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ION-SELECTIVE ELECTRODES BASED ON CALCIUM HYDROXYLAPATITE AS A TOOL FOR ANALYSIS OF VARIOUS ENVIRONMENTAL OBJECTS, FOOD AND RAW MATERIALS

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Abstract: *A method of the potentiometric determination of Ca^{2+} and HPO_4^{2-} ions in some food and raw products using the original ion-selective electrodes with calcium hydroxylapatite has been developed. The plasticized ion-selective electrodes were constructed of calcium hydroxylapatite on PVC substrate. Investigation of the electrode characteristics proved the linear parts on the Ca^{2+} and HPO_4^{2-} V-A dependencies. The slope coefficients also were calculated for the both ions. Preliminary treatment of the electrodes in the Ca^{2+}solutions results in significant changes in the both slope coefficients, which approach to the theoretical values.*

Keywords: *food; environmental objects; ion-selective electrodes; calcium hydroxylapatite*

1. Introduction

Deep modernization of the food processing branch is required in order to enhance its competitive advances and to mitigate consequences of the economical crisis, industrial depression and decrease in the labour productivity. A series of actions such as economical changes along with technical reequipment, development of resource- and energy-saving technologies and processes, ensuring thorough control of the food and raw materials quality should be taken to support this strategy.

Various physico-chemical and biological methods are widely involved in such analytical technologies.

Potentiometry of the environmental objects, food and raw materials quality using the ion-selective electrodes is an advanced and powerful method of investigation. It is express and accurate method that is capable to work with samples from one-two tenth to 1 ml, usually no sample pretreatment is needed, the method can be applied directly to the turbid mixtures, viscous substances without filtration, distillation or extraction. This way, the method is highly suitable to be employed in the automatic and well-controllable mode [1, 2]. However, new solid-ion selective electrodes with high endurance and stable output signal should be designed in order to perform analytical determination of some compounds including ions Ca^{2+} and HPO_4^{2-}.

One of the advantageous methods of synthesis for such electrodes presupposes formation of the electroactive layer directly from calcium hydroxylapatite in course of its synthesis.

Calcium hydroxylapatite (Ca-HOA) can be found in nature and also synthesized. This is the basic phosphate $Ca_{10}(PO_4)_6(OH)_2$, it

is non-toxic and almost dissoluble compound [3].
This paper deals with investigation of possible utilization of the hydroxylapatite as the electrode-active substrate for designing of the ion-selective electrodes.

2. Experimental

A method of chemical depositions from the solutions of calcium nitrate and ammonia hydrophosphate at pH=9-10 according to reaction $10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 8NH_4OH = Ca(PO_4)_6(OH)_2\downarrow + 20NH_4NO_3 + 6H_2O$ has been used to synthesize the stoichiometric calcium hydroxylapatite.
The crystals growth and deposition took place gradually then the sediment was washed by water, then ethanol and dried at 105 ^{0}C.
The electrode has been made using PVC as substrate. This substance was dissolved in cyclohexanone. Then the powder of pure Ca-HOA was mixed with the 10 % solution of PVC to form a suspension with the ratio Ca-HOA:PVC = 1:50. This suspension was applied on the graphite rod and then dried at the room temperature during a day and night. If required, the above operations could be repeated several times.
A series of the sample solutions containing of $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ with concentrations of the both compounds ranged from 10^{-5} to 10^{-1} mol/dm^3 has been prepared to investigate some electro-analytic parameters of the system.
Two types of the electrodes were used to find a pattern of dependence of the Ca-HOA electrode's potential on concentration of ions Ca^{2+} and HPO_4^{2-}. First type of electrode was untreated while the second one was kept in the solution of $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ with concentrations of the compounds 10^{-3} mol/dm^3 for a day and night prior the investigation.

