

Short Communication

Preparation of Phosphate Ion-Selective Membrane Based on Silver Salts Mixed with PTFE or Carbon Nanotubes

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Received: 14 November 2017 / Accepted: 13 December 2017 / Published: 28 December 2017

A sensitive phosphate sensor has been prepared by constructing a solid membrane disk consisting of variable mixtures of silver phosphate, silver sulfide, and PTFE (Type 1 membrane) or silver phosphate, silver sulfide and nanotube (Type 2 membrane). The ternary membranes exhibit greater selectivity over the wide range of concentration. The membrane with the composition of 50.00% PTFE; 41.66% Ag_3PO_4 and 8.33% Ag_2S was selected as our preferred membrane. The membranes exhibited linear potential response in the concentration range of 1×10^{-1} to 1×10^{-5} M. Their detection limit is about 5×10^{-6} M. The membranes have a long lifetime and can be stored in air when they are not in use. The best performance for nanocomposite sensor was obtained with membrane of the following composition: 78.00% Ag_3PO_4 ; 20.00% Ag_2S , and 2.00% carbon nanoparticles. The membrane had a slope of 32.6 mV toward HPO_4^{2-} ions in the range between 1×10^{-1} and 1×10^{-5} M with a detection limit of 5.45×10^{-6} M. The proposed sensors were found to be applicable over a pH range between 3 and 7.

Keywords: ion selective electrode, monohydrogen phosphate, potentiometry, carbon nanotubes, PTFE.

1. INTRODUCTION

Phosphate rocks are a non-renewable natural resource, mainly found in sedimentary and igneous deposits. Weathering and erosion of rocks lead to phosphorus release in form of phosphate ions, which are soluble in water. Most of the phosphate is washed out into the natural waters during leaching processes [1]. Phosphates could be found in aquatic systems as dissolved, colloidal and particulate fractions both as inorganic or organic compounds that may be biotic or abiotic particles [2].

Changes in physical-chemical conditions and biological activities cause fluctuation of phosphate concentrations in natural waters. Seasonal pH change, concentration of dissolved carbon dioxide and total dissolved calcium concentration affect phosphates' availability [3]. It is very important to mention that phosphates and their derivatives can have wide applications in different industrial branches e.g. pharmaceutical and food, as well as in advanced technology, e.g. for lasers and sensors production. Due to the wide usage of phosphate, the need for phosphate regulation and monitoring in the environment cannot be overstated [1, 4].

There are proposed analytical methods for measuring low concentrations of phosphate ions by UV-Vis spectrophotometric methods such as molybdenum blue, complex of molybdophosphate with basic dye compounds [5]. On the other hand, an alternative method for phosphates determination is potentiometry using ion-selective electrode. Potentiometric methods are simple, low-cost, accurate and rapid [5-11]. The design and construction of both, phosphate selective electrodes and membranes, have been ongoing for decades. A major concern in the construction of phosphate ion-selective electrodes is choosing sensing material. Due to the very high hydration energy of phosphates, ion-selective membranes have a very poor selectivity for phosphates [12].

This paper reports the construction of a suitable ion-selective electrode based on silver salts and PTFE or carbon nanotube.

2. EXPERIMENTAL

2.1. Reagents

All reagents were prepared from analytical reagent grade chemicals unless otherwise specified and all the solutions were made with double distilled water.

A standard solution of 0.1 M lead (II) nitrate was prepared by dissolving 16.5605 g of lead (II) nitrate in 500.0 mL double distilled water. Solution of sodium hydrogenphosphate was prepared by weighting 17.9071 g Na_2HPO_4 and dissolved in double distilled water. Silver nitrate solution (0.1 M) was prepared from silver nitrate. Further concentrations of silver nitrate were prepared by diluting the standard solution. The sodium sulfide solution was prepared by dissolving a certain amount of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in double distilled water. Concentration of such solution was determined with lead (II) nitrate standard solution. SAOB-II solution was prepared dissolving 20 g NaOH, 8.75 g ascorbic acid and 16.75 g EDTE-a in 250 mL double distilled water.

