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HIGH THROUGHPUT ION SELECTIVE ELECTRODES BASED ON PHOSPHOMOLYBATE IONOPHORES FOR BARIUM ION DETECTION

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ABSTRACT

The study centered on the facile synthesis of an ion-active substance, specifically an ionophore formed from a barium center and phosphomolybdic acid, with subsequent spectral characterization to confirm structure and coordination; building on this, a systematic evaluation of Ba^{2+}-sensitive ion-selective electrodes (ISE) based on a family of heteropoly acids (including phosphomolybdate and related polyoxometalates) demonstrated clear advantages in selectivity, response, and stability for these receptors; electrodes were then fabricated incorporating the synthesized ionophore within a membrane environment (detailing the membrane composition, loading, and potential additives to balance charge and mobility), and their electrochemical response was thoroughly tested over a Ba^{2+} concentration range ranging from 10^{-1} to 10^{-6} mol L^{-1}, yielding calibration characteristics such as slope, linear range, and response time, with the limit of detection (LOD) for Ba^{2+} determined through standard analytical procedures; the work thus broadens the understanding of how phosphomolybdate-based ionophores perform in Ba^{2+}-selective sensing relative to other heteropoly-acid–based receptors, informs optimization of membrane composition for improved selectivity against common interfering ions, and provides a framework for comparing performance with existing Ba^{2+} ISE, including considerations of stability, reproducibility, and practical deployment in environmental or industrial monitoring which is highlighted in sustainable development goal (SDG) 3.

Keywords: ISE, Phosphomolybdates, Barium Ion, Electrode, Potential. SDG3

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INTRODUCTION

Due to the rapid development of industry and agriculture, the demand for fast, accurate, and relatively simple methods for monitoring metal ions is increasing drastically, and particularly the demand for ISE is high.[1,2,3] ISE exhibits selectivity for a specific ion in aqueous solutions and can determine the concentration of a particular ion in the aqueous solution depending on the electrode potential. This greatly simplifies the process of qualitative and quantitative analysis of a specific ion in a mixture of various ions.[4] It is known that electrodes for alkali and alkaline earth metal ions based on metal sulfides and organic ionophores have such disadvantages as low sensitivity, selectivity, and short operating lifetime. In this regard, it is urgent to develop ISE with high sensitivity, electrode activity in a wide pH range in which the electrode works, and with high selectivity.[5-7] This requirement is met by ionic association of cations with heteropolyacids-phosphotungstate, phosphomolybdate ions, etc., which have high specificity,

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fastness, and sensitivity. In this regard, it is also urgent to develop ion-selective electrodes for alkali and alkaline earth metals with ion-selective plasticized membranes.[8]

Due to the sufficient stability of the electrode active compound (EAC) prepared using phosphoromolybdic acids, a wide range of linearity of functions and a low limit of detection of cations are ensured.[9,10] In this regard, it is of great importance to study the relationships of the process of obtaining highly efficient ISE based on heteropoly acids and determine their optimal conditions. Particularly, methods for determining Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, etc. ions in industrial and pharmaceutical products, soil, groundwater and surface water using found of great scientific and practical importance.[11]

Ba^{2+} can originate from natural mineral weathering or industrial discharges; sensitive, selective sensors facilitate timely intervention. Many regions establish maximum permitted concentrations for barium in water; robust sensors support enforcement and risk assessment. Early detection reduces exposure risk in communities dependent on potentially affected water sources. For this reason, the development of straightforward methods for preparing ISE aligns with the sustainable development goal (SDG) 3 strategy. Several research groups are actively working on the development of highly efficient ISE, including sulfate, double carbonate $Li_2CO_3 \cdot BaCO_3$ and glass-ceramic matrix $SiO_2 \cdot B_2O_3 \cdot P_2O_5$, dihydro- and hydrophosphate selective electrodes, as well as microelectrodes, selenite-selective electrodes, sulfite-selective electrodes, and nitrate-selective electrodes.[12-17]

In this article, highly efficient Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+} selective electrodes that can operate over a wide concentration and temperature range were prepared and their properties were studied.

