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Selective Potentiometric Method for Determination of Nitrile in Water Samples Using New PVC Membrane Sensors

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The performance characteristic of sensitive PVC-nitrile sensor was investigated for the quantification of nitrile ions in water samples, based on the use Cis-(2-thiophene-carbonitrile)-Bis-(2,2'-bipyridyl)ruthenium(II)tetrafluoroborate (ionophore A) and Cis-(trichloro-acetonitrile)-Bis-(2,2'-bipyridyl)ruthenium(II)tetrafluoroborate (ionophore B). The sensors are prepared by incorporating of A and B ionophores into a plasticized poly vinyl chloride (PVC) sensors to form electrodes I and II, respectively. The best performance was obtained using casting solutions of composition: *o*-nitrophenyloctylether(*o*-NPOE): PVC: ionophore ratio (wt %) of 63:30:7, respectively. The sensors exhibit significantly enhanced selectivity toward nitrile ions over the concentration range 1.0×10^{-5}-1.0×10^{-2} mol L^{-1} with a lower detection limit of 7.0×10^{-5} and 5.0×10^{-5} mol L^{-1} and a Nernstian slope of 57.0±0.71 and 55.1±0.33 mV decade^{-1} at pH 12 for both electrodes I and II. The sensors show stable and fast response time (≤11 s) and can be used for about 120 days without any considerable variation in the response of potential for electrodes I and II, respectively. The proposed sensors show good segregation of nitrile in presence different ions. The proposed method is successfully applied for determination of nitrile ion in environmental samples using potentiometric method.

Keywords: PVC sensor; Environmental samples; Nitrile determination; Cis-(2-thiophene-carbonitrile)-Bis-(2,2'-bipyridyl)ruthenium(II)tetrafluoroborate (ionophore A) and Cis-(trichloro-acetonitrile)-Bis-(2,2'-bipyridyl)ruthenium(II)tetrafluoroborate (ionophore B)

1. INTRODUCTION

Nitriles [1] toxicity is very important to be recognized, they occur a fundamental starting material in many organic and industrial processes [2] (e.g., mining and plating) and cyanide can be released into the air from burning plastics and coal. They have been investigated in relationship with environmental problems [3] and are involved in a large variety of biological processes [4]. Liquid chromatographic separations in organic and pharmaceutical chemistry were reported [5-7]. Toxicity of cyanide deactivates the electron transport chain along mitochondria membrane and disrupts respiration for all aerobic organisms[8,9]. some neuromuscular diseases, goiters and cretinism can be caused by chronic exposure to cyanide. The decreasing of iodine which produced by thyroid [10] due to interfere with cyanide where this interference leads to physical and mental retardation. Many foods such as flax, cassava, sorghum, bamboo shoots, and bitter almonds contains cyanide naturally where it is generated by microorganism [11,12]. Therefore, various techniques and methods were used for determination and evaluation cyanide such as volumetric and gravimetric titrations[13], ion chromatography (IC) [16, 17], high performance liquid chromatography (HPLC) [14, 15], amperometry [21, 22], voltammetry [18-20], plarography [23], potentiometry (solid state membrane ion selective electrodes) [24-26], atomic absorption spectroscopy (AAS) [27, 28] and fluorimetry [29]. Developments of ion-selective electrodes (ISEs) is very important to monitor ionic species. ISEs cannot be utilized for direct quantification of most different organic anions. Conversion of covalently bound species into their ionic counterparts by decomposition or chemical transformation [30] should be occurred before the determination. Moreover, the nitrile quantifications based on ISEs are simple, low cost, rapid, wide concentration range, accurate and precise and also usable to colored and turbid solutions [31-34]. These make ISEs as very attractive alternative tool for anions metals [26]. In United Stated, the contamination of drinking water with cyanide is usually from an industrial source or leaking from waste sites. Cyanide is classified as toxic inorganic contaminate in drinking water [35].

The aim of present work refers to study the response characteristics of the investigated ion selective membranes to some organic nitriles and to develop a selective and simple method for their potentiometric measurements. The choice of the investigated compounds resulted from their important role and action as potential physiological hazards and there is no simple methods for their quantification.

