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Article

Anion Recognition: Fabrication of a Highly Selective and Sensitive HPO_4^{2-} PVC Sensor Based on a Oxo-Molybdenum Methyl-Salen

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Um sensor de monohidrogenofosfato (MHP) altamente seletivo e sensível foi obtido, através da preparação de uma membrana de PVC, contendo oxo-molibdênio com ligantes derivados do salen (MS) como carregador neutro, brometo de hexadeciltrimetil amônio (HTAB) como aditivo catiônico e benzilacetato (BA) como solvente plastificante mediador. A membrana sensora exibe uma resposta linear no intervalo de concentração de 1,0 × 10^{-1} a 4,0 × 10^{-7} mol L^{-1} de MHP. O eletrodo mostra uma inclinação Nernstiana de –28,6±0,3 mV década^{-1} em pH 8,5. O sensor proposto também exibe um tempo de resposta menor que 15s. O limite de detecção do sensor é 2,0 × 10^{-7} mol L^{-1} (~20 ng mL^{-1}), e pode ser usado por um período superior a oito semanas, sem alterações significantes na resposta. A seletividade do sensor, com relação a outros ânions comuns, orgânicos e inorgânicos (por exemplo, cloreto, brometo, iodeto, nitrato, sulfito, sulfato, carbonato, perclorato, cianeto, tiocianato, diidrogenofosfato, pirofosfato de tetrasódio e íons tripolifosfato de sódio) é excelente. A utilidade prática do sensor foi demonstrada pelo uso como eletrodo indicador na titulação potenciométrica de MHP com íons Ba^{2+} e pela determinação direta de MHP em amostras de fertilizantes granular e líquido e em amostras de água de descarte.

A highly selective and sensitive monohydrogen phosphate (MHP) sensor has been fabricated by constructing a poly vinyl chloride (PVC) matrix membrane containing a new oxo-molybdenum methyl-salen (MS) as a neutral carrier, hexadecyltrimethyl ammonium bromide (HTAB) as a cationic additive, benzylacetate (BA) as a plasticizing solvent mediator. The membrane sensor exhibits linear potential response in the concentration range of 1.0 ×10^{-1} – 4.0 × 10^{-7} mol L^{-1} of MHP. The electrode displays a Nernstian slope of -28.6 ± 0.3 mV decade^{-1} in the pH of 8.5. The proposed sensor also exhibits a fast response time of <l5 s. The detection limit of the proposed sensor is 2.0 × 10^{-7} mol L^{-1} (~20 ng mL^{-1}), and it can be used over a period of eight weeks without significant changes in its response. The selectivity of the sensor with respect to other common organic and inorganic anions (e.g. Chloride, bromide, iodide, nitrate, sulfite, sulfate, carbonate, perclorate, cyanide, thiocyanate, dihydrogen phosphate, tetrasodium pyrophosphate, and sodium tripoly phosphate ions) is excellent. The practical utility of the sensor has been demonstrated by using it as an indicator electrode in the potentiometric titration of MHP with Ba^{2+} ions and for the direct determination of MHP in granular and liquid fertilizer samples as well waste water samples.

Keywords: monohydrogen phosphate, PVC membrane, sensor, oxo-molybdenum methyl-salen, potentiometry

Introduction

Phosphate levels in freshwaters have increased in the past 50 years, which may have a negative effect on aquatic ecology and water quality.[1] Recent studies show that leaching of PO_4^{2-} as small as 10 µg L^{-1} from agricultural land can contribute to eutrophication.[2] Thus, due to the increasing use of phosphate fertilizers in agricultural industries, monitoring of phosphate ions is very important.

The main methods for determination of phosphate ions in real samples are ion chromatography and spectrophotometric methods such as molybdenum blue, complex of molybdophosphate with basic dye compounds and indirect lanthanum chloranilate methods.

The development of novel sensors for fast, accurate, sensitive and selective determination of monohydrogen phosphate (MHP) ion in various species is of great interest

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due to its existence in clinical, environmental, agricultural and medical systems. Recently, a number of hydrogen phosphate membrane sensors based on different ion carriers such as dialkyl and diaryltin derivatives, uranyl salophen, vanadyl salen, vanadyl salophen, bis-thiourea and modified calix arene have been reported.[3-16]

In recent years, we have introduced a number of selective membrane sensor for different anions such as Cl^-, Br^-, I^-, SO_4^{2-}, NO_2^-, SCN^-, HPO_4^{2-}, and I_3^-.[12,16-26] In this report we introduce the synthesis of a oxo-molybdenum methyl-salen and its application in fabrication of a highly selective and sensitive MHP membrane sensors for fast monitoring of MHP in various granular fertilizers as well as waste water of fertilizer industry.

