free radicals in this drug. EPR results for digoxin were compared to results obtained for the others thermally sterilized drugs [7].

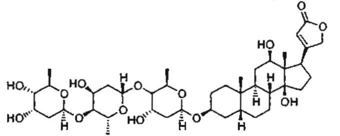

Fig. 1. Chemical structure of digoxin [6].

Heating process of powdered digoxin sample was done according to Norms [2] for thermal sterilization at the following conditions (T – temperature, t – time): T = 160°C and t = 120 minutes, T = 170°C and t = 60 minutes, and T = 180°C and t = 30 minutes.

EPR analysis for digoxin was done 0.5 hour, 15 and 45 days after sterilization. EPR measurements were done at room temperature. EPR spectra were recorded in the range of microwave power of 2.2-70 mW. g-Factor, amplitudes (A), integral intensities (I), and linewidth (ΔB_{pp}) of the spectra were determined. The shape of the EPR spectra was analysed. Free radical concentration (N) was determined by the use of ultramarine as the reference.

EPR spectra were not obtained for the non heated digoxin. As was expected free radicals do not exist in the original drug sample. EPR spectra were detected for the all thermally sterilized samples. The spectra revealed complex character, their asymmetry depends on microwave power. The lowest free radicals concentration was found for the digoxin sterilized at temperature 180 °C during 30 minutes. Free radicals concentrations in sterilized digoxin change during storage as the result of oxygen interactions with the samples.

Acknowledgements This study was supported by Medical University of Silesia in Katowice.

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APPLICATIONS OF EPR, UV AND DRIFT METHODS TO ANALYSES OF DIFFERENT METFORMIN PROBES

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The pharmaceutical active substance exists together with the support components in tablets. These components may interact with the basic pharmaceutics and as result the effectiveness of the drug may be changed. The interactions of the individual components in the large amount of commercially used drugs tablets are not well known. EPR, UV, and DRIFT spectroscopies, are proposed to test the complex pharmaceutical tablets. The exemplary drug as metphormin was examined in this work.

Metformin is the is an oral antidiabetic drug in the biguanide class. It is the first-line drug of choice for the treatment of type 2 diabetes, in particular, in overweight and obese people and those with normal kidney function[1-2]. Chemical structure of metformin is shown in Figure 1 [1-2].

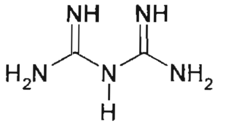

Fig. 1. Chemical structure of metformin [1].

The antioxidative properties are the most interesting feature of the tested drug. The interactions with free radicals were examined by an X-band (9.3 GHz) EPR spectroscopy. The interactions of different metformin tablets with DPPH free radicals were studied. The quenching of EPR lines of DPPH by the drug samples was determined. The UV spectra of the solutions of different metformin tablets were also compared. The UV measurements were done by the use of OCEAN OPTICS spectroscop.

The important problem is the microbiological purity of metformin. The thermal sterilization is proposed by pharmaceutical norms [2]. The free radicals formation in the exemplary thermally sterilized metformin probes was tested by EPR method. The DRIFT method was applied to check the chemical stability of metformin at the thermal sterilization conditions. DRIFT spectra were recorded on a Bio-Rad FTS 165 spectrometer equipped with a Harrick Praying Mantis diffuse reflectance accessory. The spectra were recorded from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} by averaging 256 scans. Potassium bromide (KBr) was used as the diluting agent (5/95 m/m sample to KBr) and stored at 120 °C before use. The studies metformin by the use of the major experimental methods confirm their practical application in pharmacy.

Acknowledgements
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APPLICATIONS OF EPR SPECTROSCOPY IN PHARMACY

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The major applications of electron paramagnetic resonance spectroscopy at X-band (9.3 GHz) in pharmacy are presented. This work is focused on the different subjects of EPR studies important to practical applications of drugs, which were performed by us earlier [1-10]. EPR method was used to examine free radicals formation during radiative [1] and thermal [2-4] sterilization of antibiotics and the others drugs. Kinetics of decay of different types of free radicals in gamma irradiated drugs were tested [1]. The conclusions are useful to determine the best conditions of their storage. The optimization of thermal sterilization of drugs was done by EPR method [2-4].