EXPERIMENTAL

Material and Methods

Polyvinylchloride (PVC), tetrahydrofuran (THF), plasticizer (dioctyl phthalate, DOP), molybdic acid (H_2MoO_4), nitric acid (HNO_3), phosphoric acid (H_3PO_4), and dibutyl phthalate were used as purchased. Phosphoromolybdic acid (PMA) was synthesized based on the methods described elsewhere.[18] Universal ionomer EV-74 (Gomel, Belarus) and ionomer I-160 were designed to determine the activity (pH values) of mono- and divalent anions and cations in aqueous solutions in conjunction with ion-selective electrodes, as well as to measure the oxidation-reduction potentials in these solutions. UV-vis absorption spectra were recorded on a double-beam spectrophotometer Shimadzu UV-2600i (Shimadzu, Japan). Standard glass cells were used throughout absorption measurements. Integrated sphere UV-2600 used to obtain diffuse reflectance data. Chemical and structural characterization was carried out using the FTIR spectrometer IRAffinity 1S (Shimadzu, Japan) equipped with an integrating sphere (MIRacle 10). Diffraction patterns recorded on Shimadzu Maxima XRD 7000 (Shimadzu, Japan). A monochromatic Kα beam was used from the copper anode. Element composition was acquired using a NexDE VS energy dispersive spectrometer (Rigaku, Japan).

Synthesis of $H_3PMo_{12}O_{40}$

Phosphomolybdic acid preparation can be described as the following reaction:

$$12H_2MoO_4(aq) + H_3PO_4(aq) + 21HNO_3(aq) \rightarrow H_3PMo_{12}O_{40}(s) + 21NH_4NO_3(aq) + 12\ H_2O(l)$$

To obtain 100 g of $H_3PMo_{12}O_{40}$, 106.6 g of molybdic acid was weighed. Molybdic acid was transferred to a 1000 ml heat-resistant flat-bottomed flask and dissolved in 500 ml of bidistilled water. This solution was heated to 80 ºC. Then, 300 ml of concentrated nitric acid was poured into another 500 ml flask, to which 200 ml of bidistilled water was added. In another flask, a 0.1 molar phosphoric acid solution was prepared from a concentrated (85%) phosphoric acid stock solution. Consequently, 500 ml of the prepared nitric acid solution was added to 460 ml of this solution. The mixture of phosphoric and nitric acids was heated to 70-80 ºC. A previously prepared solution of hot molybdic acid was added to this hot mixture of acids in small portions under constant stirring. In this case, a yellow precipitate was formed. The resulting solution was left for 24 hours to allow the process to complete. Then the precipitate was separated from the solution by filtration on a porous filter. The resulting precipitate was washed with distilled water until all the phosphate ions were completely washed out and dried in a Petri dish. The precipitate was first

dried at room temperature for 5 days, then in a thermostat at a constant temperature of 105 ºC. As a result, a yellow powder of phosphoromolybdic acid 96.8 g was obtained.

Synthesis of $Ba_3(PMo_{12}O_{40})_2$

For the synthesis of the ionophore $Ba_3(PMo_{12}O_{40})_2$, the determination of the amount of barium ion is necessary for a barium-selective electrode, for which 0.1 M solutions of phosphoromolybdic acid ($H_3PMo_{12}O_{40}$) and barium chloride ($BaCl_2$) were used. The reaction to describe for the synthesis can be described as:

$$3BaCl_2(aq) + 2H_3PMo_{12}O_{40}(s) \rightarrow Ba_3(PMo_{12}O_{40})_2(s) + 6HCl(aq)$$

The end product has a vivid green-yellow color (Fig.-1).