Experimental

Reagents

Reagent grade benzyl acetate (BA), dibutyl phthalate (DBP), nitrobenzene (NB), acetophenone (AP), hexadecyltrimethylammonium bromide (HTAB), tetrahydrofuran (THF), and high relative molecular weight PVC were purchased from Merck chemical company and used as received. The sodium or potassium salts of the anions, NH_4VO_3, $(NH_4)_6Mo_7O_{24}.4H_2O$, KH_2PO_4 used (all from Merck or Aldrich) were of the highest purity available, and used without any further purification except for vacuum drying over P_2O_5. Doubly distilled de-ionized water was used throughout.

Synthesis of MS

The Schiff-base, bis(2-hydroxy-acetophenone)ethylendimiimine, was prepared according to the literature through the well known, as follows: 1,2-diaminoethane (0.3 g, 5 mmol) was dissolved in 40 mL ethanol and then transferred into a 250 mL three-necked flask. Under reflux, 1.36g (10 mmol) of 2-hydroxy-acetophenone in 40 mL ethanol was added dropwise to the flask. The mixture was stirred for 50 min, under reflux, and the cooled to room temperature. The solid product was filtered, and the product was recrystallized from chloroform.

Dioxomolybdenum(VI) complex with bis(2-hydroxy-acetophenone)ethylenediimine $[MoO_2(Me_2Salen)]$ (Figure 1) was prepared in a manner similar to that reported by Gonzales and Nagaraja.[27] Anal. Calc. for $C_{18}H_{18}MoN_2O_4$: C, 51.19; H, 4.30; N, 6.63; Mo, 22.73. Found: C, 50.97; H, 4.21; N, 6.74; Mo, 22.60%. ^{1}H NMR ($CDCl_3$): δ 7.2-8.4 (m, 8H, aromatic ring), 2.46 (s, 6H, Me), 3.1 (t, 4H, $-CH_2-$). IR (KBr) ν_{max}/cm^{-1}: 948 (ν_{Mo}=0); 1620($\nu_{C=N}$).

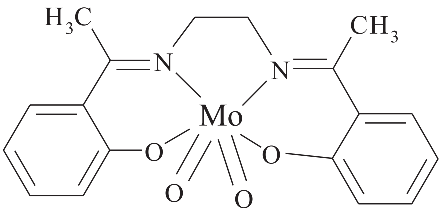

Figure 1. Structure of MS.

Preparation of electrodes

Membrane solutions were prepared by thoroughly dissolving 7.0 mg of the oxo-molybdenum methyl-salen (MS), 58.0 mg of BA, 33.0 mg of PVC and 2.0 mg of HTAB in 3 mL of fresh THF. The resulting solution was evaporated slowly until an oily mixture was obtained. A Pyrex tube (5 mm o.d) was dipped into the mixture for about 10 s so that a nontransparent membrane of 0.3 mm thickness was formed. The tube was then pulled out from the mixture, and kept at room temperature for 10 h. The tube was then filled with an internal solution (1.0×10^{-3} mol L^{-1} MHP). The electrode was finally conditioned for about 12 h by soaking in a 1.0×10^{-2} mol L^{-1} MHP solution. A silver/silver-chloride electrode was used as the internal reference electrode.

Potential measurements

All emf measurements were carried out with the following assembly: Hg_2Cl_2, KCl (satd.)‖sample solution | membrane | internal solution 1.0×10^{-3} mol L^{-1} MHP| Ag-AgCl. A Corning ion analyzer 250-pH/mV meters was used for potential measurements at 25.0±0.1 °C.

Determination of orthophosphate by colorimetric method

The molybdovanadophosphoric acid method was used as colorimetric method in this work. According to this method, addition of molybdate to an acidic solution containing orthophosphate and vanadate, results in the formation of yellow-orange molybdovanadophosphoric acid having the P:V:Mo ratio of 1:1:11.

