

Surface-analytical and EPR studies on sediment samples in Herăstrău Lake, Romania

E. D. SELEȚCHI*, C. NEGRILĂ^a, O. G. DULIU, C. V. ȚURCAȘ^b

University of Bucharest, Department of Atomic and Nuclear Physics, Măgurele, Romania

^a*National Institute of Research and Development for Materials Physics, Bucharest, Romania*

^b*University of Bucharest, Faculty of Chemistry, Bucharest, Romania*

X-Ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) have been used to investigate the elemental composition, chemical and electronic state of elements that exist within the Herăstrău Lake (Bucharest, Romania) sediments. XPS spectra were obtained by irradiating the sediment samples with an Al source of X-rays (1486.6 eV). C, N, O, F, Na, Mg, Al, Si, S, Cl, K, Ca, V, Mn, Fe, Co, Ni, Cu, Zn, and Pb have been determined by XPS and AES techniques. The analysis of Electron Paramagnetic Resonance (EPR) spectra revealed an additional free radical peak in the center of Mn^{2+} sextet, at a $g = 2.0038$, attributed to SO_3^- species as well as a very intense and broad signal due to Fe^{3+} ions.

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1. Introduction

The biodiversity and dynamics of ecosystems researches lead to the conclusion that eutrophication is the greatest threat to lake water quality. Increasing inputs of biologically accessible forms of phosphorus and nitrogen respectively deposited as gases, particles or soluble ions in rain cause algae growth in the lake, contributing to the decreasing of water transparency. In some cases, the concentration of heavy metals (Cr, Mn, Co, Ni, Cu, As and Pb) or the other pollutants in sediments and soil exceeded the "minimum threshold of safety" established by Government and Environmental Protection Agencies [3].

Situated in the northern residential part of Bucharest, Romania, around a beautiful lake with a surface of 0.7 km², Herăstrău Park is divided into two areas: a natural/rustic zone: the Village Museum and an active/public domain for recreation activities. Swimming and fishing are prohibited by Romanian legislation whereas only small boats are allowed on Herăstrău Lake. The residue forming toxic substances of anthropogenic origin can disturb the ecological equilibrium of this area. On 17th October 2006, a petrol pollution of Herăstrău Lake was noticed by local authorities. For this reason, sediment samples collected from Herăstrău Lake have been subjected to surface-analytical and electron paramagnetic resonance analysis.

Among the many surface-analytical methods, X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) have been used in a variety of fields including environmental science. X-ray Photoelectron Spectroscopy also known as Electron Spectroscopy for Chemical Analysis (ESCA) is a widely used technique based upon the photoelectric effect that studies the composition and electronic state of the surface region of a sample. Quantitative electron spectroscopy is usually applied under an assumption of ideally flat surfaces and electron elastic scattering effects are ignored [9,10]. The

determination of the core electron binding energy, defined as the difference between X-ray photon energy and kinetic energy of the photoelectron, which can be measured by the analyzer allows the identification of elements. Small shifts in the binding energies provide powerful information regarding sample chemical states and short-range chemistry [8]. XPS is a suitable method for the analysis of sediments, partly because it is less destructive than other techniques.

Auger Electron Spectroscopy is an analytical method based upon the measurement of the kinetic energies of the emitted (Auger) electrons permitting element analysis and chemical state analysis with a high spatial resolution of several 10 nm.

Some measurements were performed to verify both hypotheses that organic matter is located at surface or inside of small soil particles [1]. Surface-analytical studies on environmental and geochemical surface processes revealed that the heavy metals such as Zn, Pb, Cu, and Sn are several times more concentrated in the surface layers than in their bulk [7].

Electron Paramagnetic Resonance (EPR) is a physical method of observing resonance absorption of microwave power by unpaired electron spins in a magnetic field. The ionizing radiation produces paramagnetic centers with long lifetimes in solids and the concentration of these centers is a measure of total radiation dose to which the sample was exposed [5]. The EPR spectra of carbonate sediments and clay minerals contain a six-line spectrum around a gyromagnetic factor $g = 2.0$ resulting from Mn^{2+} ions within a carbonate matrix and a signal from isolated Fe^{3+} ions incorporated as impurities within minerals [2]. Silica often shows signals similar to those observed in calcite and aragonite: CO_3^{2-} , SO_3^{2-} and SO_3^- and the size of an EPR signal represents the number of the lattice defects which house single unpaired electron [4, 6].