2. EXPERIMENTAL

2.1. Apparatus

All electrochemical measurements were made using Orion research digital pH/millivolt meter 611 at 25 ±1 ◦C. Silver-silver chloride (Ag/AgCl) double-junction reference electrode (Metrohm 6.0726.100) was used in conjugation with nitrile-PVC selective electrodes. The adjustment of pH for all measurements were performed using Jenway 3510 pH meter. The internal filling solution of the investigated ion selective electrode was a 0.01 mol L^{-1} nitrile compound solution.

2.2. Reagents

The analytical grade of all the reagents were used for all experiments using deionized water. Cis-(2-thiophene-carbonitrile)-Bis-(2,2'-bipyridyl)ruthenium(II)tetrafluoroborate (ionophore A) and Cis-(trichloro-acetonitrile)-Bis-(2,2'-bipyridyl)ruthenium(II)tetrafluoroborate (ionophore B) were newly prepared by the authors. Different benzylnitrile solutions of 10^{-2} to $l0^{-5}$ M of were prepared using absolute ethanol. The plasticizer o-nitrophenyloctylether (o-NPOE) was purchased from Sigma, Merck, Fluka. Hydrazine and sulphate anions are used as interfering materials. Tetrahydrofuran (THF) was purchased from Aldrich Chemical Co. (Milwaukee, USA). Poly (vinyl chloride) (Breon S 110/0P) was got from BP Chemicals International (Barry, UK).

2.3. Samples

Tab water (sample was supplied from Umm Al Qura university, Makkah, Saudi Arabia). Drinking, mineral, chlorinated and ozonated water samples were collected from local distribution network at Makkah city, KSA.

2.4. Procedures

2.4.1. Preparation of ion selective electrodes (ISEs)

A plasticized polymer membrane was formed by mixing 360 mg of ortho-nitrophenyl octyl ether with 40 mg of ionophore A or B then combined with 170 mg of poly vinyl chloride (PVC) for utilizing to form electrodes I and II, respectively. The sensor was optimized by soaking in 0.1 mol L^{-1} nitrile compound solution for at least two days before use and was stored at 4 ^{o}C in the same solution when not in use.

2.4.2. Determination of nitrile in spiked water samples

Filtration of all water samples was occurred through 0.45μm cellulose membrane filter prior to analysis then about 15 mL transferred to a 25 ml beaker then adjusted the solution to pH 12 after added certain amount of nitrile compound then content was treated by potentiometric calibration curve using the new membrane sensors as sensing electrodes. The reproducibility and recovery of the proposed method was checked by repeating the used method several times.

2.4.3. Calibration of the new ISE

Aliquot of nitrile solution (20 mL, 1.0×10^{-5}-1.0×10^{-2} mol L^{-1}) was transferred to a 25-mL after added certain amount of NaOH till pH12 value with continuous stirring then immersion of the new ISE with a reference electrode was occurred for calibration process. The EMF was measured after stabilization to ±0.2 mV then a calibration curve was established by plotting the measured potentials as a function of -log [nitrile]. The resulting curve was used for subsequent quantification of unknown nitrile compounds concentration.

3. RESULTS AND DISCUSSION

3.1. Composition of nitrile-selective electrode

Certain amount of ionophore (A) or ionophore (B) was incorporated in PVC membranes plasticized with ortho-nitrophenyloctyl ether (*o*-NPOE) solvent mediators as the plasticizer and subjected to preliminary investigations. The best performance was obtained using casting solutions of composition: *o*-nitrophenyloctyl ether (*o*-NPOE): PVC: ionophore ratio (wt %) of 63:30:7, respectively. The electrode characteristics are given in Table 1.

Table 1. Response characteristics of nitrile-PVC membrane sensors.