Ammonium metavanadate, 0.25% solution. Dissolve 1.25 g of NH_4VO_3 in 250 mL of hot water. Cool the solution and add 10 mL of conc. HNO_3. Allow the solution to stand overnight, filter (if necessary), and dilute with water to 500 mL. Store solution in a polyethylene container.

Ammonium molybdate, 5% solution. Dissolve in 250 mL of water (at about 50 °C) 25 g of $(NH_4)_6Mo_7O_{24}.4H_2O$. Allow the solution to stand overnight, filter (if necessary), dilute with water to 500 mL, and store in a polyethylene container. Standard phosphorus (V) solution (KH_2PO_4): 1 mg mL^{-1}.

Procedure

10 mL of HCl 10% (m/m), is added to the 100-500 mg of each sample. Then the solution is filtered after 10 min shaking. The resulted solution was diluted to 250 mL. To the slightly acidic sample solution containing not more than 0.3 mg of P, add successively 2.5 mL of nitric acid (1+1), 2.5 mL of the vanadate solution, and 2.5 mL of the molybdate solution, mixing the solution after the addition of each reagent. Dilute the solution to volume with water in a 25 mL standard flask. After 30 min, measure the absorbance at 400 nm against a reagent blank solution.[28]

Results and Discussion

UV-Vis study

The preferential response towards MHP is believed to be associated with the coordination of MHP with the central metal of the ion-carrier MS. With UV/Vis spectra, as illustrated in Figure 2, it was possible to distinguish the interactions between the central metal and MHP. The substantial increases in the absorbance at 292.5 nm after the contact of the carried solution with a monohydrate phosphate-containing phase suggested that the absorbing species had increased in size and axial coordination was thought to take place. At the same time, the effects of other anions such as chloride, bromide, sulfate, perclorate on the spectrum of the carrier were investigated and no detectable changes in the UV/Vis spectra were noted. These results revealed that the oxo-molybdenum methyl-salen has especial tendency to the MHP ions respect with other common anions. The obtained results denoted that the mechanism of the response of the membrane sensor to MHP is based on coordination of MHP ion to oxo-molebdenum and its rapid exchanges with the solution containing MHP ions.

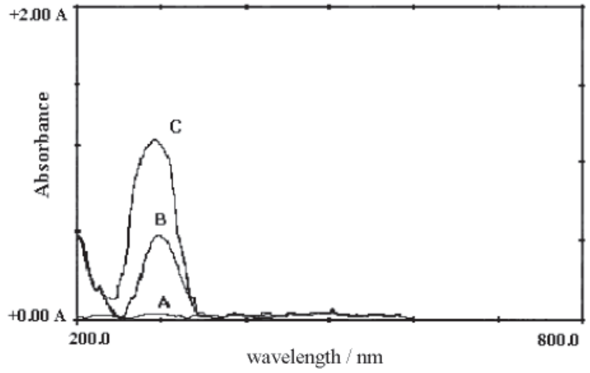

Figure 2. UV/Vis absorption spectra of acetonitrile solution of 5.0 × 10^{-5} mol L^{-1} K_2HPO_4 solution (A), 5.0 x 10^{-5} mol L^{-1} MS in the absence of K_2HPO_4 (B) and 5.0 × 10^{-5} mol L^{-1} MS titrated with 5.0 × 10^{-5} mol L^{-1} K_2HPO_4 solution (C).

Thus, in the next experiments MS was used as a suitable active component in the fabrication of a number of PVC-membrane sensors for a wide variety of common inorganic anions including chloride, bromide, iodide, nitrate, sulfite, sulfate, carbonate, perclorate, cyanide, thiocyanate, dihydrogen phosphate, tetrasodium pyrophosphate, and sodium tripoly phosphate ions, the potential responses of which are shown in Figure 3. As can be seen from Figure 3, while the slopes of the linear parts of the potential responses of the sensors for all other anions tested, are much lower than those expected by the Nernst equation, the resulting MHP potential response shows a near-Nernstian behavior.