The EPR examination was performed for model and natural melanins [5-10], and complexes of melanins with drugs and metal ions [6-10]. The different types of paramagnetic centers in melanin samples were characterized. o-Semiquinone free radicals ($S = 1/2$) [5-10] and biradicals ($S = 1$) [9-10] were studied. The changes in paramagnetic centers system in melanins after their complexing by drugs were described [6-10]. The effect of the presence of metal ions on formation of free radicals complexes with drugs was determined [6, 9-10]. The results [5-10] bring to light the role of melanins paramagnetic centers as the source of toxic effects in tissues during pharmacotherapy.

Acknowledgements These studies were supported by Medical University of Silesia in Katowice.

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EPR APPLICATIONS TO EXAMINATION OF OILS

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The application of electron paramagnetic resonance in food chemistry to test the antioxidative properties of the wide group of oils is proposed. The interactions of different oils with free radicals were examined. The EPR spectra of DPPH located in the oils were measured. The integral intensities of the EPR spectrum of solution of DPPH in ethanol and the EPR spectra of DPPH in the individual oils were compared.

The EPR measurements were done by the use of RADIOPAN spectrometer with modulation of magnetic field 100 kHz. The EPR spectra were numerically recorded by system of JAGMAR Firm (Kraków). Microwave frequency was measured by MCM detector of EPRAD Firm (Poznań). The low microwave power of 2 mW was used to avoid microwave saturation of the spectral lines.
The oils *Camelina sativa* were studied.

During storage and thermal treatment of edible oils, there are adverse effects of fatty acid metabolism, resulting in the intermediate peroxyl radicals. These changes relate mainly to oil, containing in its composition of polyunsaturated fatty acids Ω-6 and Ω-3, which readily undergo oxidation processes [1]. Not very popular in Poland, Camelina sativa oil contains almost 90% of unsaturated fatty acids, including 36.1% α-linolenic acid (Ω-3), which plays an important function in preventing and treating many diseases of the cardiovascular system [2].

It was observed that the quenching of the EPR lines of DPPH depends on the origin and composition of the oils. The interactions of the tested oils with free radicals changes after thermal treatment of the liquid samples. The usefulness of EPR spectroscopy to selection of the valuable oils in diet was proved. The evolution of the antioxidative properties during processes of food preparation was discussed.

Acknowledgements
This study was supported by Medical University of Silesia in Katowice.

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EPR STUDIES OF FREE RADICALS IN DIFFERENT PLANT SAMPLES

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Free radicals in the decoctions of drying and steam sterilized vegetables studied by the use of an X-band (9.3 GHz) electron paramagnetic resonance (EPR) spectroscopy. The first-derivative EPR spectra were recorded by RADIOPAN (Poznań, Poland) spectrometer with magnetic modulation of 100 kHz at room temperature. The total microwave power (M_o) produced by klystron was 70 mW. Microwave frequency was directly measured by MCM101 recorder of EPRAD Firm (Poznań, Poland). The numerical acquisition of the EPR spectra was performed by the Rapid Scan Unit of JAGMAR Firm (Kraków, Poland).

The parameters of the EPR spectra were analysed by spectroscopic programs of JAGMAR Firm (Kraków, Poland) and LabView 8.5 Firm (National Instruments). g-Factors, amplitudes (A), integral intensities (I), linewidths (ΔB_{pp}) of the EPR spectra were determined. g-Values were obtained from the resonance condition. Free radical concentrations (N) in the samples were determined. Ultramarine was used as the reference. A ruby crystal (Al_2O_3: Cr^3) permanently placed in a resonance cavity was used as the second reference.