Parameter	Nitrile-PVC membrane sensors	
	Electrode (I)	Electrode (II)
Slope, (mV decade^{-1})	57.0	55.1
Intercept, (mV)	203.8	177.2
Correlation coefficient, (r)	0.9700	0.9900
Lower limit of detection, (mol L^{-1})	7.0×10^{-5}	5.0×10^{-5}
Lower limit of linear range, (mol L^{-1})	1.0×10^{-4}	1.0×10^{-4}
Response time (s)	9	11
Working pH	12	12
Life span/week	14	16

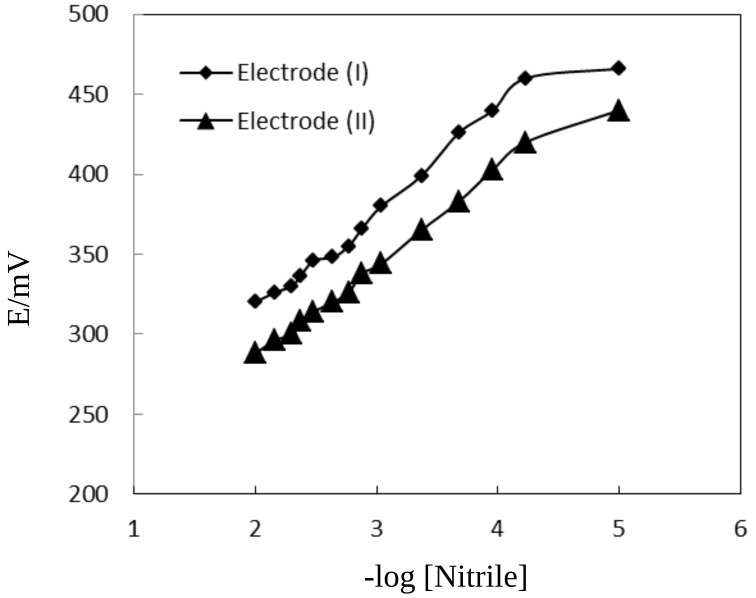

Figure 1. Calibration curve of the nitrile membrane sensors.

The electrochemical response of the sensors was recorded for nitrile along the concentration range of 1.0×10^{-5} - 1.0×10^{-2} mol L^{-1} at 25 °C for both electrodes (I & II). The obtained results showed that the PVC sensors have Nernstian response of 57.0±0.71 and 55.1±0.33 mV decade^{-1} for electrodes I and II, respectively (Fig. 1). The LOD for the electrodes was found to be 7.0×10^{-5} and 5.0×10^{-5}

mol L^{-1} for electrodes I and II, respectively. This LOD was obtained when the linear regions of the calibration curves were extrapolated to the baseline of concentration potentials [36, 37].

3.2. Effect of pH

The acidity of the investigated solutions is one of the most important factors that affects of the performance of practically all sensors. The effectiveness of pH on the behavior of membrane sensors responses was evaluated using 10^{-2} and 10^{-3} mol L^{-1} nitrile compounds solutions and in presence of different buffer solutions such as universal and acetate buffer but there is no response of electrodes was observed in test solutions of pH less than 12 but in strong alkali solutions (10 mol L^{-1} NaOH), the C = N group undergoes the high polarizing power with cognizable dipole moment (D = 3.5) [38] and allows the unionized but strongly polar organic molecules to be sensed at the investigated membrane of the electrode.