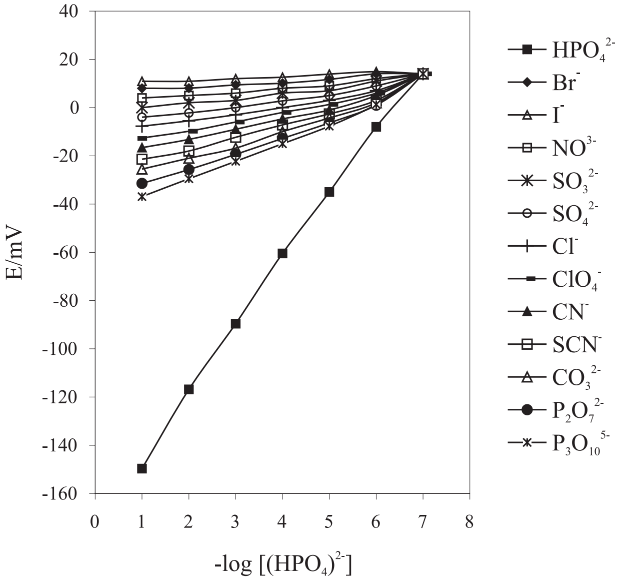

Figure 3. Potential responses of different ion-selective electrodes based on MS.

Membrane characteristics

The properties of the membranes, namely sensitivity, detection limit, response time, lifetime, selectivity, and chemical stability depend on the ratio of electro-active phase, and the binder materials. Membranes with different compositions were prepared and preliminary studies revealed that a membrane having a composition of 7.0: 2.0: 33.0: 58.0 of MS: HTAB: PVC: BA gave the best response characteristics (Table 1, membrane F).

The influences of the solvent mediators (AP, DBP, BA and NB), ionic additive (HTAB), and amount of

Table 1. Composition of membrane ingredients

Membrane	PVC / (%)	Plasticizer / (%)	HTAB / (%)	MS	Slope / (mV decade^{-1})	Linear range	D. L.
A	33	BA, 62	—	5	-12.9 ± 0.3	1×10^{-4}-2×10^{-2}	6.0×10^{-5}
B	33	BA, 61	—	6	-14.2 ± 0.3	5×10^{-5}-5×10^{-3}	1.0×10^{-5}
C	33	BA, 60	—	7	-15.3 ± 0.3	5×10^{-5}-9×10^{-2}	2.0×10^{-5}
D	33	BA, 59	—	8	-14.8 ± 0.3	5×10^{-5}-4×10^{-3}	1.0×10^{-6}
E	33	BA, 59	1	7	-24.9 ± 0.3	1×10^{-6}-5×10^{-2}	7.0×10^{-7}
F	33	BA, 58	2	7	-28.6 ± 0.3	4×10^{-7}-1×10^{-1}	2.0×10^{-7}
G	33	NB, 58	2	7	-25.6 ± 0.3	2×10^{-6}-5×10^{-1}	8.0×10^{-7}
H	33	DBP, 58	2	7	-26.2 ± 0.3	5×10^{-6}-5×10^{-1}	1.0×10^{-6}
I	33	AP, 58	2	7	-25.8 ± 0.3	1×10^{-6}-1×10^{-2}	8.0×10^{-7}
J	33	BA, 65	2	—	-3.6 ± 0.30	5×10^{-4}-5×10^{-2}	4.0×10^{-4}

the active component on the performance of the membranes were also considered, and the results are summarized in Table 1. As seen, these data reveal that four different plasticizers used, have almost the same results if the optimum composition is used. However, because BA is a low polar solvent (in comparison with NB with high polarity and BA, and DBP with low polarity), leading to the extraction of MHP and interfering ions within the relatively lower lipophile anions such as Cl^-, Br^-, and NO_3^-, which may have positive effects on the selectivity behavior of the sensor, BA was chosen as the solvent mediator. This may seem to lead to the poorer extraction of MHP ion, having a relatively high charge density, but this seemed to be compensated by the selective complexation of MS with the MHP ions. This way, not only was the slope of the sensor response maintained, but its selectivity pattern was also improved.

The optimization of permselectivity of membrane sensors is known to be highly dependent on the incorporation of additional membrane component. In fact, it has been demonstrated that, the presence of lipophilic positively charged additives improves the potentiometric behavior of certain selective sensors not only by reducing the ohmic resistance,[23,24] improving the response behavior, and selectivity,[25,26] but also, in cases where the extraction capability of the ionophore is poor, by enhancing the sensitivity of the membrane electrodes. Moreover, the additives may catalyze the exchange kinetics at the sample-membrane interface.[29] Table 1 shows that if 2% of HTAB is present as a suitable additive, the slope of the proposed sensor increases from -15.3 (membrane C) to -28.6 mV decade^{-1} (membrane F).

