

## The study of the properties of the hydroxyapatite/electrolyte interface\*

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A physicochemical property of hydroxyapatite (HAP)  $[\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6]$  surface was studied and parameters of electrical double layer of the hydroxyapatite/NaCl solution system were described. The study sample of hydroxyapatite was synthesized. The structure of the hydroxyapatite was confirmed using X-ray diffraction (XRD), its particle size by PCS (photon correlation spectroscopy) AFM and SCM microscope and its surface properties by means of adsorption-desorption of nitrogen (ASAP), Raman spectra,. Then the point of zero charge and the isoelectirc point were measured.

### 1. INTRODUCTION

Hydroxyapatite  $[\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6]$  is the structural prototype for the main inorganic constituent of bone and teeth, is also one of the principal minerals in commercial phosphate ores. The surface chemistry characteristics of hydroxyapatite is important in understanding the growth, dissolution and adhesion mechanisms of bone and teeth tissues and in enrichment of minerals such as flotation and flocculation [1,2,3]

Methods of hydroxyapatite preparation may have influence on specific chemical properties of adsorbent surface. The high purity, high density and desirable microstructure ceramic hydroxyapatite has been prepared using processes: microemulsion synthesis, sol-gel, co-precipitation or hydrothermal

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\*This article is dedicated to Professor Roman Leboda on the occasion of his 65<sup>th</sup> birthday

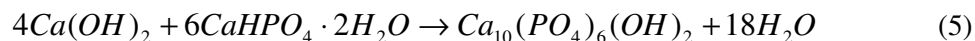
reactions [1]. The study of the electrical double layer structure for the hydroxyapatite/electrolyte solution interface reveal that the  $\text{pH}_{\text{pzc}}$  and  $\text{pH}_{\text{iep}}$  data lie in a wide range, from 4.35 for dental HAP up to 8.6 for synthetic samples, and it is very difficult to compare them. The main reason for this is the fact that all experimental results were obtained for HAP samples of different origin, stoichiometry and purity, under various experimental conditions, and by different experimental techniques. However the solubility of HAPs in determination of surface charge density and  $\text{pH}_{\text{pzc}}$  by means of potentiometer titration should be taken into account. The studies of the electrical double layer at the hydroxyapatite/electrolyte solution interface shows that besides  $\text{Ca}^{2+}$  and phosphate, the  $\text{H}^+$  and  $\text{OH}^-$  are potential determining ions[4,5]. The charge on hydroxyapatite arises as a result of the various reactions of surface hydroxyl groups and unequal adsorption from solution of ions of opposite charge [6,7]. Because hydroxyapatite is a basic salt, there was two types of groups on the surface: hydroxyl and phosphatic. It is no doubt that the phosphatic groups have more acid character than hydroxyl one, those has alkaline character. The reactions of surface groups at the hydroxyapatite that create surface charge are following:



The goal of this paper is characterization of hydroxyapatite prepared, determination of  $\text{pH}_{\text{pzc}}$  and  $\text{pH}_{\text{iep}}$  points, establishing of zeta potential on pH dependence and determination of calcium ions dependence on pH and electrolyte concentration.

## 2. EXPERIMENTAL

The sample of hydroxyapatite have been synthesized on the basis of prescription described in the literature [2]. The synthesis reaction occurs as follows:



Aqueous solutions of reagents were prepared by dissolution of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  (0.5162 g) and  $\text{Ca}(\text{OH})_2$  (0.1482 g) in 40 ml deionized water respectively. For pH=9, the initial solution was adjusted by adding  $\text{CH}_3\text{COOH}$  solution. The ready-adjusted solution was put in a teflon vessel and heated at  $120^\circ\text{C}$  for 24h, and then cooled to a room temperature in natural way. Next the precipitate was filtered and washed with deionized water. Finally, the solid was dried at  $60^\circ\text{--}100^\circ\text{C}$ . To remove ionic type contaminations, which might influence the measurements, the hydroxyapatite was washed with double distilled water until constant conductivity about  $0.05 \mu\text{S}/\text{cm}$  was achieved.

