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Potentiometric Determination of Cyanide in Polluted Water Samples Using Screen-Printed Electrode modified with Ruthenium(II) Complexes Ionophores

Tamer Awad Ali[1], *Gehad G. Mohamed*[2,3], *Amr L Saber*[4,5,*], *Layla S. Almazroai*[5]

[1] Egyptian Petroleum Research Institute (EPRI), 11727, Cairo, Egypt.
[2] Chemistry Department, Faculty of Science, Cairo University, 12613, Giza, Egypt.
[3] Egypt Nanotechnology Center, Elsheikh Zayed, 6th October City, Giza, Egypt.
[4] Chemistry Department, Faculty of Science, Zagazig University, Zagazig, Egypt.
[5] Chemistry Department, Faculty of Science, Umm Al Qura University, Makkah, Saudi Arabia
[*]E-mail: alshefny@yahoo.com

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This paper reported a potentiometric cyanide sensors, based on the use of *cis*-(4-nitrobenzonitrile)-bis-(2,2'-bipyridyl)ruthenium(II)hexafluorophosphate (ionophore A) and *cis*-(3-formylbenzonitrile)-bis-(2,2'-bipyridyl)ruthenium(II)hexafluorophosphate (ionophore B). The sensors are prepared by incorporating of A and B ionophores into plasticized screen-printed sensors to form electrodes I and II, respectively. The best performance was obtained with a paste composition of graphite: *o*-NPOE:PVC: ionophore (A or B) ratio (w/w, mg) of 472.5:200:220:7.5. Significantly, the sensors exhibited enhanced selectivity toward cyanide ion over the concentration range 5.0×10^{-6}-1.0×10^{-2} and 2.0×10^{-6} –1.0×10^{-2} mol L^{-1} with a lower detection limit of 5.0×10^{-6} and 2.0×10^{-6} mol L^{-1} and a Nernstian slope of 58.57±0.88 and 59.09±0.31 mV decade^{-1} at pH range from 3.0 to 8.0 and 3.0 to 9.0 for electrodes I and II, respectively. Influence of the paste composition and possible interfering ions on the response properties of the electrodes was investigated. Fast and stable response, good reproducibility and long-term stability are demonstrated. The sensors showed response time of <13 and 9 s and can be used for about 170 and 190 days without any considerable divergence in their potential response for electrodes I and II, respectively. Selectivity coefficients determined by fixed interference method (FIM) indicated high selectivity for cyanide ion. The proposed sensors showed fairly good discrimination of cyanide from many metal ions. This method was successfully applied for potentiomertric determination of cyanide in environmental samples, and the results obtained agreed with those obtained with liquid chromatography (HPLC).

Keywords: Screen-printed sensor; Selectivity; Environmental samples; cyanide determination; ruthenium(II) complexes ionophores

1. INTRODUCTION

Nitriles, R-C ≡ N [1], and in particular acetonitrile, are a class of compounds of relevant importance, and represented a fundamental starting material in organic and industrial processes [2]. They are studied in relationship with environmental problems [3] and are involved in a large variety of biological processes [4]. Also, acetonitrile represented the solvent of election, together with water, for an enormous number of liquid chromatographic separations in organic and pharmaceutical chemistry [5-7].

The toxicity of cyanide to all aerobic organisms can be attributed to preventing the chain transport of electrons in the mitochondria membrane and prevented respiration [8, 9]. Also, it interfered with iodine uptake by the thyroid [10]. Chronic exposure to cyanide can cause goiters, some neuromuscular diseases, and cretinism where the deficiency in iodine results in physical and mental retardation. Cyanide occurred naturally in many foods (e.g., cassava, flax, sorghum, bamboo shoots, and bitter almonds) [1] and is naturally generated by microorganisms (fungi, algae, and bacteria) [11, 12].

Therefore, a research was done for cyanide determination using different techniques and methods such as, its determination and evaluation by volumetric, gravimetric and complexometric titrations [13], high performance liquid chromatography (HPLC) [14, 15], ion chromatography (IC) [16, 17], voltammetry [18-20], amperometry [21, 22], polarography [23], potentiometry (solid state membrane ion selective electrodes) [24-26], atomic absorption spectroscopy (AAS) [27, 28] and fluorimetry [29].