2.2. Preparation of electrode materials

Next reagents were used for the preparation of membranes: silver powder, extra fine grade, 99.95%, 500-1200 nm, obtained from Inframat Advanced Materials, Manchester, USA and home-made silver sulfide, silver phosphate and polytetrafluoroethylene (PTFE) or silver sulfide, silver phosphate and carbon nanotubes. Carbon nanotubes were purchased from Sigma Aldrich (USA).

The first type of membrane was prepared by mixing silver sulfide, silver phosphate, polytetrafluoroethylene (PTFE), second type of membrane was prepared by mixing silver phosphate and carbon nanoparticles with the addition of linseed oil. The composition of electroactive material is presented in Table 1 and Table 2.

Table 1. Composition of electroactive materials for Type 1 membranes

Number	Type 1	Mass (g)	w(%)
1.	PTFE	1.20	50.00
	Ag ₃ PO ₄	1.00	41.66
	Ag ₂ S	0.20	8.33
2.	PTFE	1.20	46.15
	Ag ₃ PO ₄	1.00	38.46
	Ag ₂ S	0.40	15.39
3.	PTFE	1.20	50.00
	Ag ₃ PO ₄	1.00	41.66
	Ag	0.20	8.33
4.	PTFE	1.20	46.15
	Ag ₃ PO ₄	1.00	38.46
	Ag	0.40	15.39
5.	PTFE	1.20	42.86
	Ag ₃ PO ₄	1.00	35.71
	Ag	0.60	21.43
6.	PTFE	1.20	40.00
	Ag ₃ PO ₄	1.00	33.33
	Ag	0.80	26.66

Table 2. Composition of electroactive materials for Type 2 membranes

Number	w(Ag ₂ S) %	w(Ag ₃ PO ₄) %	w(carbon nanotubes) %
1.	50.00	49.00	1.00
2.	30.00	68.50	1.50
3.	20.00	78.00	2.00
4.	55.00	42.50	2.50
5.	61.00	36.00	3.00
6.	50.00	50.00	0.00

2.3. Electrode assembly

After mixing electroactive materials, they were pressed at 700 MPa for 1.5-2 hours at room temperature. Prepared membranes were placed in specially constructed multi-purpose Teflon® body [13] and the stainless steel disk (Type 1 membrane) provided electric contact.

The Type 2 membranes were prepared by mixing electroactive materials with linseed oil. After homogenization of the mixture, the mixture was placed in a plastic tube with an immersed copper wire in the centre. The electrodes were dried at room temperature for 48-72 hours. [14]

2.4. Potentiometric measurements

External reference electrode was double junction electrode (DJRE) purchased from Orion (USA). The potentiometric measurements were carried out by means of Mettler Toledo pH-meter (USA) and magnetic stirrer, Železnik MM 510 (Slovenia). The potential that builds up across the membrane electrode was measured using the following electrochemical cell:

External reference electrode (DJRE)|| test solution| ISE

The potential was recorded after adding HPO_4^{2-} solution in magnetically stirred with pH value 9.2. The investigated potentiometric concentration range was from 1.0×10^{-6} M to 1.0×10^{-1} M.

3. RESULTS AND DISCUSSION

3.1. Calibration curve

The multi-purpose electrode body with solid-state contact made in the laboratory was used for measuring Type 1 membranes. The replacement of selective membranes is quick and easy, and the cleaning and polishing of the electrode surface is easily feasible.

Membrane contact was accomplished over stainless steel disc and signal (potential change) was transferred by a coaxial cable to the instrument. There are various contacts of the membrane and instrument described in the literature [15, 16]. Solid-state contact with membrane characterizes certain advantages compared to the liquid electrolyte contact [17].

The measuring range of ion-selective electrode refers to the linear part of the calibration curve. According to IUPAC definition, the measuring range of an ion selective electrode is defined as the activity range between the upper and lower detection limits [5]. Figure 2 states the potentiometric responses of Type 1 membranes at pH 9.2. All membranes show linear responses in the range concentrations of HPO_4^{2-} 10^{-1} to 10^{-5} M. Response characteristic of membranes are presented in Table 3. The electrode containing 8.33% of Ag_2S showed the best response characteristics with a slope of 21.0 mV per decade, however, the slopes of the other tested membranes were significantly lower.