3. Results and Discussion

It is known [4] that the electrode-active compounds should comply with some requirements: have as low as possible value of solubility product; exhibit ionic type of conductance and be non-toxic and easily accessible. Ca-HOA comply with all these requirements: its solubility product is $1.0\cdot10^{-134}$ [5], high ionic conductivity was reported in [6] while easy and cheap syntheses were also shown. Toxicity investigation of the substance proved its complete safety [7]. It can be expected that the Ca-HOA based electrode should be sensitive to the both types of ions: calcium and phosphates. That is why these ions were selected to find experimentally a character of the electrode potential dependence on the ions' concentration.
Dependence for the first type electrode (without preliminary keeping in the solutions) on Ca^{2+} concentration is shown in Fig. 1. Three different parts with different slopes can be identified in this line. The first and the third parts exhibit low slope meaning that the electrode potential depends on Ca^{2+} concentration insignificantly within the corresponding ranges of Ca^{2+} concentrations.

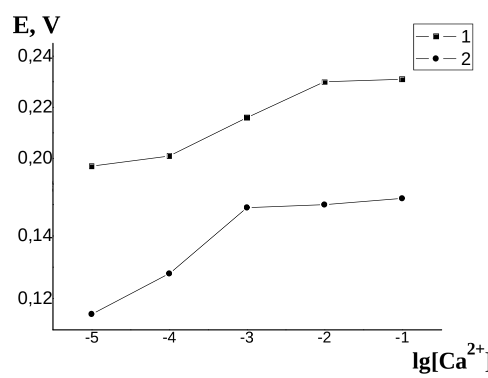

Figure 1. Dependence of the equilibrium potential of the plasticized electrode on concentration of Ca^{2+}: 1 – Type 1 electrode (untreated); 2 – Type 2 electrode (pretreated).

The second part lies from concentrations 10^{-4} to 10^{-2} and exhibits the slope coefficient 0.0145 V/decade, which is close to the theoretical value 0.01475 V/decade calculated for the 4-charge ions. Since the experimental dependence was determined for the double-charged ions Ca^{2+}, the slope coefficient had to be close to the value 0.0295 V/decade. The significant discrepancy fixed in our experiments can be caused by the effect of some side ions on the electrode potential.

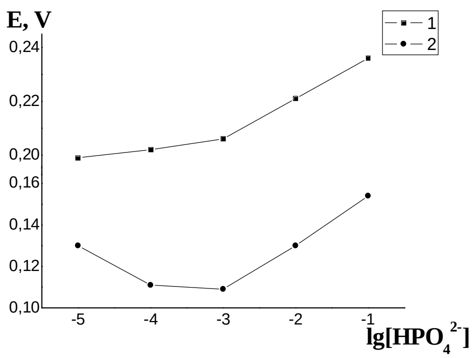

Figure 2. Dependence of the equilibrium potential of the electrode on concentration of HPO_4^{2-}: 1 – Type 1 electrode (untreated); 2 – Type 2 electrode (pretreated in the 10^{-3} mol/dm^3 solution of $Ca(NO_3)_2$).

An ion-selective electrode can usually be kept before the usage in the solution containing the respective ions in order to enhance its characteristics [8]. The curve 2 in Fig. 1 represents results of investigation of such pretreated ion-selective electrode after the day and night long keeping in the 10^{-3} mol/dm^3 solution of $Ca(NO_3)_2$. The curve shows a dependence of the electrode potential on Ca^{2+} concentration.

It can be seen that the slope coefficient of the curve 2 is different and equal to 0.022 V/decade within 10^{-5}–10^{-3} mol/dm^3 (compare with 0.0145 V/decade for the untreated electrode).

Therefore, it can be concluded that pretreatment of Ca-HOA electrode makes an effect on its slope coefficient bringing it closer to the theoretical value for the double-charged ions (0.0295 V/decade).

Fig. 2 represents similar dependencies of the electrode potential on the phosphate ions concentration. This dependence has two parts for the untreated electrode (Fig. 2, curve 1). The electrode potential changes insignificantly within the first part (concentration of HPO_4^{2-} 10^{-5}–10^{-3} mol/dm^3) and slope coefficient is 0.0035 V/decade. In the second part ranged from 10^{-3} to 10^{-1} mol/dm^3 HPO_4^{2-}, the slope coefficient is 0.015 V/decade. Similarly to the previous case, these values are different from the theoretical value for the double- and triple charged ions (0.0295 V/decade and 0.0197 V/decade respectively).