Amongst the many analytical techniques available, the development of chemical sensors was spectacular achievements in recent past. However, out of the many electrochemical sensors reported, only a few were documented to be sufficiently selective to permit easy and reliable determination while the remaining ones need improvement with regard to selectivity, reproducibility, response time and sensitivity [30]. Determination of anions using ion-selective electrodes (ISEs) have enhanced the activity of various organic species of interested anions to be measured directly and selectively and, in most instances, without prior separation of them from the formulation matrix. Moreover, the determinations based on ISEs are low cost, rapid, simple, precise, accurate, wide concentration range, and applicable to colored and turbid solutions [31-34]. These make ISEs as very attractive alternative tool for anions determination [26]. Thus, many efforts during the last three decades were focused on the introduction of different forms of ISEs to improve the potentiometric characteristics of these electrodes. Various inorganic and organic species were successfully determined using chemically modified carbon paste electrodes (CPEs) as potentiometric sensors [35-45]. Compared to other types of ISEs, potentiometric CPEs possess advantages of stable potentiometric response, very low ohmic resistance, ease of regeneration and simple of preparation [46, 47]. The latter property is due to the formation of a very thin film of the pasting liquid coated on to the small particles of carbon powders [48]. The properties of the modifier materials used to import selectivity towards the target species were the main factor to explain the operation mechanism of the CPEs. So, CMCPEs exhibited high selectivities by application of appropriate ionophore into their composition which the primary species can be measured without any interferences and separation steps [49].

The described sensor was made by thick-film and planar technologies are employed for developing solid-state sensors having high reproducibility, low cost and small size [43, 50-54]. Screen-printing is especially recommended as simple and fast method for mass production of disposable electrochemical sensors [55-57]. Thick-film technologies are predominantly used for fabrication of amperometric devices [58]. pH sensors were one of the first types of potentiometric sensors investigated for possible implementation through thick-film technology [59].

Therefore, cyanide-modified screen-printed electrodes (MSPEs) were applied in this work for determination of free cyanide ion using potentiometric method. According to our knowledge this is the first report on cyanide selective electrode based on the chemically modified screen-printed electrode using potentiometric method. The present method was also successfully applied to determine the concentration of cyanide ion in water samples.

2. EXPERIMENTAL

2.1. Reagents

All the reagents were of the analytical grade. Deionized water was used throughout the experiments. *cis*-(4-Nitrobenzonitrile)-bis-(2,2'-bipyridyl)ruthenium(II)hexafluorophosphate (Ionophore A) and *cis*-(3-formylbenzonitrile)-bis-(2,2'-bipyridyl)ruthenium(II)hexafluoro-phosphate (Ionophore B) were prepared [59]. Potassium cyanide was supplied from Sigma-Aldrich. While, tricresylphosphate (TCP), dioctylphthalate (DOP), dibutylphthalate (DBP), *o*-nitro-phenyloctylether (*o*-NPOE) and dioctylsebacate (DOS) were purchased from Alfa-Aesar, Sigma, Merck, Fluka and Merck, respectively. 4-Nitrobenzonitrile and 3-formylbenzonitrile were supplied from Sigma-Aldrich. Graphite powder (GP, synthetic 1–2 µm) (Aldrich) was used for the fabrication of different electrodes. Phosphate, carbonate, fluoride, formate, citrate, tartrate, thiosulfate, nitrate, glycine, hydrazine and sulphate, chloride, iodide, bromide, bicarbonate, chlorate, acetate, sulphite, oxalate anions are used as interfering materials.

2.2. Samples

Different water samples were collected from different places. Samples 1, 2, 3 and 4 were supplied from power station combined (Nubaria, Beheira, Egypt), cooling tower waters (Sugar Company), Delta Company for Fertilizers and Chemical Industrial (Mansoura, Dakahliya, Egypt) and tap water (Cairo university, Giza, Egypt), respectively.

2.3. Apparatus

Jenway 3505 pH-meter was used for laboratory potential measurements. Silver-silver chloride double-junction reference electrode (Metrohm 6.0726.100) in conjugation with different ion selective electrode was used. Thermo-Orion (model Orion 3 stars, USA) was used for pH measurement. Before carrying analysis, all glassware's used were washed carefully with distilled water and dried in the oven before use.