The surface-analytical techniques used in conjunction with EPR measurements allowed to determine the elemental composition of sediment samples from Herăstrău Lake. Quantitative analyses were performed in order to investigate the pollution level of this area.

2. Experimental

The X-ray photoelectron spectra were acquired using a VG ESCA 3MK II – EUROSCAN electron spectrometer employing Al-K α source of X-rays (1486.6 eV). The analysis chamber was maintained at UHV ($p \gg 10^{-9}$ torr) and the sample position was oriented at $\theta = 45^\circ$ in the respect to the analyzer. Data acquisition was performed using a computer interfaced digital pulse counting system. XPS spectra were processed by using Spectral Data Processor software (SDP 2.3). Auger electrons are measured in XPS together with the photoelectrons.

Each element produces a characteristic set of XPS peaks at characteristic binding energy (E_b) values. These peaks correspond to the electronic configuration of the electrons within atoms. The intensity of the peaks is a measure for the surface concentration. The detected photoelectron peak intensity obtained from a volume element extending from a surface to a depth h is written:

$$I_h = I_0 A D F \left(\frac{E}{E_0} \right) \rho \frac{d\sigma}{d\Omega} \Omega_0 \frac{1}{\cos\theta} \int_0^h e^{-\frac{z}{\lambda_c(E) \cos\theta}} dz \quad (1)$$

where I_0 is the incident X-ray flux, A is the analyzed area, Ω_0 is the acceptance angle of the analyzer, $d\sigma/d\Omega$ is the differential cross-section for photoemission, D is the detector efficiency, F is the fraction of photoelectrons of energy E delivered to the detector by the analyzer at an energy E_0 , $\lambda_c(E)$ is the photoelectron inelastic mean free path (2-5 nm) and $\exp(-z/\lambda_c(E) \cos\theta)$ is the probability that a photoelectron escaping the sample in direction θ measured from the surface normal. Quantification of atomic fraction C_x of i elements detected can be obtain from:

$$C_x = \frac{N_x}{\sum_i N_i} = \frac{I_x/S_x}{\sum_i I_i/S_i} \quad (2)$$

where I_i is the peak intensity for element i and S_i is the sensitivity factor for the peak i .

The EPR measurements were performed at room temperature by using an X-band JEOL JES MX 3X spectrometer provided with a TE₀₁₁ cylindrical resonant cavity and 100 kHz modulation frequency. The g -factors of the observed signals have been determined by using a 2,2-diphenyl-1-picryl-hydrazil (DPPH) as well as CaO:Mn²⁺. The samples in powder form were placed into quartz tubes with a 3 mm inner tube diameter. The position of tube in the cavity was not changed during the whole experiment in order to ensure the uniform and reproducible measurements of the sample. The optimal conditions of ESR measurement were: microwave

frequency 9.50 GHz, field modulation amplitude 3.2 G, microwave power 6 mW, sweep time 10 min, response time 0.3 s. The g spectroscopic splitting factor of unknown signal was determined using the standard signal with a known g_0 factor:

$$g = g_0 / \left(1 - \frac{\Delta H}{H_0} \right) \quad (3)$$

The magnetic field separation ΔH between the third and fourth line and the resonance field H_0 were considered 8.69 mT and 339 mT respectively at the X-band frequency.

3. Results and discussion

Photoelectron spectroscopy uses photo-ionization and energy-dispersive analysis of the emitted photoelectron to study the composition and electronic state of the surface region of a sample. The binding energies identify the elements from which the electrons were emitted. The X-ray photoelectron spectrum of sediment sample from Herăstrău Lake, in the wide range 0–1200 eV shows intensity of photoelectrons of the elements in the compounds versus their binding energies (Fig. 1). The elemental composition of sediment sample was strongly dominated by O 1s (528-533 eV) and C 1s (284-286.4 eV).

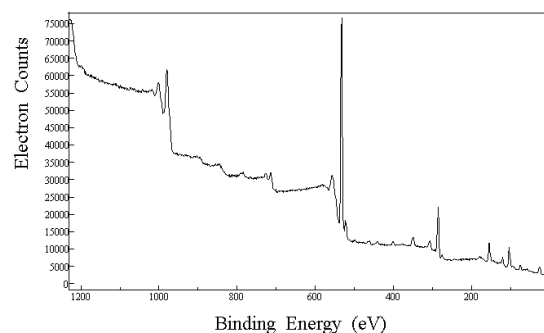


Fig. 1. The X-ray photoelectron spectrum of sediment sample in the range 0–1200 eV.