Working concentration range and slope

The potential response of the membranes as a function of MHP activity is shown in Figure 4. It is seen that membrane F shows a wide working concentration range (1.0×10^{-1} - 4.0×10^{-7} mol L^{-1}) with a detection limit of 2×10^{-7} mol L^{-1} (~20 ng mL^{-1}), and a Nernstian slope of -28.6±0.3 mV *per* decade of activity.

Lifetime and reproducibility of the sensor

The membranes were used over a period of eight weeks without showing any significant changes in the slope and detection limit of the sensor. During usage, the membranes were stored in 0.01 mol L^{-1} MHP solution and were re-equilibrated with 0.1 mol L^{-1} MHP solution whenever any drift in potentials was observed (Table 2). Repeated monitoring of potentials (20 measurements) at 1.0×10^{-3} mol L^{-1} concentration gave a standard deviation of 0.4 mV.

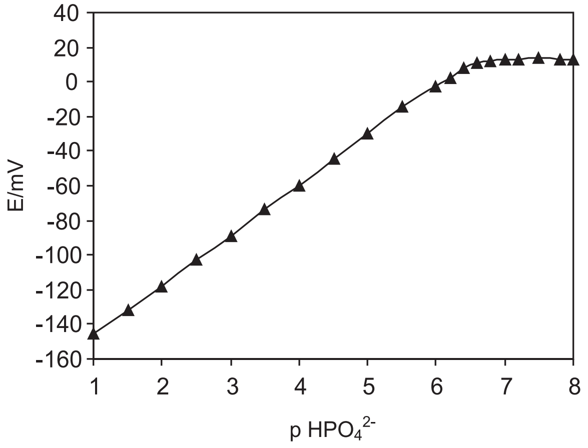

Figure 4. Calibration curves of phosphate electrode based on MS.

Dynamic response time

Dynamic response time is one of the important factors for any ion-selective electrode. In this study, the practical response time was recorded by changing the MHP concentration in solution; over a concentration range 1.0×10^{-1} mol L^{-1} to 1.0×10^{-6} mol L^{-1}. The actual potential *versus* time traces is shown in Figure 5. As can be seen from Figure

Table 2. The lifetime behavior of the monohydrogen phosphate

Period	Slope / (mV decade^{-1})	Detection Limit / (mol L^{-1})
1 week	-28.6 ±0.2	2.0×10^{-7}
2 weeks	-28.6 ±0.1	2.0×10^{-7}
3 weeks	-28.5 ±0.5	3.0×10^{-7}
4 weeks	-28.3 ±0.4	4.0×10^{-7}
5 weeks	-28.2 ±0.3	4.0×10^{-7}
6 weeks	-28.2 ±0.3	6.5×10^{-7}
7 weeks	-28.1 ±0.2	8.0×10^{-7}
8 weeks	-27.9 ±0.5	9.0×10^{-7}
9 weeks	-28.8 ±0.4	2.0×10^{-6}
10 weeks	-28.4 ±0.3	3.0×10^{-6}

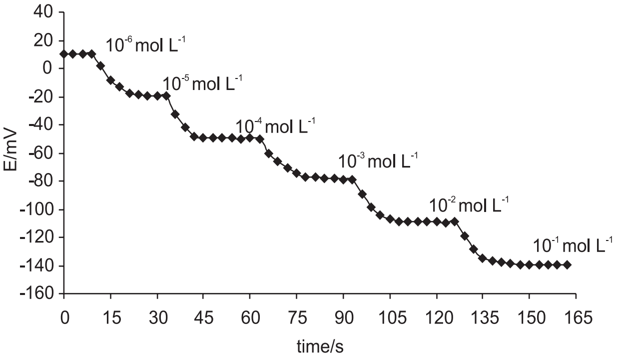

Figure 5. Dynamic response time of the potentiometric sensor for different concentration of phosphate.

5, in the whole concentration range**,** the electrode reaches its equilibrium response in a very short time (<15 s). This is most probably, due to the fast exchange kinetics of complexation-decomplexation of MHP ion with the MS at the test solution-membrane interface.