3.3. Response time

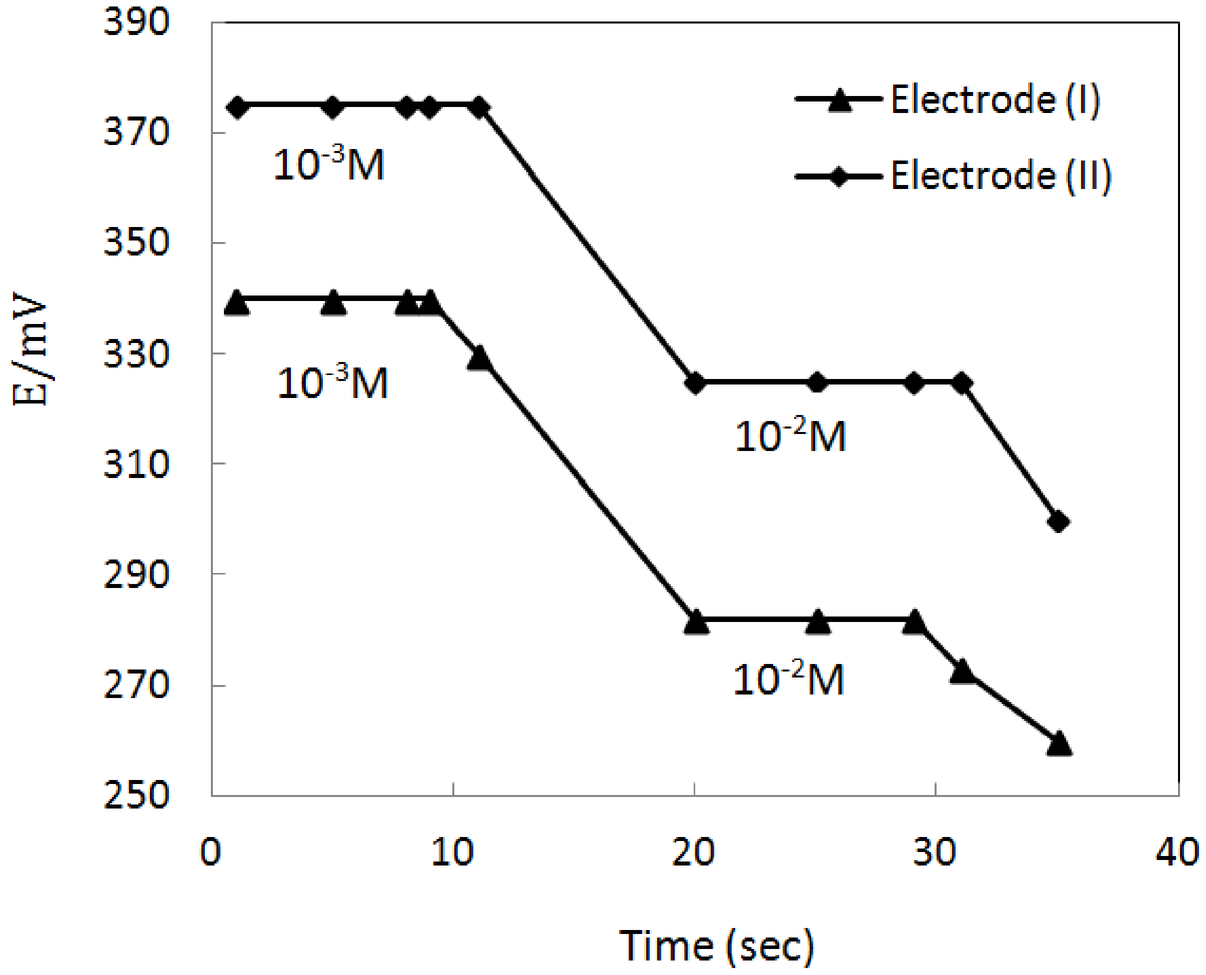

Figure 2. Dynamic response time of the electrodes for step changes in the concentration of nitrile ion.

A series of nitrile solutions were used to measure the static response time of the electrodes after successive immersion of the membranes. The obtained static response time was 9 and 11 seconds for 1.0×10^{-2} and 1.0×10^{-3} mol L^{-1} for electrode (I) and electrode (II), respectively. Figure 2 shows the relation between the actual potential against time. The potential reading was stable for approximately 3 minute, however slow change was observed within the resolution of the meter.