The prepared hydroxyapatite sample has been characterized using X-ray diffraction (XRD), adsorption-desorption of nitrogen (ASAP), PCS (photon correlation spectroscopy), Raman spectra, AFM and scanning microscope. Zeta potential was measured in the NaCl as a background electrolyte in three concentrations as a function of pH. Because for the studied system  $\kappa a \gg 1$  the zeta potentials were calculated using the Smoluchowski equation. Calcium ions concentration has been measured by ionselective electrode. Then the point of zero charge and the isoelectric point were measured. A crystallographic structure of samples was confirmed by XRD using DRON-3 diffractometer using  $\text{CuK}\alpha$  radiation and nickel filters.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the peaks of X-ray diffraction patterns. We observed peak characteristic for hydroxyapatite:  $25,9 - 35\%$ ;  $31,75 - 100\%$ ;  $32,96 - 55\%$ ;  $39,84 - 20\%$ ;  $46,7 - 40\%$ ;  $49,5 - 30\%$ . Between them it can be seen peaks characteristic for calcium carbonate ( $2\theta = 29,4 - 100\%$  and  $39,407 - 28\%$ ). Calcium carbonate was formed probably during washing out of the sample with distilled water [8].

The specific surface of the hydroxyapatite samples was determined by adsorption-desorption of nitrogen using ASAP 2405 (Accelerated Surface Area and Porosimetry, Micromeritics Instruments, Co.). Table 1 present structural parameters of hydroxyapatite.

The particle size and polydispersity coefficient has been determined by PCS (Photon Correlation Spectroscopy) using Zetasizer 3000 by Malvern. The average size of polydispersic samples was 420 nm.

Figure 3 shows Raman spectra. The one band in the spectra may be suspect of the presence of carbonate ions in the studied sample [9,10].

Most bands at the Figure 2 are characteristic for pure hydroxyapatite but only band at  $1080.27 \text{ cm}^{-1}$  may be connected with  $\nu_3(\text{PO}_4)$ , as well as with carbonates presence in the sample.

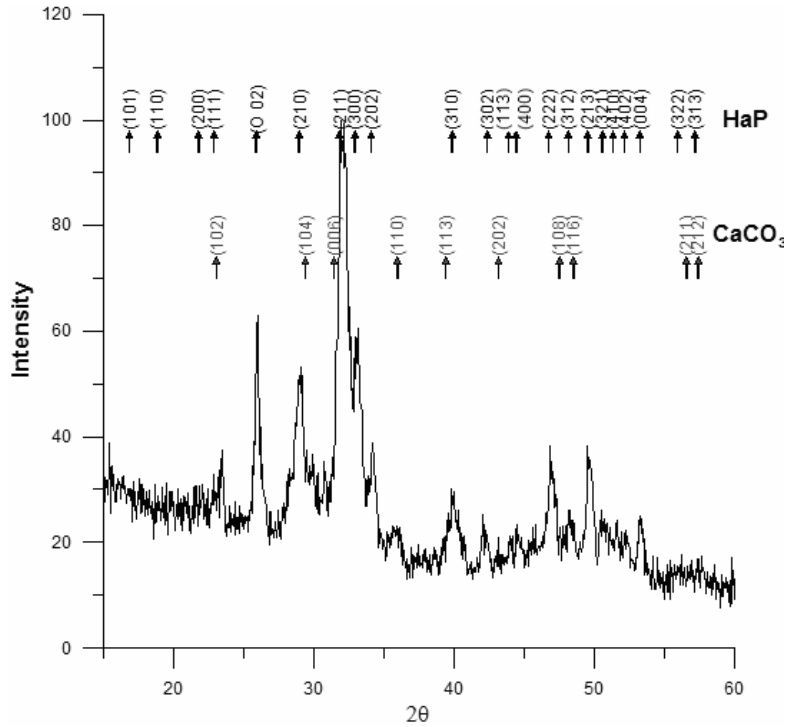


Fig. 1. Powder X- diffraction pattern.

Tab. 1. Selected structural parameters.