Fig.-1: The Appearance of Synthesized $Ba_3(PMo_{12}O_{40})_2$

Fig.-2: Membrane Prepared for Barium Selective Electrodes

ISE Membrane Preparation Process

The ISE membrane is a plasticized polymer film (here, matrix) with an ionophore embedded in it. Electroactive compounds synthesized on the basis of EAC and metal chlorides: calcium, strontium, magnesium, and barium were used as ionophores. The polymer matrix was made of PVC and a plasticizer. DOP or dibutyl phthalate (DBP) was used as a plasticizer. In the experiments, plasticized ISE film membranes were prepared by mixing PVC, plasticizer (DOP), and EAC in tetrahydrofuran. The EAC content in the resulting film was 5% of the membrane mass; the PVC plasticizer ratio was 1:2 by weight (Fig.-2). The membranes used for the preparation of ion-selective electrodes were prepared according to the following method. In a 20 ml beaker, 32% PVC powder (from the total mass of the mixture of all components used), 5% ionophore, and 63% plasticizer were dissolved in THF. The solution was poured into a Petri dish with a diameter of 10 cm (the diameter is 10 cm) and left for 24 hours until THF completely evaporated. An elastic transparent membrane with a thickness of 0.3-0.5 mm was formed. An ion-selective electrode capable of detecting barium ions in aqueous solutions was prepared from the resulting membrane (Fig.-4). The membrane electrode (Fig.-4) consists of a cylindrical Teflon body (Teflon material), to the end of which a plasticized membrane is attached with a special glue. The glue is prepared as follows: 0.5 g of dibutyl phthalate, 5 ml of cyclohexanone, and 0.25 g of PVC are poured into a beaker, heated in an oven, cooled, and allowed to thicken. The potential-detecting ion, 1.5 mol ($1 \cdot 10^{-5}$ – $1 \cdot 10^{-4}$ M), and 1-2 drops of 3 M KCl were added to the electrode body. A silver wire coated with a silver chloride salt was used as the internal reference electrode. The external reference electrode was performed by an ESR-10101 silver chloride AgCl electrode filled with a saturated KCl solution. Before measurements, the ISE with a plasticized membrane was kept in solutions of salts of potential-detecting ions of different concentrations for 12-24 hours.

Preparation of the ISE for the Experiment

A $1 \cdot 10^{-2}$ mol/l $BaCl_2$ solution was poured into the barium ion-selective electrode in a 0.1 mol/l KCl background, and a current conductor made of silver wire was connected. The conversion of the ISE to a working form was achieved by soaking in a 0.1 mol/l $BaCl_2$ solution for 2 days. After completion of the work, the electrodes were stored in a $1 \cdot 10^{-2}$ mol/l $BaCl_2$ solution.

RESULTS AND DISCUSSION

The amount of metal ions in the obtained EAC was determined by gravimetric, photocolorimetric, and complexometric methods. Results of elemental analysis of the synthesized metal dodecamolybdenum phosphates are presented in Table-1.

Table-1: Elemental Content of Phosphomolybdates.

Chemical formula of ionophore	Amount of components in the synthesized substance							
	Cation		Anion $(PMo_{12}O_{40})^{3-}$					
	Grams	Mass %	Phosphorus		Molybdenum		Oxygen	
			Grams	Mass %	Grams	Mass %	Grams	Mass %
$H_3PMo_{12}O_{40}\cdot$	3.024	0.163	30.97	1.690	1151.28	63.107	639.6	35.040
$Ba_3(PMo_{12}O_{40})_2$	117.27	6.048	30.97	1.575	1151.28	59.412	639.6	32.965

Results of energy dispersive X-ray fluorescence spectroscopy analysis of the obtained $Ba_3PMo_{12}O_{40}$ confirm Ba: P: Mo molar ratio is 3: 2 : 2 (Fig.-3).