Decoctions were prepared from dried, sterilized and unsterylised vegetables. Parsley, leek, onion and parsnip roots were studied. Vegetables to study were drying and steam sterilized by Jaworski Vegetable Drying Plant (Błonie, Poland).

Dried vegetables can be stored for several months and then used to prepare the dishes. To maintain their nutritional value during storage it is necessary to remove the microflora. One way to protect against microbiological contamination of food is steam sterilization, which can cause inactivation of antioxidant contained in it, and the formation of free radicals [1, 2, 3].

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ANTIOXIDATIVE PROPERTIES OF ELAGIC AND FOLIC ACIDS

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Electron paramagnetic resonance studies of interactions of elagic acid and folic acid with free radicals were performed.

Folic acid (pteroyl-L-glutamic acid) belongs to the group of vitamin B. Folic acid consists of pteridin derivative (2-amino-4-hydroxy-6-methylpteridin), p-aminobenzoyl acid (PABA) and glutamic acid [1]. The active form of folacin is 5,6,7,8-tetrahydrofolic acid (THF). THF plays crucial role as a co-enzyme in many metabolic reactions in the human body.

Recent data from couple cosmetic manufactures shows that folic acid has regenerative properties and protects skin against premature ageing and negative influence of UV light [2].

Folic acid can be easily decomposed by UVA. UV-induced folic acid photolysis not only cause folic acid degradation in the body and in a consequence it's deficiencies for all biochemical processes, but also results in solar- induced DNA damage, possibly resulting in the initiation process of skin cancer. Photoirradiated folic acid generates pterine-6-carboxylic acid (PCA) and p-aminobenzoyl-glutamic acid. PCA induces DNA photooxidation specifically at consecutive G residues through electron transfer [3, 4].

Ellagic acid is a polyphenol - a dimeric derivative of gallic acid. This compound exhibits antioxidant, antiproliferative and chemopreventive properties. Ellagic acid exerts its effects via activation of various signaling pathways, including apoptosis, protection from oxidative DNA damage and alteration of growth factor expression [5, 6].

The aim of this work was to compare antioxidative properties of elagic and folic acids. The antioxidative properties of the equimolar mixture of these two types of acids were examined. The influence of UV (UVA and UVB) irradiation on the ability of elagic and folic acids, and their equimolar mixture to interactions with free radicals was determined.

EPR spectra were measured by the use of an X-band (9.3 GHz) spectrometer produced by RADIOPAN Firm (Poznań, Poland). Magnetic modulation of 100 kHz was used. Microwave frequency was measured by the recorder of EPRAD Firm (Poznań, Poland). EPR spectra of DPPH methanol solutions and DPPH located in the tested samples were compared. The quenching of the EPR signal of DPPH by the examined samples was determined as the measure of their antioxidative properties. The EPR spectra were recorded with the low microwave power of 2.2 mW to avoid the microwave saturation of the signals. The numerical acquisition of the EPR data was done. The spectroscopic programs of the JAGMAR Firm (Kraków, Poland) were used. The different antioxidative properties of the tested acids were discussed. The changes of their interactions with free radicals after UV irradiation was shown.

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EPR STUDIES OF CLADOSPORIUM CLADOSPORIOIDES COMPLEXES WITH AMPHOTERICIN B

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Free radicals in *Cladosporium cladosporioides* cultured with amphotericin B were spectroscopically studied. The effect of drug concentrations on free radicals concentrations and properties were examined. The following concentration of complexing agent were used [$\mu g/cm^3$]: 1.8, 4.5, 8.1. Amphotericin B is the antifungal drug [1], which is often used intravenously for systemic fungal infections (e.g., in critically ill, comorbidly infected or immunocompromised patients). Two amphotericins: amphotericin A and amphotericin B are known, but only B is used clinically [1].
EPR spectra of the melanin complexes were measured by the use of an X-band (9.3 GHz) spectrometer of RADIOPAN Firm. The numerical acquisition of the spectra was done by the system of EPRAD Firm. Free radicals concentrations were determined. g-Values of the complexes were compared. The influence of microwave power in the range of 2-70 mW on the parameters of the EPR spectra was tested. The results were compared to our earlier data for free radicals in *Cladosporium cladosporioides* melanin and its complexes with flucytosine – the other typical antifungal drug [2-5]. EPR spectra of the analysed natural melanin samples were compared to EPR spectra of model eumelanin – DOPA-melanin.