3.4. Life time

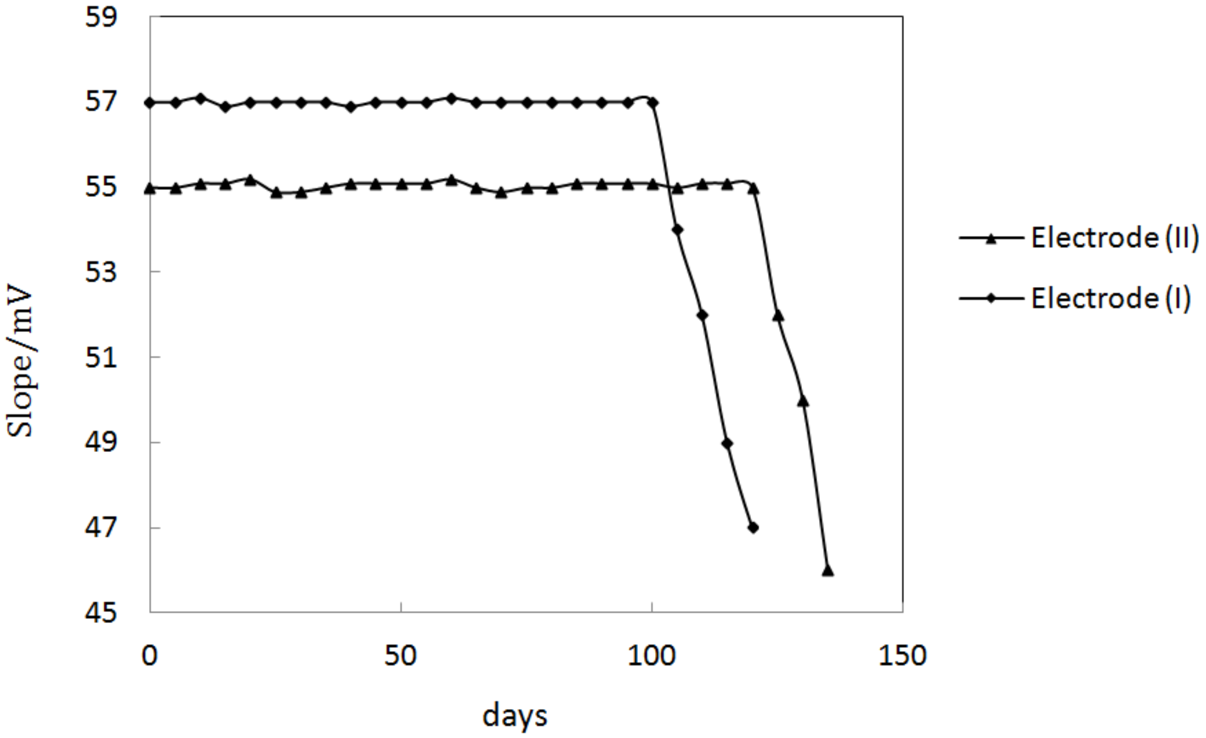

Figure 3. Life time on the performance of nitrile-PVC-electrodes

Sensor lifetime is defined as the operational or storage time required for the sensitivity, along the linear concentration range. The lifetime of the sensor were found to be dependent on the matrix of the investigated solution and the analyte measured by the sensor, therefore regular calibrations were performed using the optimized electrodes sensors to evaluate their useful lifetime tested over a period of more than 100 and 120 days for electrodes (I) and (II), respectively (Fig. 3). During that period, the calibration curves of optimized electrodes were periodically obtained and the slopes and detection limits were measured in freshly prepared nitrile solutions and based on the obtained results the lifetimes of electrodes were determined. The proposed sensor operates correctly over a period of 120 days without observing any significant change in the detection limit, working concentration range, or the slope. After this period, electrodes exhibit a slight variation in the slope and limit of detection. This may be due to leakage of the ion-associate complexes to solution.

3.5. Effect of interfering ions

Table 2. Selectivity coefficients of different ions using electrode (I) and electrode (II).

Interfering ions (B)	$-\log K^{\mathrm{FIM}}_{\mathrm{A,B}}$ [(a)]	
	Electrode (I)	Electrode (II)
Br^-	2.43	2.85
NO_3^-	3.33	3.69
I^-	2.61	2.42
Cl^-	2.77	2.83
HCO_3^-	4.80	4.73
F^-	3.53	3.63
ClO_3^-	4.56	4.57
$C_2O_4^{2-}$	4.66	4.65
CO_3^{2-}	3.68	3.83
SO_4^{2-}	3.84	3.78
HPO_4^{2-}	2.69	2.87
SO_3^{2-}	3.23	3.68
CH_3COO^-	4.13	4.29
$S_2O_3^{2-}$	2.69	2.93
Citrate	5.11	5.23
Formate	5.41	5.63
Glycine	5.21	5.45
Tartrate	4.32	4.54
Hydrazine	5.22	5.33

[a] Selectivity coefficients found by fixed interference method.