BET surface area [m <sup>2</sup> /g]	26.34
Langmuir surface area [m <sup>2</sup> /g]	33.71
BJH cumulative adsorption surface area of pores between 1.7 and 300 nm diameter [cm <sup>3</sup> /g]	0.12
BJH cumulative desorption surface area of pores between 1.7 and 300 nm diameter [cm <sup>3</sup> /g]	0.12
Average pore diameter (4 V/A by BET) [nm]	15.08
BJH adsorption on average pore diameter (4 V/A) [nm]	15.75
BJH desorption on average pore diameter (4 V/A) [nm]	8.39

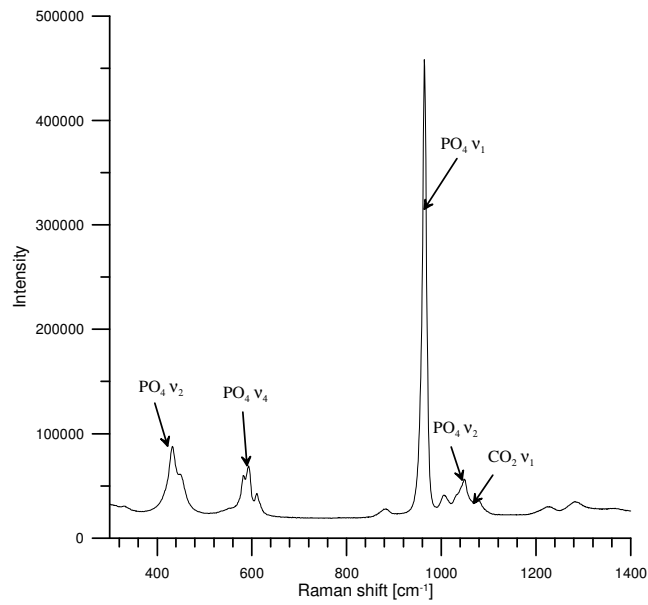
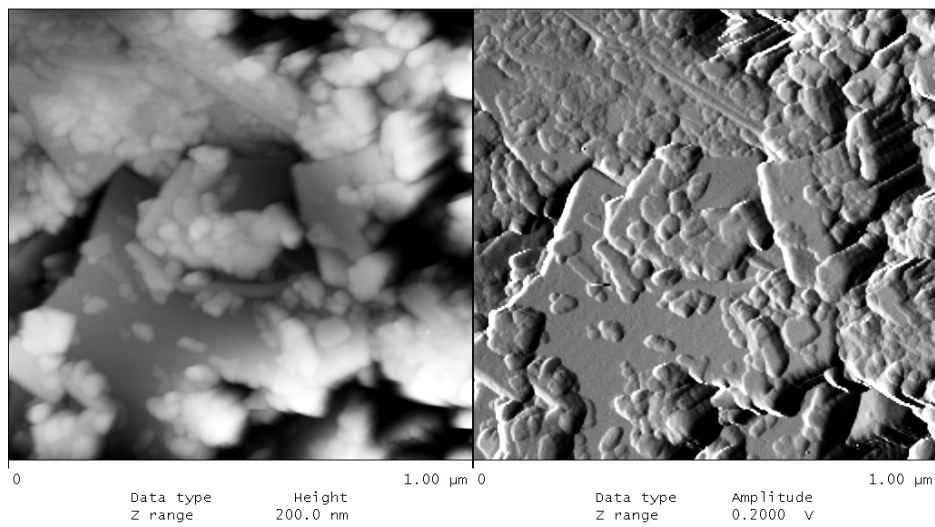


Fig. 2. Raman spectra.

Figure 3 shows AFM micrographs of several hydroxyapatite samples. It shows formation of monodisperse change crystals.



hyd-mw.002

Fig. 3. AFM micrograph of hydroxyapatite.

Photo at Figure 4 made by scanning microscope, shows hydroxyapatite particles dimensions and surface structure. As can be seen, besides large particles about 20  $\mu\text{m}$  that are aggregates, also smaller of 1  $\mu\text{m}$  are visible. Because crystallite dimension calculated from XRD by means Scherrer method is 36nm, it leads to conclusion that hydroxyapatite particles observed in the Figure 4 are aggregates that are huge amount of small crystals that together forms porous structure.

