

A New Phosphate Selective Electrode and Its Application in Some Foods

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A highly sensitive phosphate selective electrode (ISE) was fabricated using Ba₃PO₄, Cu₂S and Ag₂S solids. The highest sensitivity of ISE was obtained with 20% Ba₃PO₄ (m/m) composition. The ISE shows a slope of about 57 mV towards the phosphate ion in the concentration range 1x10⁻¹ M - 1x10⁻⁶ M. The ISE characterization was performed. The ISE was judged to be accurate in the presence of possible interfering ions. The amount of phosphate in foods was measured as real sample analysis and the proposed ISE was accepted as a reliable, sensitive and easy-to-make sensor device for phosphate analysis in food samples.

Keywords: Ion selective electrode, Phosphate, Determination, Food sample

1. INTRODUCTION

Phosphate is an important food source for living organisms. The products containing phosphate in a wide range concentration are used in many fields, especially in pharmacy, medical, clinical chemistry, industrial and environmental [1]. Chromatographic [2], spectrophotometric [3] and ion selective electrode (ISE) [4] could be found in literature in for determining phosphate ion in real samples.

ISEs prepared with water-soluble salts have many advantages such as sensitive, durable, short response times and easy preparation. In recent years, the phosphate ISEs showed remarkable improvements for the analysis in real sample analysis. Many ion selective electrodes have been prepared using different phosphate carriers [5-18].

The first solid state phosphate selective electrode was prepared from silver sulfide, lead sulfide and lead hydrogen phosphate salts. This electrode was used for potentiometric precipitation titration of phosphate and lanthanum [19]. Another solid electrode prepared a silver phosphate-based phosphate-selective electrode using the electrochemical method of silver over platinum. The sensitivity of this

electrode is about 20 mV and it is sensitive to chloride ion [20]. In one study, a tungsten-based potentiometric electrode was prepared to measure the phosphate (HPO_4^{2-}) concentration in the aqueous solution. The training of this electrode is 29 mV [21]. A solid membrane phosphate sensor was prepared from poorly soluble salts of silver and phosphate. The membrane electrode had a 32.6 mV slope [22]. Recently, modified molybdenum electrode with molybdenum dioxide and molybdenum phosphate on its surface, phosphate ion selective electrode was used. Its slope at pH 9.0 was measured to be approximately 28 mV [23]. Cobalt-phosphate selective electrode with cobalt matrix was prepared and used in environmental analysis. Cobalt-phosphate selective electrode with cobalt matrix was prepared and used in environmental analysis. This electrode sensitivity was measured between (pH 4.0-6.0) between 35 and 50 mV [24].

In this study, ISE was prepared by using Ba_3PO_4 , Cu_2S and Ag_2S for phosphate ion determination. These salts were prepared in the laboratory. This electrode is easy to prepare and low in cost compared to other electrodes. Direct determination with ISE is possible. Electrode life is longer. The selectivity and sensitivity of the ISE were determined in the presence of potentially interfering ions, and the proposed sensor was confirmed to be a reliable ISE in food samples such as beef, beans, garlic, and dried apricots.

2. EXPERIMENTAL

2.1. Materials and Reagents:

Barium phosphate, silver sulfur and copper (I) sulfur were prepared in the laboratory. Other metal solutions were prepared from nitrate and chloride salts (Merck). Phosphate buffer was prepared using di-potassium hydrogen phosphate and potassium di-hydrogen phosphate (Merck). All reagents are of analytical grade. All solutions were prepared using twice purified water.

2.2. Instruments:

An external Ag/AgCl reference electrode with a Jenway 3040 pH/ion meter was used for potential measurement. Atlas auto touch pellet hydraulic press was used in the preparation of the ISE pellets. Potential values were measured at room temperature.

2.3. Preparation of electrode:

Ba_3PO_4 , Cu_2S and Ag_2S were mixed in certain proportions to have a total mass of 0.3 g according to previously published work [25]. The compositions of the proposed ISEs were abbreviated as Ba10 for 10% Ba_3PO_4 + 40% Cu_2S + 50% Ag_2S , Ba20 for 20% Ba_3PO_4 + 40% Cu_2S + 40% Ag_2S , Ba25 for 25% Ba_3PO_4 + 35% Cu_2S + 40% Ag_2S and Ba30 for 30% Ba_3PO_4 + 40% Cu_2S + 30% Ag_2S .