The complete Nernst equation is composed of Nernst factor, sensitivity factor and selectivity factor. The Nernst equation can be modified by the sensitivity of the electrode, $S/100\%$. Due to the interference of other ions, the selectivity of electrode was never 100% [1].

HPO_4^{2-} is major specie among all derived of phosphoric acid with share around 98.95% at pH value of 9.2. At pH value of 9.2 can be found in about 0.70% of PO_4^{3-} and 0.98% of H_2PO_4^- . Although PO_4^{3-} and H_2PO_4^- occur in a significantly small fraction comparing to HPO_4^{2-} , both of them can affect to membrane slope, probably in synergistic effect since they react with silver ions in membrane and yield complex containing both PO_4^{3-} and H_2PO_4^- . Mentioned effect leads to slope decrease from 29.5

mV per decade (theoretically Nernstian slope) to about 20 mV. On the other hand, at alkaline solution, the formation of Ag₂O can occur. In such occasion, Ag₂O is deposited on the membrane and affects the membranes' response characteristics too. Substantial Ag₂O influence can be expected for membranes containing high share of Ag and/or Ag₂S, in our case this applies to Type 1 membranes. One of the effects of Ag₂O influence is causing significant decrease of the slope. On the other hand, it should be stressed that the Type 1 membranes retain their positive characteristics (e.g. response time, slope, and linear dynamic range) for a few years.

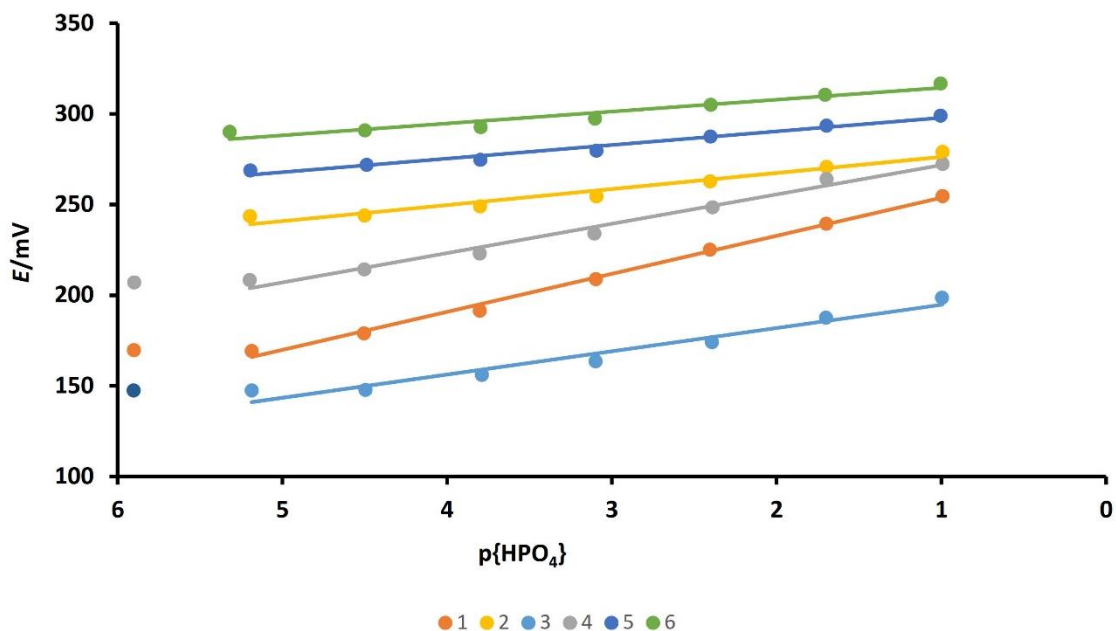


Figure 1. Calibration curves for the electrode membranes containing: *w*(Ag₂S) 1) 8.33%, 2) 15.39%, and *w*(Ag):3) 8.33%, 4) 15.39%, 5) 21.43%, 6) 26.66% respectively.