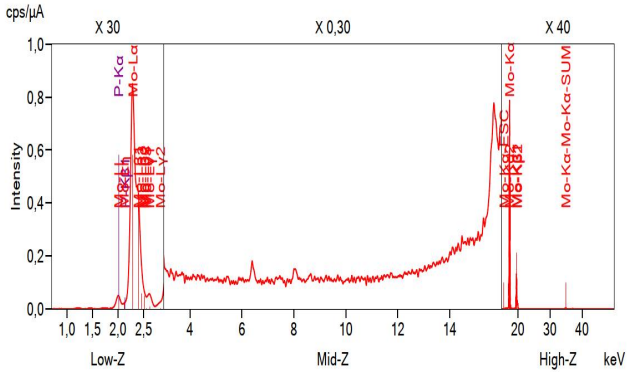

Fig.-3: EDS XR Spectrum of $Ba_3(PMo_{12}O_{40})_2$

The decrease in the weight of the synthesized metal dodecamolybdenum phosphate samples to a constant weight value at a temperature of 105 ºC was 2.5-3.5% of the initial sample weight. This change in the sample weight is probably due to the evaporation of water molecules and other volatile substances adsorbed on the surface of the synthesized samples. By thermogravimetric analysis, a second jump, a change in mass, was observed in the temperature range of 110-125 ºC. Using the results of thermogravimetric and gravimetric analysis, the amount of water in moles corresponding to one mole of the synthesized electrode active compounds was calculated, and their molecular formula and molecular weight were determined (Table-2).

Table-2: Results of Water Content in the EAC

No	Chemical formula of the EAC	EAC crystallization water	Anhydrous EAC	Water content in 1 mol of EAC	
				Grams	Moles
1	$H_3PMo_{12}O_{40}$	2058.948	1824.87	234.078	13.00
2	$Ba_3(PMo_{12}O_{40})_2$	2137.198	1939.12	198.066	9.49

Thus, it was found that the composition of the metal dodecamolybdenum phosphates obtained as a result of the experiments corresponds to the following: $Ba_3(HMo_{12}O_{40})_2.9{,}5\ H_2O$.

The electrode performance interval of the developed barium ISE was determined, and the final result was obtained on the concentration-dependent operating range (Fig.-5).

The graph shows a negative linear correlation between analyte concentration and measured potential, with a slope of 1.2 mV/molar, consistent with the Nernst equation for a divalent ion. The high R^2 value (0.968) indicates a strong linear fit, suggesting the system behaves ideally over the tested concentration range. Range of linearity: No significant outliers are present, and error bars remain small, confirming measurement precision. The electrode showed the following characteristics: linearity range is 10^{-1}-10^{-5} M of Ba^{2+}; limit of detection (LOD) 0.035 µg/mL; limit of quantification (LOQ) 0.117 µg/mL.

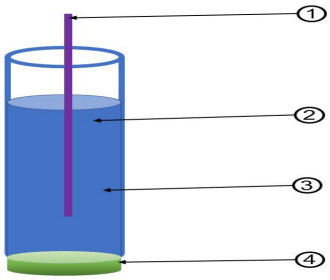

Fig.-4: Construction of a Liquid ISE with a Plasticized Membrane. (1 – internal reference electrode; 2 – standard solution; 3 - Teflon body; 4 – plastisized membrane)

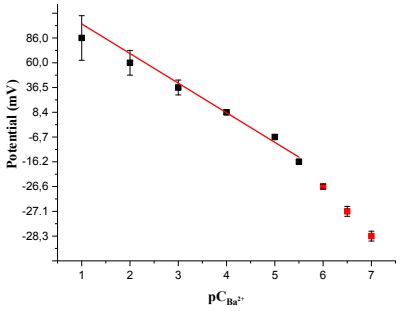

Fig.-5: Dependence of the Electrode Potential of an ISE Based on Ba^{2+}-EAC for the Detection of Barium Ions in the Solution

CONCLUSION

A novel ionophore for barium ion was synthesized based on the EAC and the corresponding metal salt, and the process of forming an optimal liquid membrane based on this ionophore was studied. Based on the resulting membrane, an ion-selective electrode capable of selectively and fast detecting barium ions in aqueous solutions was fabricated, and the operating range of this electrode was measured. The patterns identified as a result of the studies allowed the selection of membrane compositions with the best electroanalytical properties, and based on them, an ISE was developed for the quantitative determination of barium ions. The conducted research conforms to the SDG 3 strategy.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-3: Good Health and Well-being*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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