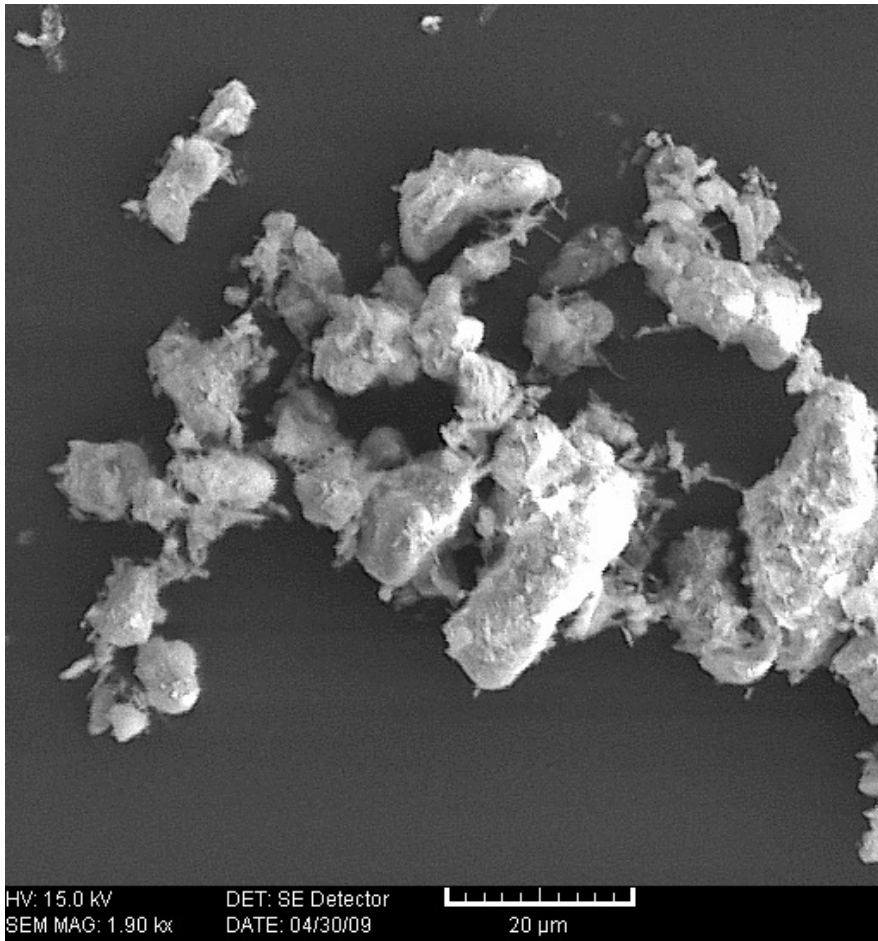


Fig. 4. Scanning microscopy.

I. D. Smičiklas et al. has given a comparison of  $\text{pH}_{\text{pzc}}$  and  $\text{pH}_{\text{iep}}$  values for hydroxyapatite that are obtained for different basic electrolytes using potentiometric titration and electrophoresis [11]. There are some samples with

the  $\text{pH}_{\text{iep}} < 5$ . L. C. Bell et. al. has also presented a juxtaposition of  $\text{pH}_{\text{pzc}}$  values [12]. They are ranged from 4.5 to 7 for different electrolytes. L. M. Rodriguez-Lorenzo et. al. have obtained a typical dependence zeta potential as a function of pH and  $\text{pH}_{\text{iep}}$  is at  $\text{pH}=7.3$ . They have investigated at the hydroxyapatite/KCl interface in pH range from 4.5 to 12 [3]. Due to process of dissolution, various weights of hydroxyapatite for potentiometric titration were taken with the purpose of determining  $\text{pH}_{\text{pzc}}$  Figure 5.

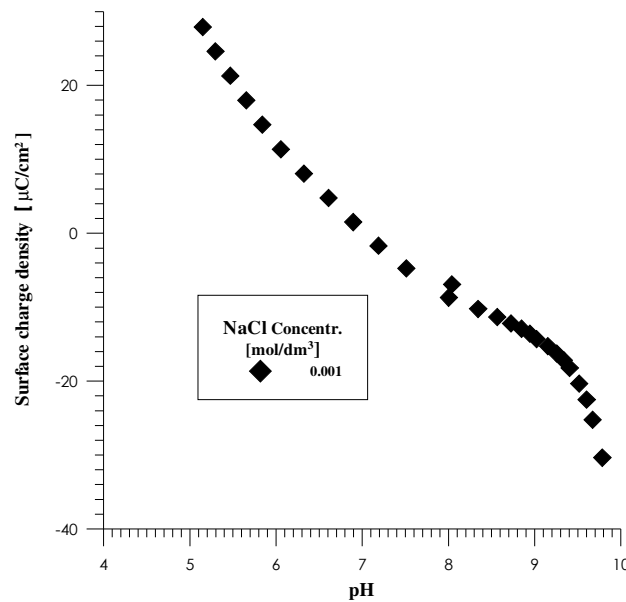


Fig. 5. Surface charge density at the hydroxyapatite / 0.001 M NaCl solution interface as a function of pH.