Effect of pH

The pH dependence of the MHP membrane sensor was tested over a pH range of 4.0-10.0 in a 1.0×10^{-4} mol L^{-1} MHP solution, and the results are illustrated in Figure 6. As it can be seen, the potential remains fairly constant in the pH range of 8.5-9.2. Beyond this range, a gradual change in the potential was detected. The observed potential drift at the higher and lower pH values could be due to the decreasing of the concentration of MHP (formation of H_2PO^{4-} and PO_4^{3-} at lower and higher pH, respectively).

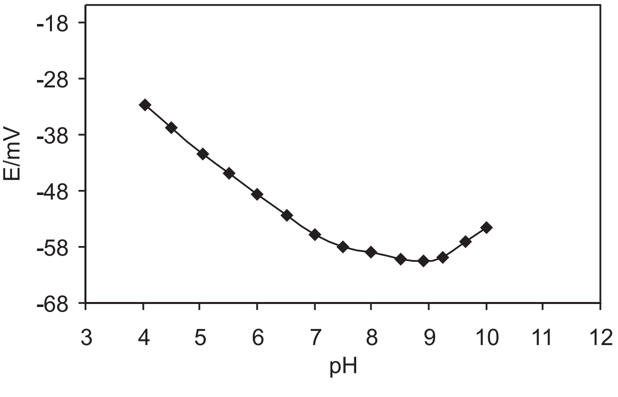

Figure 6. The effect of the pH of the test solution (1.0×10^{-4} mol L^{-1}) on the potential response of the membrane sensor.

Potentiometric selectivity

The influence of interfering ions on the response behavior of ion-selective membrane electrodes is usually described in terms of selectivity coefficients. The potentiometric selectivity coefficients of the MHP membrane sensor were evaluated by the matched potential method (MPM) and separation solution method (SSM).[30] The resulting values of the selectivity coefficients are given in Table 3. As shown in Table 3, for all common anions tested, the selectivity coefficients are in the order of 1.0×10^{-4} or smaller, which seems to indicate negligible interference**s** in the performance of the electrode assembly. Such remarkable selectivity of the MHP membrane sensor over other common anions, reflects the high affinity of the MS used as ion carrier toward the MHP ions.

Table 4, compares the response time, detection limit, linearity concentration range and major interfering ions (log K < -4) of the proposed sensor with those reported for previously reported MHP membrane sensors. As it is seen, the sensor in the case of the response time and detection limit is superior to the best previously reported MHP ion selective membrane electrodes.[12,16]

Table 3. Selectivity coefficients of various interfering ions

Anion	$K_{A,B}$ (MPM)	$K_{A,B}$ (SSM)
Br^-	5.2 X 10^{-6}	4.6 X 10^{-6}
Cl^-	1.5 X 10^{-5}	1.9 X 10^{-5}
SO_4^{2-}	1.0 X 10^{-5}	2.4 X 10^{-5}
ClO_4^-	3.2 X 10^{-5}	4.6 X 10^{-5}
SCN^-	2.5 X 10^{-5}	1.8 X 10^{-5}
I^-	6.0 X 10^{-6}	5.2 X 10^{-6}
NO_3^-	1.0 X 10^{-5}	1.4 X 10^{-5}
CO_3^{2-}	3.2 X 10^{-5}	2.2 X 10^{-5}
SO_3^{2-}	1.0 X 10^{-5}	1.5 X 10^{-5}
CN^-	4.0 X 10^{-5}	2.7 X 10^{-5}
$P_2O_7^{4-}$	5.0 X 10^{-5}	2.5 X 10^{-5}
$P_3O_{10}^{5-}$	5.0 X 10^{-5}	3.0 X 10^{-5}

Analytical application

The membrane sensor was successfully used in the potentiometric titration of MHP with Ba^{2+} solutions. A 25.0 mL (1.0×10^{-4} mol L^{-1}) solution of MHP was titrated with 1.0×10^{-2} mol L^{-1} solution of Ba^{2+} (Figure 7). As it is obvious from Figure 7, the sharp break point corresponds

Table 4. The characteristics of the proposed sensor were compared with those of the best previously reported

Reference	LDR / (mol L^{-1})	DL / (mol L^{-1})	Response time / (s)	Selectivity coefficient range for common Ion
16	1.0×10^{-6}- 1.0×10^{-1}	5.0×10^{-7}	< 20	-4.90 to -3.60
12	5.0×10^{-6}- 1.0×10^{-1}	5.0×10^{-6}	< 25	-4.31 to -3.07
This Work	4.0×10^{-7}- 1.0×10^{-1}	2.0×10^{-7}	< 15	-4.72 to -3.30