The functional group C-C with the binding energy 285 eV has been used as the reference for calibration (Fig. 2).

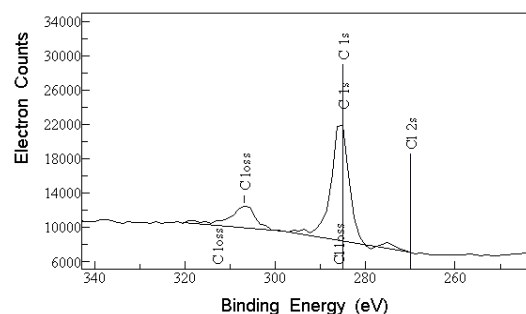


Fig. 2. C 1s X-ray photoelectron spectrum.

The position of the signal of carbon in the range 284-286.4 eV suggests that carbon is bonded to nitrogen and oxygen. Carbon and nitrogen could be assigned to organic matter. Measurement results showed that the surface concentration of carbon exceeds that of the bulk samples [1]. XPS analysis identifies the functional groups present on sediment samples (Fig. 3).

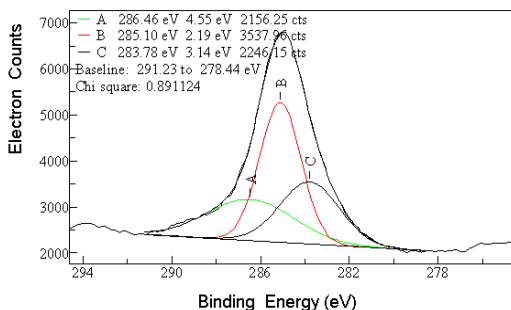


Fig. 3. Cls high resolution X-ray photoelectron spectrum.

Auger parameter energy of 398 eV carried-out slight traces of NH_3 and ammonium salts (Fig.4.).

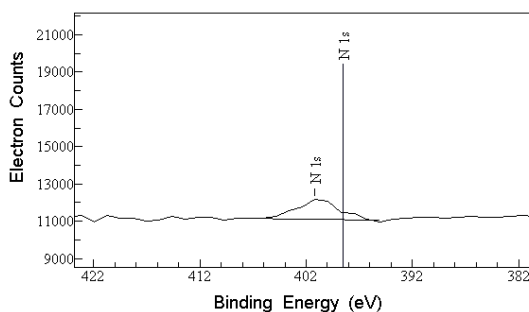


Fig. 4. N 1s X-ray photoelectron spectrum.

The metal oxides (Al_2O_3 , Fe_2O_3) occur in the range of 528-531 eV, SiO_2 at 533 eV, phosphates and nitrates arise at 531-533 eV and silicates occur at 532-533 eV (Fig. 5.). Two lines corresponding to transitions to the doublet and quartet final states occur due to coupling of the unpaired O 1s electron and the two unpaired electrons of the outermost p orbital in the final cationic state.

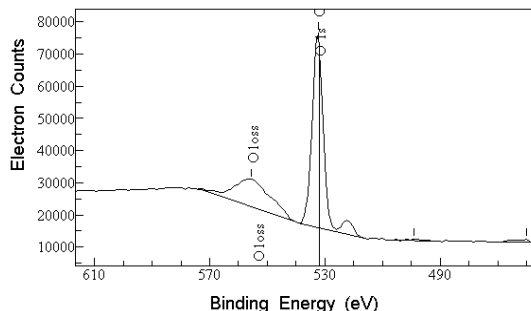


Fig. 5. - O 1s X-ray photoelectron spectrum showing a very intense peak at a binding energy of 531 eV.

The X-ray photoelectron spectra of sediment samples from Herăstrău Lake also exhibited line intensities of electrons in the 2s orbital of O (24 eV), in the 1s orbital of Na (1071 eV) correlated to Na_3PO_4 and Na_2SO_4 , in the 2s orbital of Mg (88.7 eV) due to MgO as well as Pb 4f correlated to PbCO_3 (138.3 eV), PbCl_2 (138.9 eV) and PbSO_4 (140 eV) (Fig. 6.). The accumulation of Pb over time in organisms can cause serious illness. Aluminium oxides, boehmite, silicates and silica have also been found in sediment samples in the range 72-150 eV. Minor signals were assigned by the 2s and 2p electrons levels of Si at a binding energy of 150 and 103 eV respectively (Fig. 7.).