The mixtures were transferred to the place of the hydraulic press, and the pellets were compressed at 6000-9000 atm pressure for 20 minutes. The copper wire in 99% purity was fixed to a glass tube using epoxy resin considering to contact the resulting pellet and to ensure no leakage.

3. RESULTS AND DISSCUSION

3.1. Characterization the ISE:

The electrode performance of IS electrodes are highly depending on the conditions such as storage and their compositions. The criteria of a suitable ISE are specified with response time, repeatability, reproducibility, LOD and LOQ, linear working range and selectivity. The usage of ISE in real sample analysis finally proves the reliability of the proposed sensor against analyze in real conditions.

ISEs prepared in a composition of 20% Ba₃PO₄, 40% Cu₂S and 40% Ag₂S (m/m) were stored in air, distilled water and pH 7 phosphate buffer for 6 h to show the optimum storage conditions, and the sensitivity of proposed ISE against phosphate ion concentrations ranging from 10⁻⁶ M to 10⁻¹ M in abovementioned composition were depicted in Fig. 1. From Fig.1, the optimum storage condition of the proposed ISE was decided as 1.0×10⁻⁴ M phosphate buffer in pH 7 with 57 mV·(pA)⁻¹ of sensitivity, while 27 mV·(pA)⁻¹ and 21 mV·(pA)⁻¹ of sensitivities were measured in air and in distilled water, respectively.

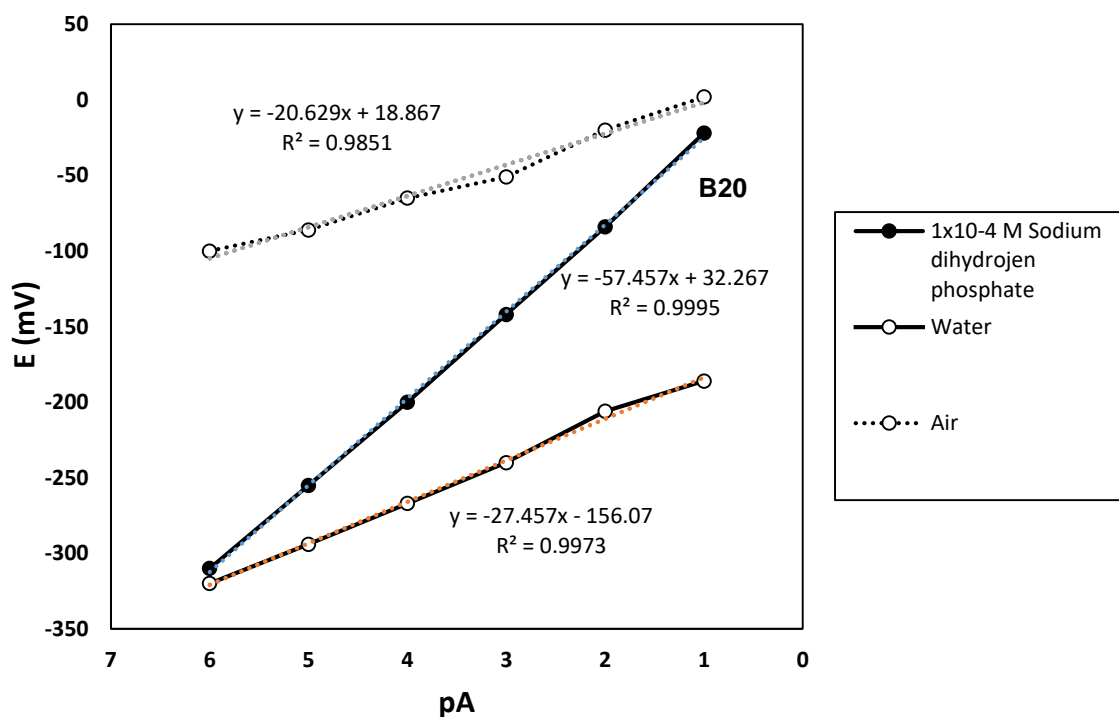


Figure 1. The effect of media on the performance of the electrode (B20).