The selectivity of an ISE is the most important feature where is detected in terms of selectivity coefficient. The selectivity coefficient values of potentiometric measurements for these membranes were measured by the IUPAC recommended (FIM) fixed interference method [39]. To calculate the selectivity coefficient, a fixed concentration of interfering ion (a_B= 1.0 × 10^{-3} mol L^{-1}) should be added to the different nitrile ion solutions ranging from 1.0 × 10^{-5} to 1.0 × 10^{-2} mol L^{-1} and the potentials were detected. The potential values detected were plotted against the activity of the nitrile ion. The linearity range of the potential response graph were extrapolated and the value (a_A) of a nitrile was obtained from the intersection point. The values of potentiometric selectivity coefficients were calculated using the equation:

$$K_{A,B}^{FIM} = \frac{a_A}{(a_B)^{Z_A/Z_B}}$$

Where a_A is the activity of the primary ion (Nitrile) at the lower limit of detection in the presence of interfering ion, Z_A and Z_B are the charge of the primary and interfering ions. The potentiometric selectivity coefficient values given in Table 2 indicate that the electrodes are highly selective to nitrile over a number of monovalent (Cl^-, Br^-, I^-, F^-, CH_3COO^-) and divalent (HPO_4^{2-}, CO_3^{2-}, SO_3^{2-}, SO_4^{2-}, $C_2O_4^{2-}$) ions.

3.6. Analytical applications

Table 3. Determination of nitrile ions in spiked water samples using electrode (I) and electrode (II).

Samples	[Nitrile] ($\mu g\ L^{-1}$)									
		(Electrode I)			(Electrode II)			AAS		
	Added	Found	R.S.D (%)	Recovery (%)	Found	R.S.D (%)	Recovery (%)	Found	R.S.D (%)	Recovery (%)
Tap water	2.0	1.95	1.054	97.50	1.97	0.908	98.50	1.94	1.436	97.00
	2.5	2.46	1.063	98.40	2.48	1.089	99.20	2.46	1.067	98.40
Mineral water	2.0	1.96	0.857	98.00	1.97	0.716	98.50	1.95	1.216	97.50
	2.5	2.47	1.081	98.80	2.48	1.174	99.20	2.47	1.019	98.80
Chlorinated or ozonated water	2.0	1.98	1.088	99.00	1.99	1.121	99.50	1.96	1.799	98.00
	2.5	2.46	1.215	98.40	2.47	0.679	98.80	2.44	1.938	97.60

The proposed electrodes (I and II) were also applied successfully to the direct quantification of nitrile ions in different real spiked water samples. Different spiked real water samples were prepared by adding aliquots of nitrile solution into the different water samples and the direct measurement of the amount of spiked nitrile in samples was done as shown in Table 3. As seen the recovery (n = 5) of nitrile at various nitrile concentrations is quantitative.

3.7. Comparison with other nitrile electrodes

Table 4. Comparing some of the nitrile-Electrode (I) and Electrode (II) characteristics with some of the previously reported nitrile-ISEs.

References	Slope (mV decade^{-1})	Response time (s)	pH	Life time (months)	Linear range (mol L^{-1})	DL (mol L^{-1})
[40]	55.0	20	5.5 – 12.0	<3	$1.0\times10^{-5} – 1.0\times10^{-2}$	5.3×10^{-6}
[41]	60.0	5 min	10.0-11.0	-	$1.5\times10^{-5} – 1.0\times10^{-2}$	9.0×10^{-6}
[42]	59.8	< 2 min	8.0 - 12.0	3	$2.1\times10^{-8} – 1.0\times10^{-1}$	1.3×10^{-8}
[43]	59.0	< 5 min	3.0-9.0	<7	$3.1\times10^{-5} – 1.0\times10^{-2}$	5.8×10^{-6}
Proposed method electrode (I) electrode (II)	 57.0 55.1	 9 11	 10 10	 14 16	 $1.0\times10^{-5} – 1.0\times10^{-2}$ $1.0\times10^{-5} – 1.0\times10^{-2}$	 7.0×10^{-5} 5.0×10^{-5}