The role of o-semiquinone free radicals of *Cladosporium cladosporioides* melanin in binding of amphotericin B was proved. The binding of drugs to melanin via free radicals was observed by us earlier [6-8]. Similar to flucytosine [2-5], mainly EPR component of the eumelanin exist in the resonance absorption curve of *Cladosporium cladosporioides* complexes with amphotericin B. Only the low amount of pheomelanin exists in the tested complexes. Concentrations of free radicals and the parameters of the spectra of the examined samples depend on the amphotericin B presence in the melanin polymer. The complexation of melanin in *Cladosporium cladosporioides* by amphotericin B may cause prolongated interactions of this drug with the whole sample. Free radicals of the examined melanin biopolymer play an important role in interactions of amphotericin with the biological systems.

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EFFECT OF MICROWAVE POWER ON EPR SPECTRAOF DOPA-MELANIN-NETILMICIN COMPLEXES WITH DIFFERENT DRUG CONCENTRATIONS - THE STUDY AT TEMPERATURES IN THE RANGE OF 110-290 K

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EPR spectra of the model eumelanin – DOPA-melanin complexes with netilmicin were measured with microwave power in the range 0.3-200 mW. The influence of microwave power on amplitudes (A), integral intensities (I) and linewidths (ΔB_{pp}) of the spectra was determined. The EPR spectra were recorded by BRUKER spectrometer at temperatures from 110 K to 290 K. Continuous microwave saturation of EPR lines was used to compare the velocity of spin-lattice relaxation processes in melanin samples. Changes of the parameters of the EPR spectra of DOPA-melanin-netilmicin complexes with microwave power for the samples differ in netilmicin concentrations were observed. The effect of microwave power on the EPR spectra of the analysed melanin complexes at different temperatures was compared.

The model DOPA-melanin was chose to studies, because eumelanin mainly exist in the natural samples of living organisms. DOPA-melanin was obtained according to the Binns method [1]. Netilmicin is the popular aminoglycoside antibiotic, which is used in the treatment of serious infections (e.g. sepsis, infections of the respiratory and urinary tract) [2-3]. Netilmicin is characterized by lowest toxicity of this aminoglycoside antibiotic and high practical applications [2]. Complexes of melanin samples with netilmicin were obtained as follows: 40 mg of melanin were incubated with 40 ml of drug solutions in 0.067 M phosphate buffer at pH 7.0. The following netilmicin concentrations were used to obtain the melanin-drug complexes [M]: $1\text{x}10^{-4}$, $5\text{x}10^{-4}$, $1\text{x}10^{-3}$, $5\text{x}10^{-3}$, $1\text{x}10^{-2}$.
Temperature EPR examination pointed out that o-semiquinone free radicals ($S = 1/2$) and biradicals ($S = 1$) exist in DOPA-melanin-netilmicin complexes. o-Semiquinone free radicals are the well known paramagnetic centers in melanins [4-8] and biradicals are the new type of detected paramagnetic centers in melanin [5, 8]. In this work we focused on microwave power and temperature effects on the EPR lines of free radicals.