3.2. Effect of electrode composition:

Electrode composition of the proposed ISE was the other main consideration defining its performance. ISEs prepared in various compositions of Ba₃PO₄, Cu₂S and Ag₂S were performed against phosphate concentrations of 10⁻⁶ M to 10⁻¹ M to determine the optimum composition of the electrode with the use of their sensitivities, and the calibration plots of the ISEs in various compositions were presented in Fig.2. The slopes of the proposed ISEs were listed in Table 1. From Fig.2 and Table 1, the optimum composition of ISE was observed as Ba20 (m/m). It is a well-known fact that barium phosphate is the main component of the ISE for phosphate sensitivity as an insoluble salt. For this reason, the content of 20% Ba₃PO₄ showed a 2.54 times higher sensitivity than the one of 10% Ba₃PO₄. On the other hand, the decrease of Cu₂S and Ag₂S content led to diminish in the sensitivity of the proposed ISE because they were increasing the conductivity of proposed ISEs [26, 27]. Herewith, the increasing content of Cu₂S and Ag₂S reduced the ISEs sensitivity to be 2.41-fold and 3.11-fold for Ba25 and Ba30, respectively. The optimum content of the proposed sensor showed a slope of 57 mV·decade⁻¹ against ten-fold increasing phosphate concentrations, and its electrochemical behavior was accepted as non-Nernstian.

Table 1. The Nernst equation slopes for ISEs prepared in various compositions.

Composition	Slope (1x10 ⁻⁶ -1x10 ⁻¹ M)	R ²	LOD (M)
Ba10 (10% Ba ₃ PO ₄ + 40% Cu ₂ S + 50% Ag ₂ S)	17	0.9936	7.8x10 ⁻⁷
Ba20 (20% Ba ₃ PO ₄ + 40% Cu ₂ S + 40% Ag ₂ S)	57	0.9999	2.4x10 ⁻⁷
Ba25 (25% Ba ₃ PO ₄ + 35% Cu ₂ S + 40% Ag ₂ S)	19	0.9987	6.5x10 ⁻⁷
Ba30 (30% Ba ₃ PO ₄ + 40% Cu ₂ S + 30% Ag ₂ S)	15	0.9875	1.0x10 ⁻⁶

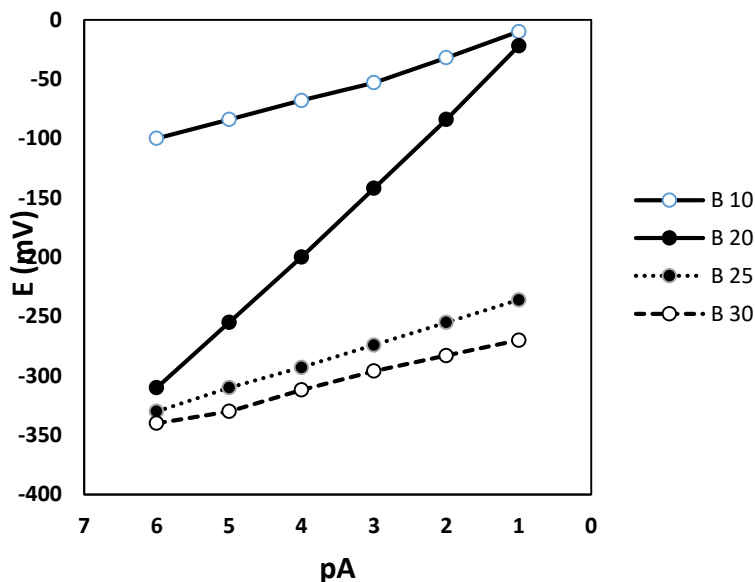


Figure 2. Calibration curves for the phosphate sensitive electrodes of different compositions.

Since the optimum electrode composition was defined by calibration plots and Nernst equation slopes to be Ba20, the composition of Ba20 was preferred in further validation steps against phosphate ion determination.

3.3. Response time:

It is expected that the proposed ISE shows a quick and accurate response against analyze [28]. For this, proposed ISEs were performed against phosphate concentrations of 10^{-6} M to 10^{-1} M and three times at same conditions to show their quick responses and accuracies, and the plots of average potentials vs. time measured from Ba20 was presented in Fig.3. The response time of Ba20 was found 30 seconds because of obtaining less than 1.0 % RSD regardless of phosphate concentrations.