2.4. Procedures

The ruthenium(II) complexes were prepared as previously reported in the literature [60]. These complexes were used as ionophores in this study for the potentiometric determination of cyanide ions.

2.5. Preparation of the modified screen-printed electrodes (MSPEs)

The working modified SPEs were printed in arrays of six couples (each 5 × 35 mm) following the procedures previously described [49, 54, 55] where a polyvinyl chloride flexible sheet (0.2 mm) was used as a substrate. This flexible sheet was not affected by the curing temperature or the ink solvent and easily cutted by scissors. The working electrodes were prepared depending on the method of fabrication and were printed using homemade carbon ink (prepared by mixing 2.5-20 mg ionophores (A or B), 200 mg TCP, 220 mg of polyvinyl chloride (PVC) (8%) and 472.5 mg graphite powder (GP). They were cured at 50 ^{o}C for 30 min. A layer of an insulator was then placed onto the printed electrodes, leaving a defined rectangular shaped (5 × 5 mm) working area and a similar area (for the electrical contact) on the other side. Fabricated electrodes were stored at 4 ^{o}C and used directly in the potentiometric measurements.

2.6. Determination of cyanide ions in spiked water samples

In a 25 ml beaker, definite concentration of cyanide ions target was added to about 5 ml water samples. The pH was adjusted to pH 5 with acetate buffer. The cyanide ion content was estimated via potentiometric calibration using modified SPEs as working electrodes. In order to check the accuracy and reproducibility of the proposed method, the measurement was repeated several times.

2.7. Calibration of the new MSPEs

Calibrated of the modified screen printed electrodes was performed by their immersion in conjunction with a reference electrode in a 25-mL beaker containing 2.0 mL of acetate buffer solution of pH 5. Then 10 ml aliquot of cyanide ion solution of concentration ranging from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} was added with continuous stirring. The potential was recorded after stabilization to ±0.1 mV. By plotting the recorded potentials as a function of -log [cyanide], the calibration graph was constructed which was used for subsequent determination of unknown cyanide concentration.

3. RESULTS AND DISCUSSION

Development of simple and precise method for determination of cyanide ions is of great importance. In this method, two Ru(II) complexes were described as ionophores for development of screen printed electrodes which used in the determination of cyanide ions is spiked water samples. Also, due to the strong ability of cyanide ions to form coordination complexes with transition metals, they can probably exchange with the hexafluorophosphates anion in the ionophores moiety and hence responsible for the increase in the sensitivity of the electrodes.

3.1. Composition of cyanide-selective electrodes

The aim of this study is to investigate the influence of paste composition on the potential response of the cyanide-screen-printed electrodes. It is well known that the electrode response such as sensitivity, working concentration range, selectivity and potential stability depends on the amount and the nature of the screen-printed electrodes components [61]. The ratio of ionophore, GP and PVC was varied in order to obtain a composition which gives a paste of best performance with regard to working concentration range, slope and response time [62]. For this purpose screen printed electrodes with paste containing varying amounts of ionophore (A) or ionophore (B), and appropriate proportion of *o*-nitrophenyloctyl ether (*o*-NPOE) as the plasticizer, were prepared and subjected to preliminary investigations. The compositions and the electrode characteristics of the paste prepared are given in Table 1.

It is clear from the data given in Table 1 that the response of the electrode increases with the increase of ionophore content to 10 and 7.5 mg of ionophore A and B, respectively. Using the optimized paste composition described in Table 1, the potentiometric response of the sensors was studied for cyanide ions within the concentration range of 5.0×10^{-6}- 1.0×10^{-2} and $2.0\times10^{-6} – 1.0\times10^{-2}$ mol L^{-1} at 25 °C for electrodes I and II, respectively. The results showed that the sensors have Nernstian response of 58.57±0.88 and 59.09±0.31 mV decade^{-1} for electrodes I and II, respectively (Figure 1).