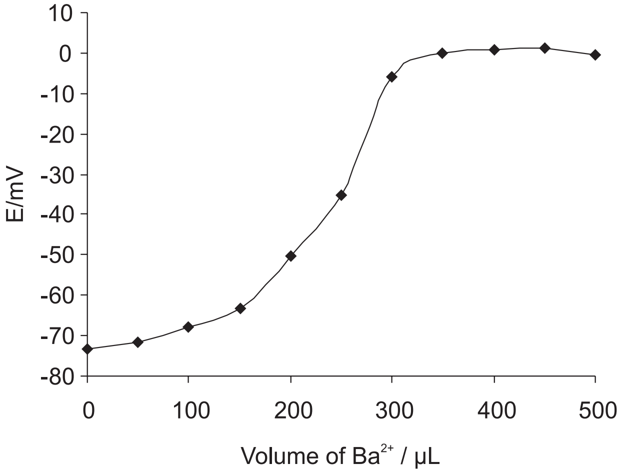

Figure 7. Titration curve 25 mL phosphate ion solution (1.0×10^{-4} mol L^{-1}) with the Ba^{2+} ion (1.0×10^{-2} mol L^{-1}) at pH 9.0.

Table 5. Determination of P_2O_5 in three samples of NPK fertilizers using colorimetry[28] and proposed monohydrogen phosphate sensor based on MS

Sample No.	ISE / (%)	Colorimetry / (%)
1	$10.26^a \pm 0.11$	$10.07^a \pm 0.05$
2	10.17 ± 0.15	10..23 ± 0.10
3	10.66 ± 0.13	10.09 ± 0.12

[a]Results are based on five measurements.

Table 6. Determination of P_2O_5 in three granular TSP fertilizers using colorimetry[28] and proposed monohydrogen phosphate sensor based on MS

Sample No.	ISE / (%)	Colorimetry / (%)
1	$42.5^a \pm 0.3$	$41.9^a \pm 0.5$
2	42.1 ± 0.5	41.5.3 ± 0.2
3	41.9 ± 0.6	42.1 ± 0.3

[a]Results are based on five measurements.

Table 7. Determination of P_2O_5 in three granular SSP fertilizer samples using colorimetry[28] and proposed monohydrogen phosphate sensor based on MS

Sample No.	ISE / (%)	Colorimetry / (%)
1	$18.4^a \pm 0.7$	$18.1^a \pm 0.2$
2	18.3 ± 0.3	18.0 ± 0.3
3	18.3 ± 0.5	18.1 ± 0.2

[a]Results are based on five measurements.

to the stoichiometry of the MHP-Ba^{2+} precipitate ($BaHPO_4$). The equivalent volume is 250 µL.

To assess the practical applicability of the sensor in real samples an attempt was made to determine MHP in the three phosphate fertilizer samples, and the results are given in Tables 5, 6 and 7 (for mixed nitrogen phosphate potassium fertilizer (NPK), triple super phosphate (TSP), and single super phosphate (SSP), respectively). As it is seen, the MHP contents obtained from triplicate measurements were found to be in satisfactory agreement with those obtained by standard method (colorimetry).[28]

The monohydrogen phosphate sensor was used for the direct monitoring of phosphate ions in the waste water samples of monocalcium phosphate industry (Faridshimi Co. Hashtgerd, Iran). 2.0 mL of each sample was taken and dissolved in distilled water in a 100 mL volumetric flask. To this solution 5.0 mL of 0.1 mol L^{-1} EDTA (pH of 10.0) was added to the flask and diluted to the mark with distilled water. The concentration of each sample was measured by the monohydrogen phosphate sensor, using the calibration method. The results obtained by the direct potentiometry and spectrophotometry are depicted in Table 8. As can be seen, there is a good correlation between the both methods.

Table 8. Determination of phosphate content in waste water samples using colorimetry and proposed monohydrogen phosphate sensor based on MS

Sample No.	ISE / (%)	Colorimetry / (%)
1	$44.9^a \pm 0.5$	$43.3^a \pm 0.7$
2	38.9 ± 0.7	38.0 ± 0.2
3	38.9 ± 0.9	37.7 ± 0.2

[a]Results are based on five measurements.

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