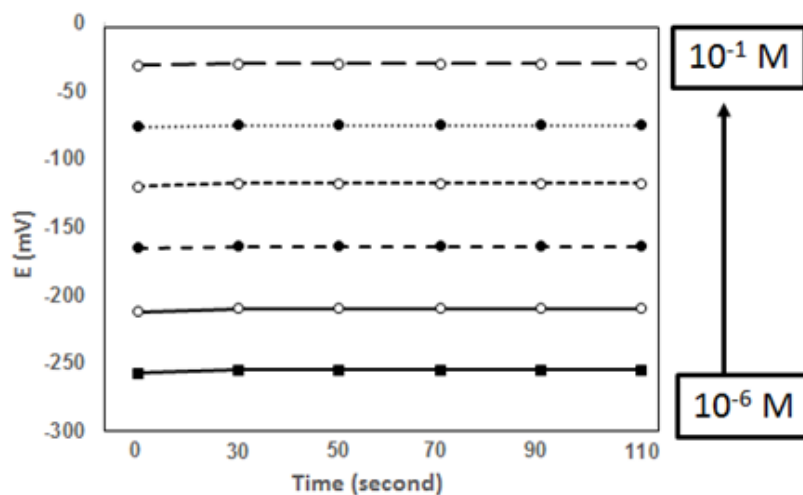


Figure 3. The dependence of response time with concentration.

3.4. pH Effect:

Mono hydrogen and dihydrogen phosphate types of phosphate were used to examine the pH effect of the electrode. Certain pH 7, 8 and 9 standard solutions were prepared using the salts of mono hydrogen and dihydrogen phosphates. Potential values of the electrode against phosphate concentrations at these pHs were measured. In this study, the electrode potential did not change with pH.

3.5. Interferences studies:

With the mixed solution method, it was determined whether the electrode was sensitive to some ions [29]. Here, the interference effect of Cl^- , NO_3^- , S^{2-} , SO_4^{2-} anions and Na^+ , Ag^+ , Ba^{2+} , Cu^{2+} cations are examined. The sensitivity of the electrode to some anions and cations are shown in Fig. 4. Selectivity coefficients given in Table 2.

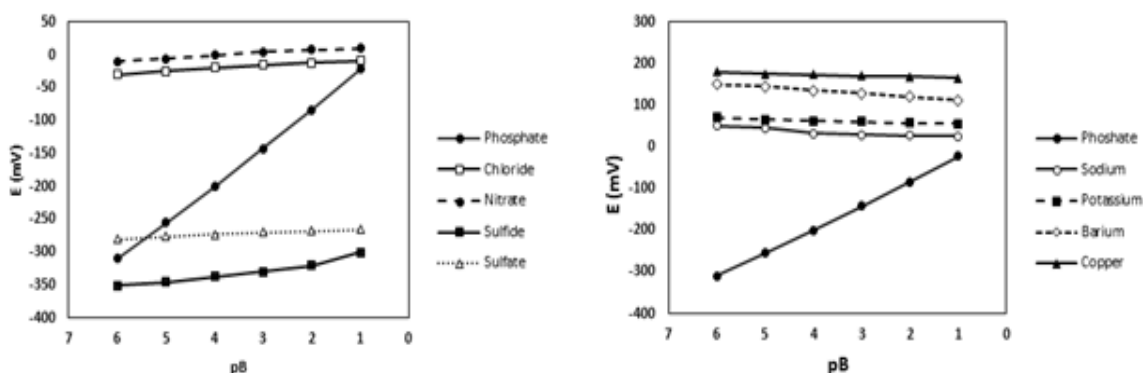


Figure 4. The interference effect of some anions and cations.