An indication of the influence of an excess of, both metallic and non-metallic components, of the active substance composition to the membrane response can be found in the literature [18], e.g. can cause collapse of "internal equilibria" of the active substance composition in the membrane.

The contact in Type 2 membrane between membrane and examined solutions was established through hole at the bottom of Type 2 membrane holder. The holder was a plastic cylinder in diameter of 10 mm.

Table 3. The potentiometric characteristics of Type 1 membranes

Membrane	Linear response range (M)	Detection limit (M)	Slope (mV/dec)	R ²
1.	1×10 ⁻⁵ – 1×10 ⁻¹	5.31×10 ⁻⁶	21.0	0.9955
2.	1×10 ⁻⁵ – 1×10 ⁻¹	3.36×10 ⁻⁶	8.84	0.9585
3.	1×10 ⁻⁵ – 1×10 ⁻¹	5.04×10 ⁻⁶	14.8	0.9931
4.	1×10 ⁻⁵ – 1×10 ⁻¹	4.25×10 ⁻⁶	16.2	0.9834
5.	1×10 ⁻⁵ – 1×10 ⁻¹	3.94×10 ⁻⁶	7.51	0.9755
6.	1×10 ⁻⁵ – 1×10 ⁻¹	2.09×10 ⁻⁶	6.58	0.9328

We prepared six membranes with a different share of nanoparticles. The best response characteristics was found in membrane 3 (Table 4). The linear response range was between 10^{-5} - 1×10^{-1} M with a potential change of 32.6 mV per decade. However, it has to be mentioned that the potential change in the first measurement was significantly lower (13.01 mV).

Figure 2 shows the potentiometric response of Type 2 membrane, but only for the best one (marked as 3 in Table 2). Table 4 shows the potentiometric characteristics of all tested Type 2 membranes. Other investigated membranes showed the potential change of only a few mV per the concentration decade. The preparation of these membranes is relatively simple. However, if the nanoparticle fraction is too large, that could cause covering the electroactive parts of membrane surface. Covered electroactive parts of membrane surface are causing unstable potential, as well as the potential change in the concentration decade which becomes negligible. Similar cases were reported previously [5].

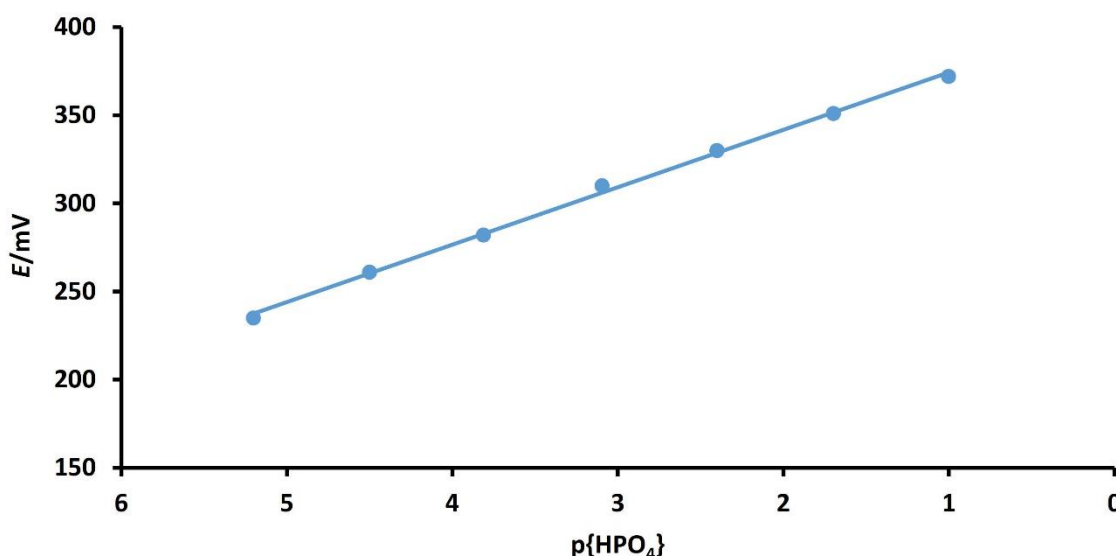


Figure 2. Calibration curve for the Type 2 membrane with a composition of 20.00% Ag_2S ; 78.00% Ag_3PO_4 ; 2.00% nanotubes.