Acknowledgements
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ELECTRON PARAMAGNETIC RESONACE IN PPI THIN FILMS

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Paramagnetic centers in pristine and iodine doped thin films of poly(1,4-phenylenemethylenenitrilo-1,4-phenylenenitrilomethylidyne) (PPI) deposited onto microscopic glass substrates under different conditions were studied. PPI is the simplest aromatic polayzaomethine, whose chain resemble poly(p-phenylenevinylene) (PPV) [1-2]. Having the same electronic structure as PPV, PPI thin films are expected to be also promising material for optoelectronic application.

The spectra were recorded at room temperature by the use of an X-band (9.3 GHz) EPR spectrometer with magnetic modulation of 100 kHz produced by RADIOPAN Firm (Poznań). Microwave frequency was measured by MCM 101 recorder of EPRAD Firm (Poznań). To avoid microwave saturation EPR spectra were measured at low microwave power of 2.2 mW. The following parameters of the spectra: amplitude (A), integral intensity (I), linewidth (ΔB_{pp}) and g-factor, were determined. The spectroscopic programs of EPRAD (Poznań) and JAGMAR (Kraków) Firms and the ORIGIN program were used in analysis. The influence of microwave power in the range of 2.2-70 mW on the EPR spectra was examined. The changes of amplitude (A) and linewidths (ΔB_{pp}) with increasing of microwave power were evaluated. The type of EPR line broadening was determined.

EPR spectra were not obtained for the original poly(1,4-phenylenemethylenenitrilo-1,4-phenylenenitrilomethylidyne) sample. Broad EPR lines were measured for PPI thin film after iodine addition to the polymer. It was shown that similar to the others conducting polymers [3-6] paramagnetic centers in PPI result from conducting state of this polymer. Paramagnetic centers in PPI chains are formed while transferring π-electrons from HOMO level of conjugated segments onto iodine atoms. The number of paramagnetic centers depends on degree of iodine doping.

Acknowledgements
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CHANGES IN PLASMA VISCOSITY UNDER THE INFLUENCE OF NIR RADIATION MONITORED BY SPIN PROBES

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Blood plasma is the liquid component of blood, consisting of around half of the total blood volume. Plasma itself is around 90% water, with the 10% remainder including proteins, minerals, waste products, clotting factors, hormones, and immunoglobins. Plasma's viscosity is determined by water-content and plasma proteins concentration. In order to obtain information on plasma environment, it is possible to use water-soluble probes such as derivatives of 2,2,6,6-tetrametylpiperidine presented on the Fig.1. The chemical properties of the spin label are presented in the table 1 [1]. The success of this type of probing of the intracellular environment is due to ability of the spin label to diffuse into cellular space or to form hydrogen bonded complexes with surface of proteins and polymers. In this experimental condition, the EPR signal of the spin probe can be used to obtain information on the microviscosity of the medium by the rotational correlation time τ_c. The hydrogen-bonding character of the nitroxide functional group may be observed directly and separately from that of the amine or hydroxyl functional group on the TAMINE or TEMPOL molecule in a low-viscosity medium. In this case the electronic structure of the nitroxide is perturbed toward the more ionic resonance form by hydrogen bonding with a consequent increase in the isotropic hyperfine splitting constant, A_N. The amine or hydroxyl hydrogen-bonding character is manifested by the rotational correlation time when a hydrogen complex is formed. In the plasma medium the spin label tumbles isotropically

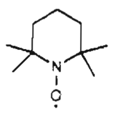	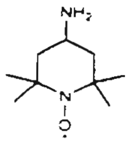	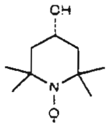
TEMPO	Amino-Tempo TAMINE	Hydroksy-Tempo TEMPOL

Fig. The chemical formula water soluble probes, derivatives of 2,2,6,6-tetrametylpiperidine

Spin probe	Tumb ling Correlation time	Acidity of hydrogen bonds α Scale from 0-1	Basicity of hydrogen bonds β Scale from 0-1 –	The molecular Volume [A³]	A_N in Non polar medium [mT]	A_N in Polar medium [mT]
Tempo	10^{-11} 10^{-10}	0	very weak	171	1,54	1,66
Tempol		0,30	0,51	177		
Tamine	10^{-11}	0	0,72	182	1,52	1,69