Table 2. Selectivity coefficients, $K_{A,B}^{pot}$, for the phosphate selective electrode in mixed interferant solutions (in the presence of 1×10^{-5} M phosphate)

Anions	$K_{A,B}^{pot}$	Cations	$K_{A,B}^{pot}$
Cl^-	2.1×10^{-4}	Na^+	1.1×10^{-4}
NO_3^-	1.3×10^{-4}	K^+	1.2×10^{-4}
S^{2-}	3.2×10^{-4}	Ba^+	4.1×10^{-4}
SO_4^{2-}	6.4×10^{-5}	Cu^{2+}	2.3×10^{-5}

3.6. Determination of phosphate quantity in food samples:

Phosphorus is an important element for human health. People get these needs from nutrients. In this study, Turkey too consumed beef, beans, garlic and dried apricots in the amount of available phosphorus were determined. The selected foods were solubilized by using the appropriate procedure in the Milestone microwave digestion system using acid and acid mixtures. The measured phosphorus amounts are given in Table 3.

Table 3. Determination of the amount of phosphorus in beef, beans, garlic and dried apricots with solid state phosphate selective electrode (mg/100 g). 90 % confidence interval and N=4. (\bar{X} : arithmetic mean, s: standard deviation, t: Student`s t test)

Sample	$\bar{X} \pm \frac{t.s}{\sqrt{N}}$
Beef	188 ± 13
Bean	423 ± 24
Garlic	203 ± 15
Dried apricots	106 ± 11

3.7. The comparison of proposed ISE by spectrophotometric method:

The amount of phosphate measured in beans using ISE and the values obtained by spectrophotometric method were compared. For phosphate determination, measurements were made at 840 nm wavelength in the spectrophotometric method. The obtained values and their comparisons can be seen in Table 4.

According to the t and F tests, the results show that there is no significant difference between the two methods in terms of accuracy and precision. It is concluded that the values measured by ISE are satisfactory and selective.

Table 4. Comparison of measured phosphate amount in beans by ISE and spectrophotometric method 90% confidence interval and N=4.

Parameters	ISE	UV Spectrophotometry
Found (mg/100 g)	423 ± 24	421 ± 27
LOD (M)	2.4x10 ⁻⁷	6.5x10 ⁻⁶
RSD (%)	0.92	1.26
t-test (t _{critical} =3.18)	1.53	2.65
F-test (F _{critical} = 9.28)	5.48	7.18

3.8. Comparison of our phosphate electrode with similar electrodes

Phosphate electrodes in the literature are prepared either from a mixture of poorly soluble salts or by using metal-phosphate salts electrochemically deposited on a metal surface. The electrode we prepared was obtained from the less soluble salts we prepared in the laboratory environment. The properties of similar electrodes and our electrode are given in table 5.

As seen in Table 5, our electrode has the highest inclination. Detection limit is low, pH can be studied between 7.0 and 9.0. It is not sensitive to other anions and cations. It has been found to be highly accurate in real sample analysis.

Table 5. Comparison of the properties of our phosphate electrode with similar electrodes.

Electrode	Slope	LOD	pH	Interferences ions	References
Ag ₂ S – PbS- PbHPO ₄	-27	5.2x10 ⁻⁷	8.3	Cl ⁻	[19]
Ag ₃ PO ₄ – modified electrode	-20	4x10 ⁻⁹	7.0-10.0	Cl ⁻	[20]
Tungsten-based electrode	-30	1x10 ⁻⁶	10.0	----	[21]
	-21	5x10 ⁻⁶	3.0-7.0	unexamined	[22]

Ag ₃ PO ₄ membrane electrode					
Molybdenum phosphate modified electrode	-28	1x10 ⁻⁶	9.0	NO ₃ ⁻ , SO ₄ ²⁻ , Cl ⁻ , HCO ₃ ⁻ , CH ₃ COO ⁻	[23]
Cobalt phosphate modified electrode	-55	5x10 ⁻⁶	4.0	NO ₃ ⁻ , SO ₄ ²⁻ , Cl ⁻	[24]
Our phosphate electrode	-57	2.4x10 ⁻⁷	7.0-9.0	not sensitive to other ions	

4. CONCLUSION

Determination of phosphorus in real samples is of great importance because of its role in human metabolism. In addition, due to the popularity of spectrophotometric and chromatographic methods, there are limited studies in the literature for phosphorus analysis with ion selective electrodes. Here, we proved a new ion selective electrode for phosphorus determination in real samples, and barium phosphate was first used to achieve ion selectivity. The optimum barium phosphate content in the pellet was found to be 20% (m/m) and the Nernst behavior was observed with a slope value of 57 mV from the calibration chart. The proven ISE has demonstrated easy preparation and use, cost effectiveness, wide operating range, fast response, long life and high selectivity. It is also insensitive to other anions and cations. ISE was considered reliable by comparing the spectrophotometric technique as a validated method.