The chart with dependence of calcium ions concentration on pH in hydroxyapatite/NaCl system is shown at Figure 6. Change of background electrolyte concentration from 0.001 to 0.1 mol/dm<sup>3</sup> had little influence on calcium ions concentration, also is visible that for  $\text{pH}=10$  calcium ions concentration is lower than electrode sensitivity which caused zero readout.

Figure 7 present the zeta potential as a function of pH for two concentrations of NaCl solution. It can be seen that increase of electrolyte concentration in the system causes the lowering of zeta potential. The point  $\text{pH}_{\text{iep}}=4.3$  for sample. It can be seen also that the point  $\text{pH}_{\text{iep}}$  is shifted towards lower values of pH. It is a result of the adsorption reactions. For background electrolyte it may occur in a porous surface that characterizes an heterogenic surface. Sample has a porous surface so that for lower electrolyte concentration double layer can be

overloaded. As a consequence holes can be closed during electrophoresis and surface features may not be revealed. The difference in the position of  $\text{pH}_{\text{IEP}}$  and  $\text{pH}_{\text{pzc}}$  may also indicate the specific anion adsorption, because  $\text{pH}_{\text{pzc}} > \text{pH}_{\text{IEP}}$ .

Discrepancy between  $\text{pH}_{\text{pzc}}$  and  $\text{pH}_{\text{iep}}$  values is caused by the method of surface charge density determination: potentiometric titration uses acid-base reactions of surface groups (engaging  $\text{H}^+$  or  $\text{OH}^-$  ions only) whereas dzeta potential is also dependent on this part of surface charge, which is caused by unequal adsorption or desorption of phosphate or calcium ions.

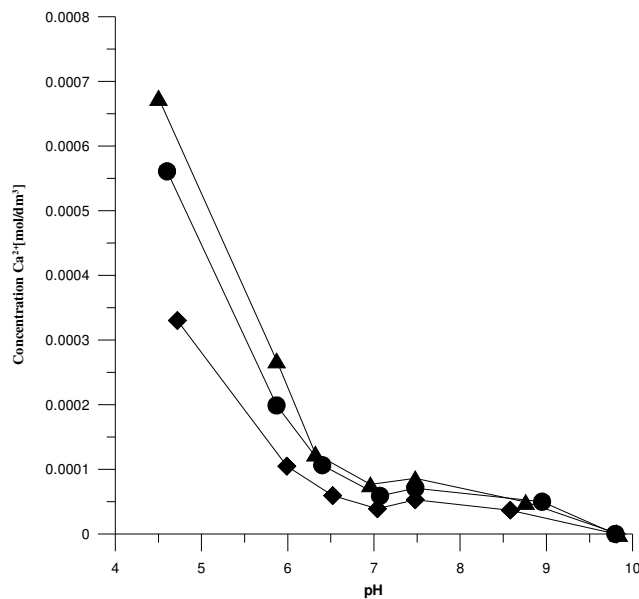


Fig. 6.  $\text{Ca}^{2+}$  concentration at the hydroxyapatite /NaCl solution interface as a function of pH.

#### 4.CONCLUSIONS

1. Investigations at the hydroxyapatite/electrolyte solution system are limited by dissolution of mineral and are narrowed to pH range 7–11.
2. The results of X-ray diffraction analysis, Raman spectroscopy and specific surface area obtained by AFM and BET indicate the relationship between the synthesis parameters and edl parameters.
3. The points  $\text{pH}_{\text{pzc}}$  and  $\text{pH}_{\text{IEP}}$  for sample are  $\text{pH}_{\text{pzc}}=6.7$  and  $\text{pH}_{\text{IEP}}=4.3$ .