Table 1 the properties of water soluble spin label: A_N Hyperfine splitting in polar and nonpolar medium [1]

The rheological measurements showed that after exposition to near infrared radiation (NIR) the plasma viscosity slightly increases. The viscosity changes were also monitored by application of the water soluble spin probes. The plasma was taken from Lower Silesia Center of Blood Donation and Blood Therapy and irradiated by wavelengths from the region 750 to 1200 nm. The experiments with the TEMPOL spin probe show decreasing correlation time effect while increase of A_N indicates hydrogen bonding between the nitroxide group and plasma. The correlation time shows enhanced hydrogen bonding through the TAMINE amine functional group, the correlation time increases. The effects of radiation strongly depends on the wavelengths. For 750 nm the correlation time decreases while for all wavelengths from the used interval 750 -1200 nm A_N was stable. Also for TEMPO spin probe for irradiated samples correlation time increased. Value of the correlation time increases for 30 minutes after exposure and later relaxed to the value before irradiation. Differences in the measured parameters indicate the diffusion of selected spin probes in the various centers of structurally inhomogeneous human blood plasma.

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AN IMAGE RECONSTRUCTION METHOD OF SPATIAL DISTRIBUTION OF OXYGEN CONCENTRATION IN EPR TOMOGRAPHY

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EPR tomography (or EPR imaging) allows obtaining cellular metabolism by measuring oxygen concentration, and based on this get information about size and localization of the tumor [1]. We present a methodology for recovering of spatial distribution of oxygen concentration in two dimensions from a set of projections. An input for the presented O_2 image reconstruction method are projections obtained with our self -made prototype of EPR tomograph. The new signal analyze technique based on rapid scan EPR method was applied. The method allows obtaining a projection of T_1 from only one spectra by measuring difference between the EPR signal amplitudes for up and down rapid magnetic field slope. This difference is T_1 dependent, and could be measured by EPR signal amplitude ratio [2].

Apart from the projections an initial image of radical density distribution [3,4] is processed by the O_2 reconstruction algorithm. The initial image is obtained by means of inverse Radon transform. We found that Ordered Subsets Expectation Maximization (OSEM) [5] algorithm is superior to traditional Filtered Backprojection (FBP) [6] method.

The O_2 concentration distribution images of the three-tube phantom containing LiPc radicals are presented in Fig. 1. The experimental parameters were: scan frequency 5 kHz, sweep width 6.6 G, magnetic field gradient 1.83 G/cm, RF frequency 212 MHz, number of projection 36, with 10.000 averages.

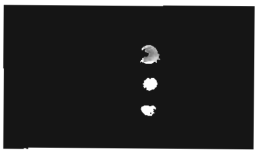

Figure 1. The O_2 concentration distribution images of the three-tube phantom containing LiPc radicals.

The initial results indicates potential usefulness of the method. More work is required to calibrate the imaging system and to quantitatively assess the accuracy of the reconstruction.

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METHOD OF GENERATING HOMOGENEOUS MAGNETIC FIELDS FOR EPR TOMOGRAPHY

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In many applications magnetic field is required to be highly homogenous over some specified volume. Especially homogeneous magnetic fields are important in magnetic resonance imaging experiments. Many systems used for medical diagnostic studies are build with solenoidal superconducting electromagnets. These solutions are expensive and in certain applications cannot be used because of limited access to the region of uniform magnetic field. In some functional NMR imaging experiments [1] and particular in EPR imaging [2] electromagnets generate low fields with possible access to the working space from all directions. A classic example of systems are air-core assemblies build with a some number of circular or square windings placed co-axially and distributed so that the leading perturbation terms in the field series expansion are eliminated [3,4].