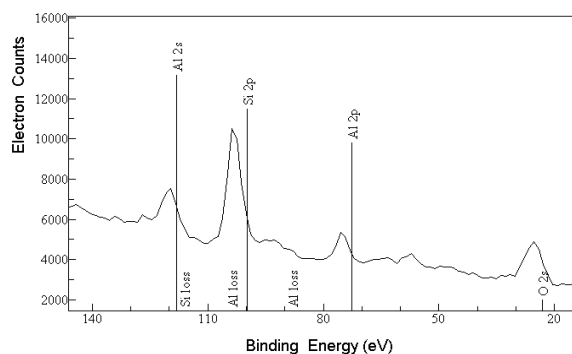


Fig. 6. - O 2s (24 eV), Al 2s (117.8 eV) and Al 2p (72.95 eV) X-ray photoelectron spectrum.

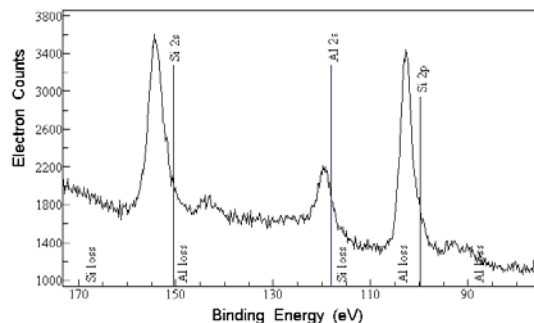


Fig. 7. Si 2s (150 eV) and Si 2p (103 eV) X-ray photoelectron spectra.

The emission from the 2p levels of the sulfur atoms gives a very broad peak in the range of 165-180 eV due to sulfur hexafluoride, sulfur oxides, sulfate and sulfite ions (Fig. 8.).

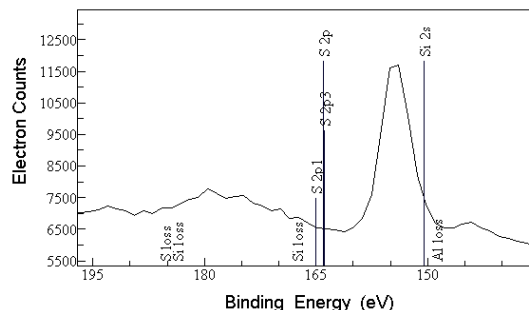


Fig. 8. S 2p X-ray photoelectron spectrum.

The chlorine spectrum exhibits traces of NaCl and KCl in the range of 198.4-198.6 eV (Fig. 9.).

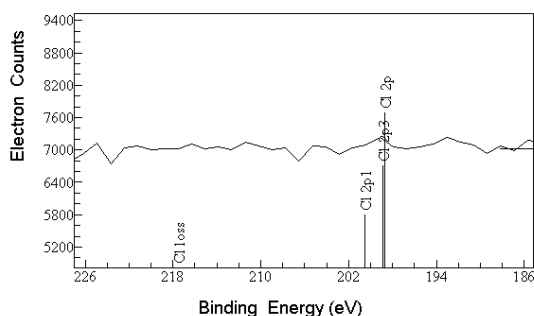


Fig. 9. Cl 2p X-ray photoelectron spectrum.

The Ca 2p XPS spectrum confirms the presence of CaO, CaCO₃ and CaS in the range of 346-347 eV, CaSO₄ at 348 eV and Ca(NO₃)₂ at 349 eV (Fig. 10). We have also found Ca 2s at 438.4 eV, K 2s (378.6 eV) and K 2p (292.8 eV) associated to KF and V 2p at 519 eV due to vanadium oxides.

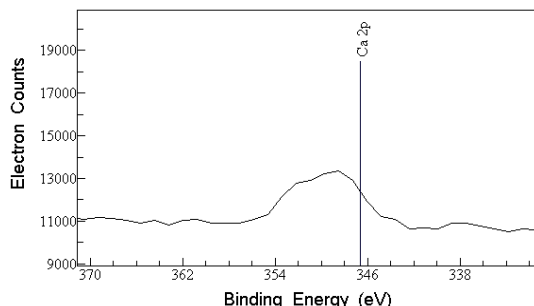


Fig. 10. Ca 2p X-ray photoelectron spectrum.