Table 4. The potentiometric characteristics of Type 2 membranes

Number	Linear response range (M)	Detection limit (M)	Slope (mV/dec)	R^2
1.	$1 \times 10^{-5} - 1 \times 10^{-1}$	*	11.6	0.9491
2.	$1 \times 10^{-5} - 1 \times 10^{-1}$	*	1.42	0.2519
3.	$1 \times 10^{-5} - 1 \times 10^{-1}$	5.45×10^{-6}	32.6	0.9980
4.	$1 \times 10^{-5} - 1 \times 10^{-1}$	*	3.44	0.9478
5.	$1 \times 10^{-5} - 1 \times 10^{-1}$	*	6.95	0.9150
6.	$1 \times 10^{-5} - 1 \times 10^{-1}$	*	5.35	0.9069

* - not calculated because correlation coefficients were not satisfied

3.2. pH effect on the membrane response

Effect of pH was tested for Type 1 membranes only. The potential response of membranes were determined by investigating membrane response in solutions where HPO_4^{2-} concentrations were 1.0×10^{-1} , 1.0×10^{-2} , 1.0×10^{-3} M, respectively. The pH value varied from 3 to 11 by adding HNO_3 or NaOH . The potential change was a function of pH value. pH influence of the Type 1 membrane No. 1 is shown in Figure 3. The response of the sensors was independent of pH influence in the range 3–7, as shown in Figure 3. Visible interference of H^+ or OH^- was not observed in this pH range. A similar effect of pH was observed for all other tested membranes.

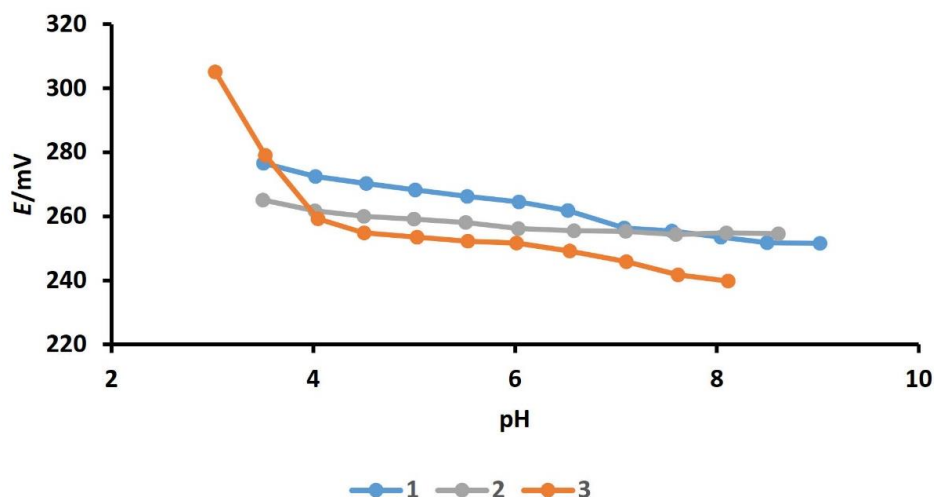


Figure 3. Effect of pH on the potential response of the electrode with ratio Ag_2S 8.33% (Type 1 membrane No.1) in the Na_2HPO_4 solutions concentration: 1) 0.100 M; 2) 0.010 M; 3) 0.001 M

Figure 4 shows the influence of pH on the electrode response for Type 2 membrane with 2% of nanotubes.