In this paper we consider the system consisting of two coaxial pairs. These circular loops have the same radius. The use of properly distributed windings of the same radius allows the radial access to the uniform field and axial access, as well. In systems based on spherical harmonic expansion with outer pair of windings of smaller radius, the axial access is limited.

The invention describes two families of solutions for the construction of the coils. These two families of designing allow to adjust the systems to the geometry desired.

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METHOD OF MEASURING T1 ELECTRON RELAXATION TIMES IN EPR TOMOGRAPHY

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EPR tomography (or EPRI) allows obtaining cellular metabolism by measuring oxygen concentration, and based on this we get information about size and localization of the tumor. It should be noted, that EPR is considered (not only by EPR experts) to be the "gold standard" for intra-cellular oxygen quantification [2, 3] and at least equivalent to electrochemical methods for extra-cellular applications.

Apart from the proposed electron relaxation times measurement method there is also the location system of imaging cancerous lesions by EPRI, which uses the traditional technique of EPR with modified electronic components operated in the radio frequency spectrum – safe for living matter. This method enables also quadrature detection by a technique based on frequency modulation allowing to register adiabatic transition and providing data on the fast pharmacokinetics of free radicals and oxygen concentration in the tissues.

So far, the most widely used techniques for measuring the relaxation time T2 and T1 are pulsed EPR methods of detection of transverse magnetization component. The main problem is the shortening of T2 relaxation time due to the presence of the gradient field. It results in significant loss of free induction decay signal (FID) which occurs during the dead time of the spectrometer. In traditional methods it is impossible to detect this signal. The new patented method of measuring relaxation time of spin-lattice T1 is devoid of these limitations because it uses rapid adiabatic passage and the detection of the longitudinal magnetization component [1].

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FAST DATA ACQUISITION METHODOLOGY IN EPR TOMOGRAPHY

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Electron paramagnetic resonance technique, applied to the detection of cancerous changes in living organisms, is focused on the use of magnetic fields in range from tens to several hundred gauss. This implies the use of radio frequencies. Optimization of automatic process control and data acquisition is an important factor influencing the total time of experiment[1]. In the developed solution direct-detection Rapid Scan technique was used, which allows one to shorten the measurement time for accumulation to only several hundred μs. The time required to perform hundreds of signals accumulation is comparable to the time required for reorientation of the gradient and transfer the recorded data.

In the developed solution a method to optimize the measurement parameters is presented. The solution allows the reconstruction of 2D concentration of radicals density distribution and the concentration of oxygen by Rapid Scan EPR technique[2]. For measurements was used a phantom consisting of three samples of LiPc (Lithium phthalocyanine). Measuring parameters were as follows: the number of projections - 36, the frequency of magnetic field scanning - 5 kHz, the amplitude of scanning - 6.6Gs, the number of signals in accumulation - 400. The total measurement time was 20 seconds.

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THE ABILITY OF Nb_2O_5 AND Ta_2O_5 TO GENERATION OF ACTIVE OXYGEN IN CONTACT WITH H_2O_2

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Hydrogen peroxide is often used as environmentally friendly oxidant. Its interaction with the surface of catalysts determines the further transformation and reaction with the oxidized molecule. Depending on the type of catalyst surface the different types of O-O bond cleavage in H_2O_2 can occur, i.e. homolytic or heterolytic, and different types of oxidative species can be generated. In this contribution the focus is on the interaction of H_2O_2 (or tert-butyl hydroperoxide (WNTB) for comparison) with two Group Five metal oxides: Nb_2O_5 and Ta_2O_5.

Commercial (CBMM-Brazil) hydrated (amorphous) and anhydrated (crystalline) Nb_2O_5 (Alfa-Aesar), Ta_2O_5 were applied. Moreover, amorphous Nb_2O_5 and Ta_2O_5 were prepared by the precipitation of $Nb(Ta)(C_2H_5O)_5$ in water. All oxides were treated with two different oxidants: hydrogen peroxide and tert-butyl hydroperoxide (WNTB) (oxidant/Nb = 1:1, 5:1). The materials were characterized by the use of XRD, UV-Vis, IR spectroscopy. However, the main technique applied in this study was EPR.