The emission from 2p levels of the iron atoms is shown in Fig. 11. The Fe₂O₃ and FeOOH chemical compounds can be found in the range of 706.8-720 eV. Elemental line F 1s appeared in the range 684-696.7 eV. The Auger parameters energies in the range of 641.4-642.6 eV due to Mn₃O₄ and MnO₂ have been attributed to Mn 2p.

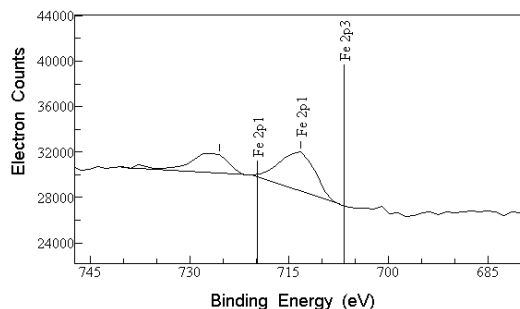


Fig. 11. Fe 2p X-ray photoelectron spectrum.

The most intense peak at 784 eV is due CoSO₄ (Fig. 12). The line intensities of electrons in the 2p orbitals of

heavy metals: Ni, Cu and Zn were found in the range 856-1021 eV.

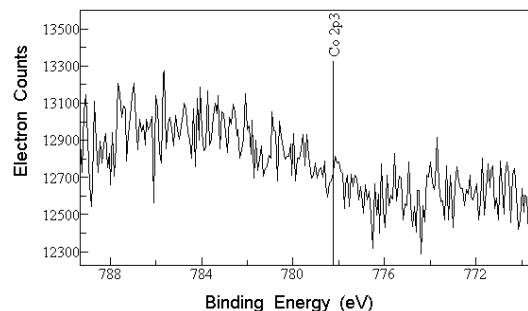
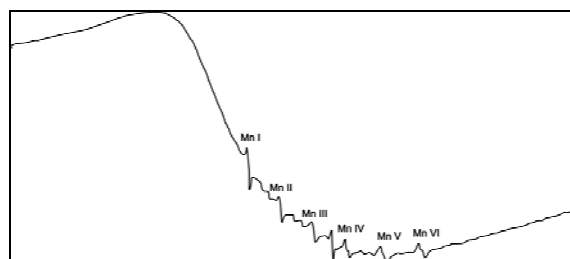
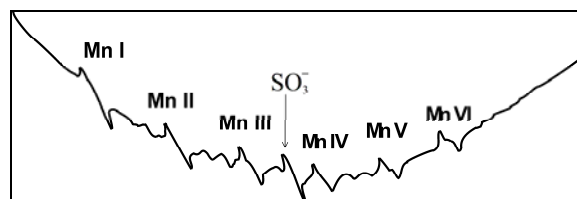


Fig. 12. Co 2p X-ray photoelectron spectrum.

The EPR spectrum of sediment samples consist of Mn²⁺ characteristic sextet with an additional free radical peak between the third and the forth lines at a $g = 2.0038$, attributed to SO₃⁻ species (Fig. 13). In the low field region we noticed a strong component due to Fe³⁺ in orthorhombic symmetry at a gyromagnetic factor $g = 4.3$.



a)



b)

Fig. 13. EPR experimental spectrum of investigated sediments: (a) The broad and intense signal is due to Fe³⁺ while in the center of the spectrum the typical Mn²⁺ sextet can be remarked. (b) The Mn²⁺ sextet showing an additional free radical peak at a $g = 2.0038$, attributed to SO₃⁻ species.

The relative concentration of elements from Herăstrău Lake sediments detected by XPS and AES techniques is listed in Table 1. The measurements revealed that the elemental composition of sediment samples is strongly dominated by carbon and oxygen. We have also found relative high concentrations of aluminum and silicon.

Table 1. Binding energy and relative concentration of elements from Herăstrău Lake sediments.