Table 1

Linear ranges in dependencies of the Ca-HOA electrode potentials on concentrations of Ca^{2+} and HPO_4^{2-} and corresponding slope coefficients (S)

Potential determining ion	Ca-HOA-electrode			
	Untreated		After pretreatment (kept in 10^{-3} mol/dm^3 $Ca(NO_3)_2$	
	Concentration range, mol/dm^3	S, V/decade	Concentration range, mol/dm^3	S, V/decade
Ca^{2+}	10^{-4}–10^{-2}	0.0145	10^{-5}–10^{-3}	0.0220
HPO_4^{2-}	10^{-3}–10^{-1}	0.0150	10^{-3}–10^{-1}	0.0225

The curve 2 represented in Fig. 2 represents a dependence of the electrode potential on concentration of HPO_4^{2-} for the pretreated electrode. It can be seen that this dependence is linear within the range of HPO_4^{2-} concentration 10^{-3}–10^{-1} mol/dm^3 and the slope coefficient is 0.0225

V/decade (compare with 0.015 V/decade for the untreated electrode).

Therefore, the electrode pretreatment influences its characteristics in the solutions of Ca^{2+} and HPO_4^{2-} and brings values of the slope coefficients closer to the theoretical magnitudes.

Another samples of the plasticized Ca-HOA electrode have been pretreated in the 10^{-3} mol/dm^3 solution of $(NH_4)_2HPO_4$ according to the above mentioned methodics. No influence of such pretreatment on the electrode characteristic in solutions of Ca^{2+} and HPO_4^{2-} was registered.

It can be summarized, that this method of potentiometric determination of Ca^{2+} and HPO_4^{2-} ions concentration can be applied to find contents of these ions in some natural objects, raw and food samples.

The plasticized electrodes based on the PVC substrate and Ca-HOA has been developed and their electrode characteristics for the Ca^{2+} and HPO_4^{2-} solutions were found, (Table 1).

4. Conclusion

Untreated electrodes show the linear dependence of the electrode potential on concentration of Ca^{2+} ranged from 10^{-4} to 10^{-2} mol/dm^3 with the slope coefficient 0.0145 V/decade. After pretreatment in the Ca^{2+} solution, the same electrode also showed the linear dependence with the slope coefficient 0.022 V/decade within the Ca^{2+} concentrations range 10^{-5}–10^{-3} mol/dm^3. Similar parameters for the HPO_4^{2-} solutions were 0.015 V/decade within 10^{-3}–10^{-1} mol/dm^3 (untreated electrode) and 0.0225 V/decade within 10^{-3}–10^{-1} mol/dm^3 (treated electrode).

Therefore, Ca-HOA can be used in the ion-selective electrodes for the food and raw materials analysis methods.

5. References

[1]. DARST R., *Ion-selective Electrodes*. Mir, Moscow. (1972).

[2]. *Electroanalytical Methods. Theory and Practice. (Ed.: F. Scholz)*. Binom, Moscow. (2006).

[3]. ORLOVSKY V., SUKHANOVA G., EZHOVA Z.H., RODICHEVA G., Hydroxylapatite Bioceramics. *Bulletin of the USSR Chemical Society*, 36, 683-688 (1991).

[4]. VLASOV Y., BYCHKOV. E., A Composition of the Chalcogenic Membrane for Determination of Cadmium Ions. *Journal of Analytical Chemistry*, 40, 1067-1070 (1985).

[5]. ZHYBAREV A, E. ZHARYKOV, AHMETSHIN. E., *A Method of Synthesis of Hydroxylapatite*. Russian Federation Patent 2505479.

[6]. KIBATLTSEV V., KOMAROV V., Express Synthesis of Hydroxylapatite Crystals. *Journal of Inorganic Chemistry*, **25**, 565-567 (1980).

[7]. FILIPPENKO V., ZYMAN Z., MEZENTSEV V., Use of the Hydroxylapatite Ceramics in the Musculoskeletal Systems Surgery. *Orthopaedics, Traumatology and Prostetics*, **3**, 141-142 (2000).

[8]. LAKSHMINARAYANH N., *Membrane Electrodes*. Khimiya, Leningrad (1979).