Hydrogen peroxide treatment of Grup Five Metal oxides leads to the change of white color to yellow one (typical of metal peroxo species [1]) only in the case of both amorphous niobium oxides (hydrated and obtained by the precipitation method). EPR and IR studies confirm the formation of Nb peroxo species. FTIR spectra of amorphous Nb_2O_5 after H_2O_2 treatment show the band at ca. 870 cm^{-1} from ν(O-O) vibration [2], whereas EPR spectra exhibit the characteristic signal assigned to $O{=}Nb(V)O_2^-$ radical species [3]. The highest intensity of the IR band and EPR signal is observed when higher H_2O_2/Nb ratio (5:1) is applied due to higher concentration of the metal peroxy radicals. The interaction of amorphous niobia with hydrogen peroxide is also confirmed by the changes in the UV-Vis spectra (the changes in the spectra in the range 300-400 nm). Contrary, interaction of amorphous Nb_2O_5 with tert-butyl hydroperoxide is much weaker (in EPR spectra of amorphous Nb_2O_5 treated with this peroxide a low intensity signal from $O{=}Nb(V)O_2^-$ radical species appears). Interestingly, the EPR spectrum of amorphous Ta_2O_5 after treatment with H_2O_2 is considerably different in comparison to the spectrum of Nb_2O_5 treated with H_2O_2. In contrast to niobia, superhyperfine structure in EPR spectrum was not observed for Ta_2O_5. Superhyperfine structure results from the unpaired electron interaction with a surface ion nucleus which has a non zero nuclear spin (for tantalum nuclear spin I=7/2). The spectrum of the oxygen radicals generated on Ta_2O_5 has a rhombic symmetry and the tensor g has three distinct components. It is important to note that the ten-hour evacuation at room temperature of both the amorphous samples (Nb_2O_5 and Ta_2O_5) treated with H_2O_2 or WNTB caused an increase in the intensity of EPR signals originating from oxygen radicals. This effect is much more visible for Nb_2O_5. The evacuation of the samples at 323-423 K did not cause the significant changes in the EPR spectra besides intensity of signals. After evacuation at 473 and 523 K for Nb_2O_5 and Ta_2O_5, respectively, EPR spectra indicate the presence of O^- radical species.

The crystalline oxides containing niobium or tantalum after interaction with hydrogen peroxide and also with WNTB do not show the presence of $O{=}MO_2^-$ radical species. It indicates that amorphous niobia and Ta_2O_5 are responsible for their unique properties in the interaction with H_2O_2.

The phenomenon of interaction of amorphous oxides with peroxides can be attributed to the M-O-M bond weaker in amorphous phase than in the crystalline one. In the amorphous phase niobium and tantalum species are more mobile than in the crystalline materials and therefore their interaction with peroxides is much easier. This effect is more pronounced in case of H_2O_2 than WNTB interaction with metal oxides.

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EPR STUDY OF ZINC AMMONIUM PHOSPHATE HEXAHYDRATE SINGLE CRYSTALS DOPED WITH VO2+ IONS

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Abstract

Electron paramagnetic (EPR) results obtained for zinc ammonium phosphate (ZAPH) single crystals, doped with VO^{2+} ions are reported with special emphasis on spectrum changes which reveal the effect of vanadyl ions on the spin Hamiltonian g and A parameters.

Vanadyl complexes have been the subject of interest to a number of researches over resent years [1-5].

EPR study of VO^{2+} : ZAPH has been done earlier by Chand et al. [6] observing only single site while in our study two inequivalent sites of VO^{2+} ion are observed. By correlating EPR and optical data various molecular orbital coefficients of the vanadyl ion in the ZAPH lattice are evaluated and the nature of bonding in the crystal is discussed.

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