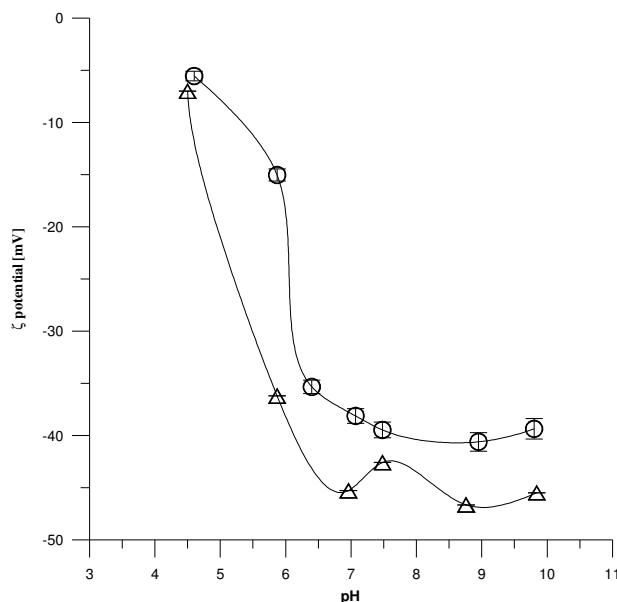


Fig. 7. The  $\zeta$  potential of hydroxyapatite/NaCl solution interface as a function of pH.

## 5. REFERENCES

- [1] R. E. Riman, W. L. Suchanek, K. Byrappa, C. Wei Chen, P. Shuk, C. S. Oakes, *Solid State Ionics* 151 393 (2002).
- [2] J. Liu, X. Ye, H. Wang, M. Zhu, B. Wang, H. Yan, *Ceramics International* 29 629 (2003).
- [3] L. M. Rodriguez-Lorenzo et al., *Biomaterials* 22, 1847 (2001).
- [4] G. Yin, Z. Liu, J. Zhan, F. Ding, N. Yuan, *Chem. Eng. J.*, 87 181 (2002).
- [5] S. Harding, N. Rashid, K. A. Hing, *Biomaterials* 26 6818 (2005).
- [6] G. R. Wiese, R. O. James, D. E. Yates, T. W. Healy, *Electrochemistry of the colloid-water interface*. In *Electrochemistry of Colloid-Water Interface*; Bockris J. O'M. Ed.; Int. Review Sci. Phys. Chem. Series 2.; Butterworths: London; 6, 53 (1976).
- [7] J. Lyklema, *Fundamentals of Interface and Colloid Science*. Academic Press London, 1995, 3.2-3.232. b) *Fundamental the Electrical Double Layers in Colloidal Systems*. In *Colloidal Dispersions*, Goodwin J. W. Ed., Special Publication No 43; Royal Soc. Chem.: London, 47 (1981).
- [8] R. A. Jillavenkatesa, Condrate Sr., *J. Mater. Sci.* 33 4111 (1998)
- [9] C. Silvaa, A. S. B. Sombrab, Raman spectroscopy measurements of hydroxyapatite obtained by mechanical alloying, *J. Phys. Chem. Solids* 65 1031 (2004).
- [10] G. Penel, G. Leroys, C. Rey, B. Sombret, J. P. Huvenned and E. Bres, Infrared and Raman microspectrometry study of fluor-fluor-hydroxy and hydroxy-apatite powders, *J. Mater. Sci.: Materials in Medicine* 8 271 (1997).
- [11] D. Smičiklas, S. K. Milonjič, P. Pfendt, S. Raičević, *Separation and Purification Technology* 18 185 (2000).
- [12] L. C. Bell, A. M. Posner, J. P. Quirk, *J. Colloid Interface Sci.*, 42 2 (1973).

## CURRICULA VITAE



**Władysław Janusz;** PhD 1981, Habilitation 2001, Professor 2007. Research areas: The main research interest covers various fields of physicochemistry of the solid dispersion (e.g. metal oxides, insoluble carbonates, silicates, phosphates) in the electrolyte solutions especially: origin of the surface charge at the solid /electrolyte interfaces, mechanism of the adsorption of ions at the solid/electrolyte interface, zeta potential measurements of dispersions, structure of the electrical double layer structure at the solid/electrolyte interface, determination of the equilibrium constants of surface hydroxyl groups at the solid/electrolyte interface, specific adsorption of ions at the solid/electrolyte interface, competition of ion adsorption, adsorption of ternary complexes at the solid/electrolyte interface, colloid stability, additionally radioisotope methods in physical and analytical chemistry.



**Ewa Skwarek** received MSc in organic chemistry, PhD in physical chemistry from the University of Maria Curie Skłodowska in Lublin in 1996 and 2005 respectively. At present, she is a lecturer in Department of Radiochemistry and Colloid Chemistry. Main field of her interests are the adsorption of ions on metal oxides and various minerals, synthesis of adsorbents and structure of the electrical double layer.