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References

1. S.A. Glazier and M.A. Arnold, *Anal. Chem.*, 60 (1988) 2540.
2. A. Alcázar, P.L. Fernández-Cáceres, M.J. Martín, F. Pablos and A.G. González, *Talanta*, 61 (2) (2003) 95.
3. B. Shyla, Mahadevaiah, and G. Nagendrappa, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 78(1) (2011) 497.
4. R. De Marco and C. Phan, *Talanta*, 60(6) (2003) 1215.
5. S.A. Glazier and M.A. Arnold, *Anal. Chem.*, 63 (1991) 754.
6. N. Chaniotakis, K. Jurkschat and A. Ruehlemann, *Anal. Chim. Acta*, 282 (1993) 345.
7. J.K. Tsagatakis, N.A. Chaniotakis and K. Jurkschat, *Helv. Chim. Acta*, 77 (1994) 2191.
8. D. Liu, W.C. Chen, R.H. Yang, G.L. Shen and R.Q. Yu, *Anal. Chim. Acta*, 338 (1997) 209.
9. S. Sasaki, S. Ozawa, D. Citterio, K. Yamada and K. Suzuki, *Talanta*, 63 (2004) 131.
10. C.M. Carey and W.B. Riggan, *Anal. Chem.*, 66 (1994) 3587.
11. T.L. Goff, J. Braven, L. Ebdon and D. Scholefield, *Anal. Chim. Acta*, 510 (2004) 175.
12. M. Fibbioli, M. Berger, F.P. Schmidtchen and E. Pretsch, *Anal. Chem.*, 72 (2000) 156.

13. W. Wroblewski, K. Wojciechowski, A. Dybko, Z. Brzozka, R.J.M. Egberink, B.H.M. Snellink-Ruel and D.N. Reinhoudt, *Sens. Actuators B*, 68 (2000) 313.
14. W. Wroblewski, K. Wojciechowski, A. Dybko, Z. Brzozka, R.J.M. Egberink, B.H.M. Snellink-Ruel and D.N. Reinhoudt, *Anal. Chim. Acta*, 432 (2001) 79.
15. S. Nishizawa, T. Yokobori, R. Kato, K. Yoshimoto, T. Kamaishi and N. Teramae, *Analyst*, 128 (2003) 663.
16. K. Jain, V.K. Gupta and J.R. Raison, *Talanta*, 69 (2006) 1007.
17. J.H. Liu, Y. Masuda and E. Sekido, *J. Electroanal. Chem.*, 291 (1990) 67.
18. N. Sato and Y. Fukuda, *Chem. Lett.*, 3 (1992) 399.
19. D. Midgley, *Talanta*, 26 (4) (1979) 261.
20. I. Vermees and E.W. Grabner, *J. of electroanal. chem. and interfacial electrochem.*, 284 (2) (1990) 315.
21. G. Chen, S. Xiao, A. Lorke, J. Liu and P. Zhang, *Journal of The Electrochemical Society*, 165 (16) (2018) 787.
22. M. Bralić, A. Parkić, J. Radić and I. Pleslić. *Int. J. Electrochem. Sci.*, 13 (2018) 1390.
23. K. Xu, Y. Kitazumi, K. Kano, T. Sasaki, O. Shirai. *Analytical sciences*, 36 (2) (2019) 201.
24. R. Zeitoun, A. Biswas. *Journal of electrochemical society*, 167 (2020) 127507.
25. G. Somer, S. Sezer, M. Dogan, S. Kalayci and O. Sendil, *Talanta*, 85 (2011) 1461.
26. G. Somer, Ş. Kalaycı and İ. Başak, *Talanta*, 80 (2010) 1129.
27. G. Somer, U. Yilmaz, and Ş. Kalaycı, *Talanta*, 142 (2015) 120.
28. R.P. Buck and E. Lindner, *Pure Appl. Chem.*, 66 (1994) 2527.
29. K. Srinivasan and G.A. Rechnitz, *Anal. Chem.*, 41 (1969) 1203.

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