Membrane sensors previously reported [63] based on magnesium(II)- phthalocyanines, iron(II)-phthalocyanines and iron(II)-bathophenanthroline dicyanoargentate showed slope values of 54.70±0.3, 59.1±0.3 and 55.0±0.4 mV decade^{-1} and linear response over the concentration range of $1x10^{-2}$-$1x10^{-5}$ mol L^{-1} $[Ag(CN)_2]^-$. MCPE based on tetra-3,4-pyridino-porphirazinatocobalt(II) complex [64] showed a Nernstian slope of 60.3 mV decade^{-1} with a linear concentration range of $3x10^{-5}$-$1x10^{-2}$ mol L^{-1}. It was obvious from these data that the proposed electrodes reported herein showed a good response and wider concentration range.

The linear regions of the calibration graphs were extrapolated to the baseline potentials in order to calculate LOD. The limit of detection (LOD) was found to be 5.0×10^{-6} and 2.0×10^{-6} mol L^{-1} for electrodes I and II, respectively. The obtained LOD values were lower than those previously reported [63-66].

3.2. Effect of plasticizer

The slope of the paste was low Nernstian and the working concentration range was narrow. The improvement in the performance was attempted by the addition of plasticizers to the paste composition. The addition of plasticizers not only improved the workability of the paste, but also contributes significantly towards the improvement in the working concentration range, stability and shelf life of the sensor [67]. The plasticizer to be used in pastes should exhibit high lipophilicity, high molecular weight, low vapor pressure and high capacity to dissolve the substrate and other additives present in the paste. Additionally, its viscosity and dielectric constant should be adequate.

Table 1. Optimization of the screen-printed ingredients.

Composition				Electrode characteristics		
Electrode Type	Ionophore (mg)	GP (mg)	PVC (mg)	Slope (mV decade^{-1})	LR (mol L^{-1})	R
	Ionophore A					
Electrode (I)	2.5	477.5	220	53.62±3.04	1.0×10^{-4}– 1.0×10^{-2}	0.955
	5	475	220	54.94±2.73	5.0×10^{-5}– 1.0×10^{-2}	0.968
	7.5	472.5	220	55.88±1.03	1.0×10^{-5}– 1.0×10^{-2}	0.995
	10	**470**	**220**	**58.57±0.88**	**5.0×10^{-6} – 1.0×10^{-2}**	**0.999**
	12.5	468.5	220	56.78±0.93	1.0×10^{-5}– 1.0×10^{-2}	0.996
	Ionophore B					
Electrode (II)	2.5	477.5	220	54.70±2.13	1.0×10^{-5}– 1.0×10^{-2}	0.969
	5	475	220	56.67±1.01	7.0×10^{-6}- 1.0×10^{-2}	0.991
	7.5	**472.5**	**220**	**59.09±0.31**	**2.0×10^{-6}-1.0×10^{-2}**	**0.999**
	10	470	220	58.15±0.58	5.0×10^{-6}-1.0×10^{-2}	0.993
	12.5	468.5	220	56.07±2.24	1.0×10^{-5}-1.0×10^{-2}	0.955