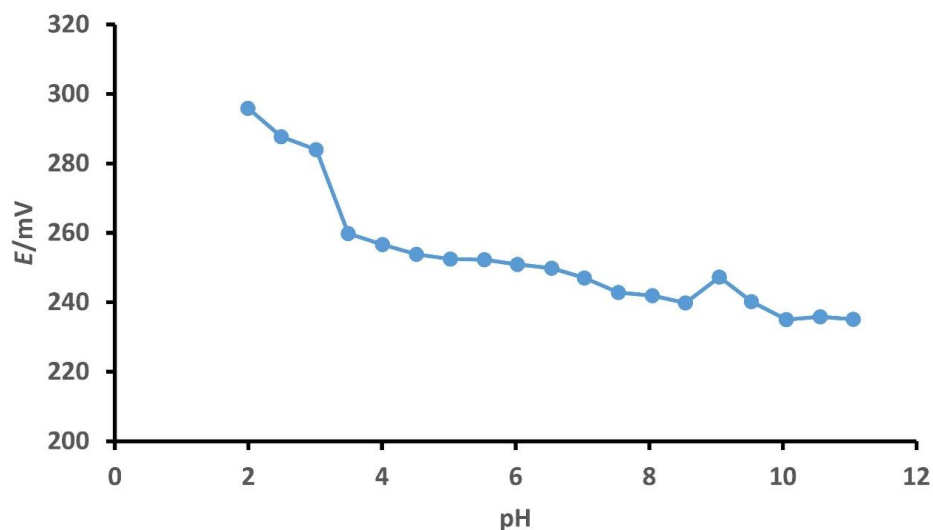


Figure 4. Effect of pH on the potential response of the electrode with 2% nanotubes in the solution Na_2HPO_4 concentration 0.10 M.

3.3. Response time

The response time of an ion-selective electrode is an important factor for any analytical application too. The response times of the membranes were measured at 10-fold increase of the HPO_4^{2-} concentration with method proposed by IUPAC [19]. Experimental conditions such as stirring, ionic concentration and composition of the testing solution, as well as the concentration and composition of the solution to which electrode was exposed. Before performing the experimental measurements, any previous usage or preconditioning of the membrane and testing temperature can have an effect on the experimental response time of a sensor [20]. Results in Fig. 5 showed that the potentiometric response time of the membrane was about 60 s in whole concentration range.

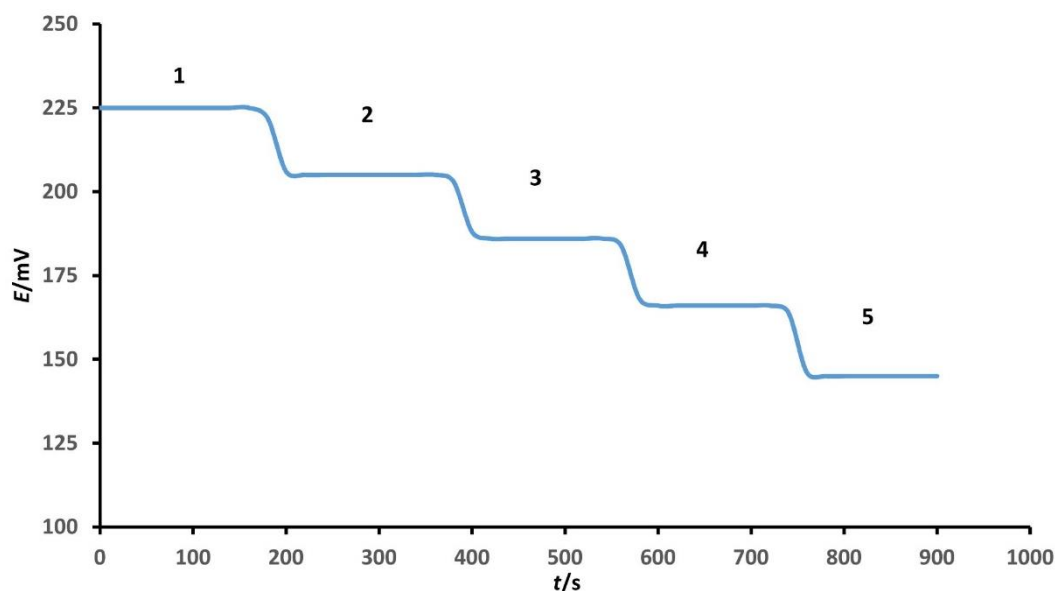


Figure 5. Dynamic response of Type 2 membrane (No. 1) on different concentration HPO_4^{2-} . 1) 1×10^{-2} M; 2) 1×10^{-3} M; 3) 1×10^{-4} M; 4) 1×10^{-5} M; 5) 1×10^{-6} M.