Atomic number	Element symbol	Element line	Binding energy (eV)	Sensitivity factor	Relative concentration (%)
6	C	1s	284-286.4	0.25	16.546
7	N	1s	398.8	0.42	0.984
8	O	1s	528-533	0.66	27.890
		2s	24	0.025	24.819
9	F	1s	684-696.7	1.00	0.103
11	Na	1s	1071	2.30	0.089
12	Mg	2s	88.7	0.15	0.689
13	Al	2s	117.8	0.17	4.866
		2p	72.95	0.18	2.298
14	Si	2s	150	0.19	7.619
		2p	103	0.25	6.618
16	S	2p	165-180	0.49	0.422
17	Cl	2p	198.4-198.6	0.61	0.169
19	K	2s	378.6	0.26	0.039
		2p	292.8	0.83	0.996
20	Ca	2p	346-349	1.05	0.827
23	V	2p	519	1.30	1.272
25	Mn	2p	641.4-642.6	1.70	0.121
26	Fe	2p	706.8-720	2.00	0.620
		3p	53	0.21	0.492
27	Co	2p	784	2.50	0.248
28	Ni	2p	856	3.00	0.241
29	Cu	2p	932	4.20	1.477
30	Zn	2p	1021	4.80	0.517
82	Pb	4f	138.3-140	3.82	0.027

4. Concluding remarks

The rapid development of XPS and AES techniques has enabled us to find the surface chemistry of sediment samples in Herăstrău Lake in order to outline the possible polluting elements of this area. One of the important findings of this study was that beside the normal relative concentrations of C, N, O, Na, Mg, Al, Si, K, Ca, and Fe characteristically to frequent sediments or soil we found traces of V and Cu. Living organisms require trace amounts of some heavy metals, including Co, Cu, Mn, V and Zn, but excessive levels can be detrimental to the organism. At the same time, it must be taken into account that the relative concentration of F, Mn, Ni, Zn and Pb is not significantly increased.

The EPR spectra of sediment samples from Herăstrău Lake are essentially the same as in the majority of carbonates, revealing an additional free radical peak in the center of Mn^{2+} sextet, at a $g = 2.0038$, attributed to SO_3^- species as well a very intense and broad signal due to Fe^{3+} ions.

References

- [1] W. Amelung, K. Kaiser, G. Kammerer, G. Sauer – Organic Carbon at Soil Particle Surfaces – Evidence from X-ray Photoelectron Spectroscopy and Surface Abrasion, *Soil Sci. Soc. Am. J.* **66**, 1526 (2002).
- [2] N. P. Crook, S. R. Hoon, K. G. Taylor, C. T. Perry – Electron Spin Resonance as a high sensitivity technique for environmental magnetism: determination of contamination in carbonate sediments, *Blackwell Synergy – Geophys. J. Int.* **49**(2), 328 (2002).
- [3] L. C. Dinescu, E. Steinnes, O. G. Duliu, C. Ciortea, T. E. Sjøbakk, D. E. Dumitriu, M. M. Gugiu, M. Haralambie – Distribution of some major trace elements in Danube Delta lacustrine sediments and soil, *J. Radioanal. Nucl. Chem.* **262**, (2), 345 (2004).
- [4] M. Ikeya - New applications of Electron Spin Resonance – Dating. Dosimetry and Microscopy. World Scientific, Singapore, New Jersey, London, Hong Kong. (1993).
- [5] M. Jonas – Concepts and Methods of ESR Dating, *Radiation Measurements* **27** (5/6), 943 (1997).
- [6] W. J. Rink – Electron Spin Resonance (ESR) Dating and ESR Applications in Quaternary Science and Archaeometry, *Radiation Measurements*, **27**, (5-6), 975 (1997).
- [7] H. Seyama, M. Soma – Surface-analytical Studies on Environmental and Geochemical Surface Processes, *Analytical Sciences*, **19**, 487 (2003).
- [8] E. Talik, W. Zarek, M. Kruczek, S. Ganschow, D. Skrzypek, E. Popiel – Characterization of olivine single crystals grown by the micro-pulling-down method and terrestrial olivine by XPS, Mössbauer, magnetic and EPR methods, *Cryst. Res. Technol.* **41**(10), 979 (2006).
- [9] J. Zemek – Electron Spectroscopy of Solid Surfaces, *Acta Physica Slovaca*, **50**(4), 577 (2000).
- [10] J. Zemek - Electron Transport at Solid Surfaces, *Acta Physica Slovaca*, **56**(4), 543 (2006).

*Corresponding author: seletchi@gmail.com