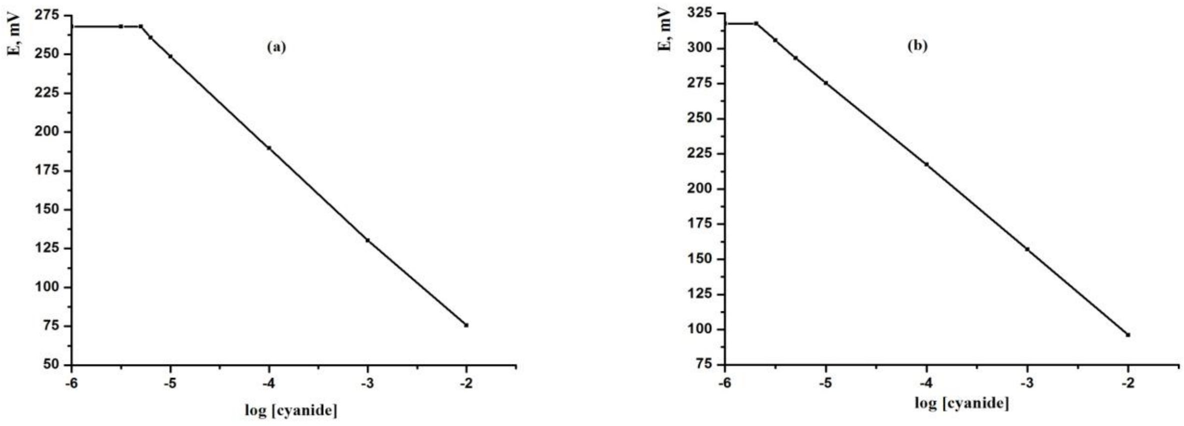

Figure 1. Calibration curves for cyanide-screen-printed electrodes: (a) Electrode I and (b) Electrode II. T = 25 ºC, pH = 5.

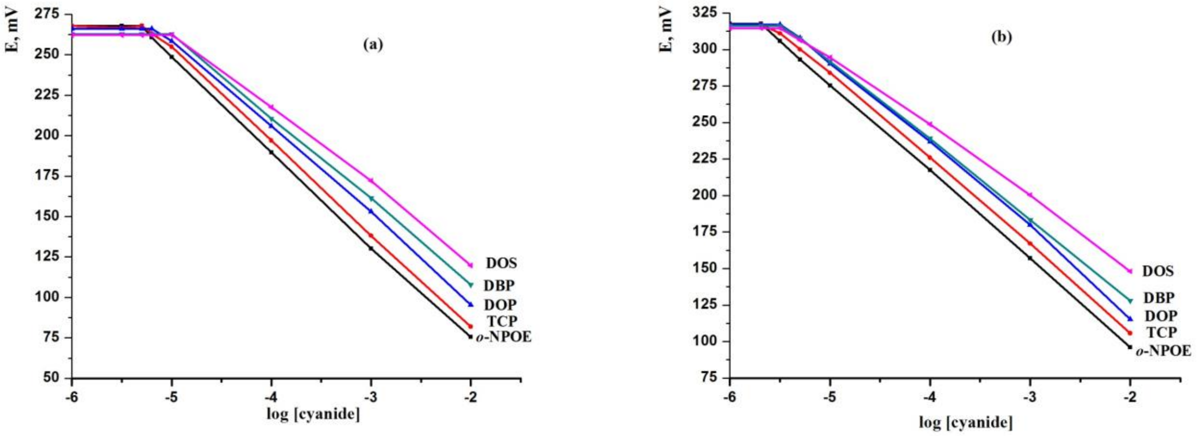

Figure 2. Effect of plasticizer type on the performance characteristics of cyanide-screen-printed electrodes: (a) Electrode I and (b) Electrode II. T = 25 ºC, pH = 5.

To examine the optimization of the electrodes composition, five plasticizers namely *o*-NPOE, DOP, TCP, DOS and DBP were used. The results obtained showed that the response performances of the paste prepared were rather different depending on the use of plasticizer. The best plasticizer was found to be *o*-NPOE and TCP for electrode (I) and electrode (II), respectively (Figure 2). The analytical performance of electrode (I) is compared with the electrode (II) using o-NPOE and TCP, respectively. The electrode (II) has the best performance with respect to Nernstian slope, detection limit, as well as the response time in comparison with electrode (I).

3.3. Response time

Measurement of the static response time of the electrodes was carried out by successive immersion of the electrodes in a series of cyanide ion solutions increased 10-fold, from 5.0×10^{-6} to $1.0{\times}10^{-2}$ and 2.0×10^{-6} to $1.0{\times}10^{-2}$ mol L^{-1} for electrode (I) and electrode (II), respectively. The data obtained were represented graphically in Figure 3. It is obvious from this figure that the electrodes have static response time less than 10 and 7 s for 1.0×10^{-2} and 1.0×10^{-3} mol L^{-1} cyanide ion concentration. In addition, the average static response times were found to be 13 and 9 s for electrode (I) and electrode (II), respectively. According to the previous data [63], the time required for magnesium(II)-phthalocyanines and iron(II)-phthalocyanines based membrane sensors varies from 10 s for $>1x10^{-3}$ mol L^{-1} to 50 s for $1x10^{-3}$ mol L^{-1} $[Ag(CN)_2]^-$, while Fe(II)-bathophenanthroline dicyanoargentate based sensor showed a response time of 20-30 s for 1×10^{-3}-1×10^{-5} mol L^{-1}. Meanwhile, the response time in variation of concentration from 1.5×10^{-4} to 1.5×10^{-3} mol L^{-1} cyanide was about 5 min [64]. It was documented that CPE [65] was found to have a response time of <2 min.