3.4. Lifetime

The Type 1 membranes (membranes based on silver salts and PTFE) showed the same response characteristics after several years, but the Type 2 membranes have lost responsive characteristics after a few days. Other authors have noted similar observations for membranes containing nanotubes [5].

3.5. Comparison of Type 1 and Type 2 membranes with similar ones

By searching the literature using Web of Science for the last five years, we have established a very few phosphate sensors similar to ours. The dominating type of phosphate sensors are fluorescent ones [21-23]. Those kind of sensors are based on very different chemical reactions, as well as used detectors (UV-Vis spectrophotometer) toward our sensors. Nevertheless, few sensors used as a detector for phosphate in various electroanalytical techniques could be found, e.g. voltammetry [24-26] and

amperometry [27]. Table 5 shows comparison for a few found potentiometric sensors proposed for phosphate determination.

Table 5. Comparison of Type 1 and Type 2 membranes towards similar ones

Sensor	Linear range	Coefficient of correlation	Slope (if applicable)	Lifetime (if applicable)	Limit of detection, M
Type 1	$1 \times 10^{-5} - 1 \times 10^{-1}$	0.9955	21.0	2 years	5.31×10^{-6}
Type 2	$1 \times 10^{-5} - 1 \times 10^{-1}$	0.9980	32.6	5 days	5.45×10^{-6}
PVC-BA[28]	$1 \times 10^{-6} - 3.1 \times 10^{-4}$ $3.1 \times 10^{-4} - 1 \times 10^{-1}$	N/A	20.9 46.2	4 days	1.0×10^{-7}
PVC-DBP [28]	$3 \times 10^{-5} - 3 \times 10^{-2}$	N/A	69.5	4 days	1.0×10^{-7}
PVC-NOPE[28]	$1 \times 10^{-5} - 1 \times 10^{-2}$	N/A	58.9	4 days	1.0×10^{-6}
Bis[29]	$5 \times 10^{-7} - 5 \times 10^{-3}$	0.995	32.0	5 hours	N/A
[30]	$1 \times 10^{-5} - 1 \times 10^{-1}$	N/A	26.9	3 months	1.9×10^{-6}

N/A – not available

By analysing data in Table 5, it can be seen that membranes containing polymer carrier, e.g. PVC like ours and ionophores [28] have narrower linear dynamic range, except those with benzyl acetate (BA). Although two kinds of PVC membranes have narrower linear dynamic range, the authors gave the same limit of detection for all three types. This statement is very ambiguous to readers. Since the authors [28] did not mention a method for membranes testing, we assumed that standard adding was performed during the test and authors started from 1.0×10^{-7} M solution. At such low concentration, the possibility of phosphate ions leaking from membranes to Nerst layer, at the border of membrane surface and solution is increasing. This phenomenon is very common for all ion-selective membranes. Among others found ion-selective membranes for phosphate, our membranes, especially Type 1 ones, emphasize their simplicity for preparation and long lifetime (at least two years), while in all cases, both dynamic range and limit of detection are very similar. We hope that our Type 1 membranes could be used for phosphate determination at pH = 3-7.

4. CONCLUSION

All the tested Type 1 membranes showed a linear response range down to HPO_4^{2-} concentrations of 10^{-5} M. However, the potential change per concentration decade is below the expected theoretic value for the bivalent ionic species. Significant pH effect to the Type 1 membranes in the pH range 5-8 was not detected. Type 1 membranes are not losing response characteristics during a few years. On the other hand, used electrode body has a simple design, it is mechanically and electrically very reliable, and allows quick and easy membrane replacement. Although Type 2 membranes have a simple design too, they did not showed satisfactory properties. Most of the prepared Type 2 membranes showed poor potential change and short lifetime. Nevertheless, Type 2 membrane

No. 3 showed an excellent slope of 32.6 mV per decade, slightly above Nernstian theoretical value. Generally, it could be stated that membranes containing nanotubes have a short lifetime.

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