A comparison with other nitrile ion-selective electrodes (ISEs) depended on different ionophores reported in the literatures was done [40-43]. Table 4 presents the major analytical characters of some nitrile ion-selective membranes. The proposed electrodes depended on Cis-(2-thiophene-carbonitrile)-Bis-(2,2'-bipyridyl)ruthenium(II)tetrafluoroborate (ionophore A) and Cis-(trichloro-acetonitrile)-Bis-(2,2'-bipyridyl)ruthenium(II)tetrafluoroborate (ionophore B) ionophores exhibit accepting behavior in many respects with those reported ionophores, such as detection limit 7.0×10^{-5} and 5.0×10^{-5} mol L^{-1} for electrode (I) and electrode (II), respectively) and electrochemical selectivity over other metal ions. Meanwhile, simple, lower cost and easily synthesis method shows that the proposed electrodes can be used widely in the future.

4. CONCLUSIONS

Ionophore (A) and Ionophore (B)-PVC electrodes offer variable techniques for the determination of nitrile ion in pure solutions and different water samples. In addition, these electrodes showed a very good selectivity to nitrile in the presence of many inorganic anions. The obtained results show high precision, accuracy and no interference with most common ions. A comparison with other potentiometric methods [40-43] indicated simply of fabrication, short response time and better selectivity of the present sensors especially in the presence of Cl^-, NO_3^-, SO_4^{2-}, $S_2O_3^{2-}$ ions.

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References

1. L. Liu, J. Dong, Y. Zhang, Y. Zhou, S.F. Yin, *Org. Biomol. Chem.*, 13 (2015) 9948.
2. K. Huang, S.A. Couchman, D.J.D. Wilson, J.L Dutton., C.D. Martin, *Inorg. Chem.*, 54 (2015) 8957.
3. Z. Getahun, C.Y. Huang, T. Wang, B. De León, W.F. DeGrado, F. Gai, *J. Am. Chem. Soc.*, 125 (2003) 405.
4. B.K. Kuruba, S. Vasanthkumar, L. Emmanuvel, *Synth. Commun.*, 46 (2016) 799.
5. J. Zhang, Q. Zhang, B. Xia, J. Wu, X.N. Wang, J. Chang, *Org. Lett.*, 18 (2016) 3390.
6. R.A. Haque, S.Y. Choo, S. Budagumpi, A.A.A. Abdullah, M.B. Khadeer Ahamed, A.M.S. Abdul Majid, *Inorganica Chim Acta*, 433 (2015) 35.
7. R. Manikandan, P. Anitha, G. Prakash, P. Vijayan, P. Viswanathamurthi, R.J. Butcher, *J. Mol. Catal. A: Chem.* 398 (2015) 312.
8. C.G. Lee, M.K. Song, J.C. Ryu, C. Park, J.W. Choi, S.H. Lee, *Chemosphere*, 153 (2016) 1.
9. O.M. Ogundele, B. Wasiu Gbolahan, A. Emmanuel Cobham, I. Azeez Olakunle, A. Abdulbasit, *Drug Chem. Toxicol.*, 12 (2016) 1.
10. R. Altenburger, S. Ait-Aissa, P. Antczak, T. Backhaus, D. Barceló, T.B. Seiler, *Sci. Total Environ.* 513 (2015) 540.
11. O.O. Fawole, T.A. Yekeen, A.A. Ayandele, T.O. Ajayi, O.O. Aina, O. Omolaso, *Atmos Pollut Res*, 33 (2014) 243.
12. G. Ofori-Sarpong, K. Osseo-Asare, I.J.M.P, 119 (2013) 27.
13. N.P. Lu, J.Q. Nian, L.F. Zhang, F. Gu, *Yejin Fenxi/Metallurgical Analysis*, 36 (2016) 62.
14. R.K. Bhandari, E. Manandhar, R.P. Oda, G.A. Rockwood, B.A. Logue, *Anal. Bioanal. Chem.*, 406 (2014) 727.
15. F.Z. Yehia, G. Eshaq, A.M. Rabie, A.H. Mady, A.E. ElMetwally, *Egypt. J. Petroleum*, 24 (2015) 13.
16. O. Destanoğlu, G. Gümüş Yılmaz, *J. Liq. Chromatogr. Relat. Technol.*, 39 (2016) 465.
17. S.A. Mahmoud, O.A. Fouad, *Sol. Energy Mater. Sol. Cells*, 136 (2015) 38.
18. L. Khalafi, M. Rafiee, F. Yadaei, *Res. Chem. Intermed.*, 37 (2011) 1047.
19. F. Shinozuka, J.T. Stock, *Anal. Chem.*, 34 (1962) 926.
20. H. Tatsuta, T. Nakamura, T. Hinoue, *Anal. Sci.*, 17 (2001) 991.
21. W. Wu, Q. Xiao, P. Zhang, M. Ye, Y. Wan, H. Liang, *Food Chem.*, 172 (2015) 681.
22. C.K. Zacharis, P. Tzanavaras, D.G. Themelis, *NATO Science for Peace and Security Series A: Chemistry and Biology*, (2012) 279.
23. N. Menek, Y. Karaman, *Dyes Pigm.*, 67 (2005) 9.
24. S.S.M. Hassan, I.H.A. Badr, A.H. Kamel, M.S. Mohamed, *Anal. Sci*, 25 (2009) 911.
25. M. Najafi, M. Mohammadi, *Sens Lett* 13 (2015) 230.
26. T.A. Ali, G.G. Mohamed, *J AOAC Int*, 98 (2015) 116.
27. M. Imamoglu, A.O. Aydin, *Fresenius Environ. Bull.*, 14 (2005) 940.
28. L. Kocúrová, I.S. Balogh, J. Şkrlíková, J. Posta, V. Andruch, *Talanta*, 82 (2010) 1958.
29. E. Miralles, R. Compañó, M. Granados, M.D. Prat, *Anal. Chim. Acta*, 403 (2000) 197.
30. T.S. Ma, and S.S.M Hassan. Organic Analysis Using Ion Selective Electrodes.Academic Press. London. Volume 1, 1982.
31. A. L. Saber, *Electroanalysis* 28 (2016) 860
32. T.A. Ali, G.G. Mohamed, *Sens. Actuators, B*, 202 (2014) 699.
33. T.A. Ali, G.G. Mohamed, E.M.S. Azzam, A.A. Abd-Elaal, *Sens. Actuators, B.* 191(2014) 192.

34. A. L. Saber,*Electroanalysis*, 25 (2013) 2707.
35. Maximum Contaminant Levels for Inorganic Con-taminants. Fed. Regist. Code of Federal Regulations, Section 162, Title 40, Revised July 1, 2002, 428.
36. T.A. Ali, A.L. Saber, G.G. Mohamed, T.M. Bawazeer, *Int. J. Electrochem. Sci.* , 9 (2014) 4932.
37. T.A. Ali, G.G. Mohamed, A.H. Said, *Chem. Eng. Commun*. 203 (2016) 724.
38. B.L. Shaw, Physical Methods in Organic Chemistry. Oliver and Boyd, London.(1965) 327.
39. G. G. Guilbault, R. A. Durst, M. S. Frant, H. Freiser, E. H. Hansen, T. S. Light, E. Pungor, G. Rechnitz, N. M. Rice, T. J. Rohm, W. Simon, J. D. R. Thomas. *Pure Appl. Chem.* 46 (1976) 127.
40. S.S. Hassan, S. Marzouk, A.H. Mohamed, N. Badawy, *Electroanalysis*, 16 (2004) 298.
41. A. Abbaspour, M. Asadi, A. Ghaffarinejad, E. Safaei, *Talanta*, 66 (2005) 931.
42. A. Yari, R. Sepahvand, *Microchim. Acta*, 174 (2011) 321.
43. N.V. Kolytcheva, O.M. Petrukhin, N.V. Filipjeva, B.Y. Spivakov, B.F. Myasoedov, *Anal. Chim. Acta*, 357 (1997) 231.