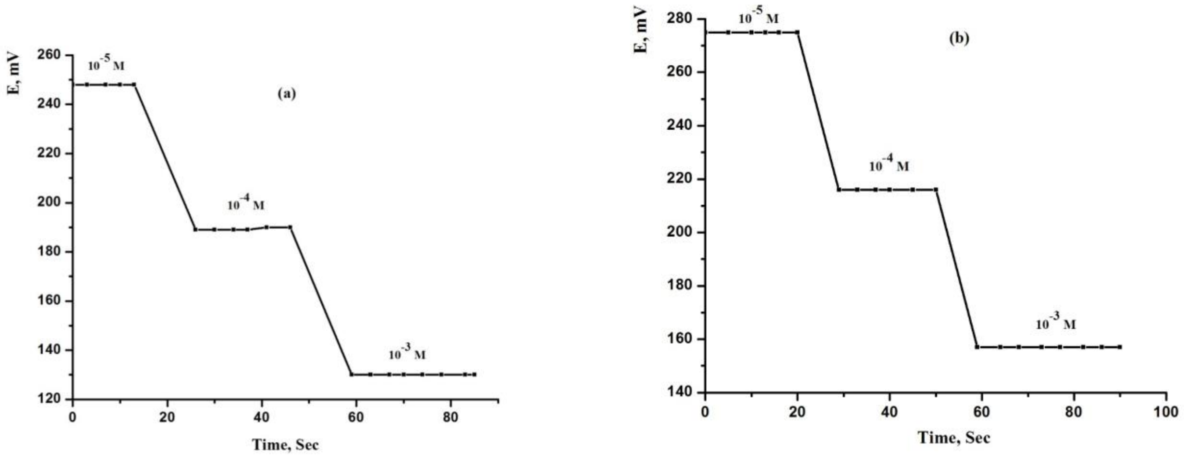

Figure 3. Dynamic response time of (a) Electrode (I) and (b) Electrode (II). T = 25 ºC, pH = 5.

The potentials remained constant for approximately 3 min, after which a very slow change was recorded. The sensing behavior of the electrodes did not depend on whether the potentials were recorded from low to high concentrations or vice versa.

3.4. Life time

Sensor life time is known as the operational time required for the sensitivity, within the linear concentration range, to decrease by a factor of 10 or 30%. The life time of the sensor was found to be dependent on the matrix of the test solution and the analyte measured by the sensor [50]. The main factor responsible for the limited lifetime of a sensor is believed to be the loss of one or more of its components while contacting with aqueous solutions. Sufficient lipophilicity of ionophores and plasticizers ensures stable potentials and long lifetimes [68]. Therefore, regular calibrations were performed using the optimized electrodes to evaluate their useful life time. It is clear from the data given in Figure 4 that the electrodes under study can be used over a period of more than 170 and 190 days for electrodes (I) and (II), respectively, without any significant change in the Nernstian slopes. After this time, a significant decrease in the Nernstian slope was observed. The calibration curves of optimized electrodes were periodically obtained during this period and the slopes and detection limits were measured in freshly prepared cyanide solutions. Based on the obtained results, the life times of electrodes were determined. Without observing any significant change in the detection limit and working concentration range, the proposed sensors operated correctly over a period of 170 or 190 days. After this period, electrodes exhibit a slight variation in the slope and detection limit. This may be due to leakage of paste ingredients from the paste to the solution. This kind of behavior has been reported for many SPE sensors. It was documented that the operational lifetime is up to 3 months without significant deviation in normal function [65].

3.5. Effect of pH

The influence of the pH of the test solution on the potential response of the paste sensor in the pH range of 1.0–11.0 (pH was adjusted by concentrated HNO_3 or NaOH) was described. It was carried out on solution containing 1.0×10^{-3} and 1.0×10^{-5} mol L^{-1} cyanide ions.

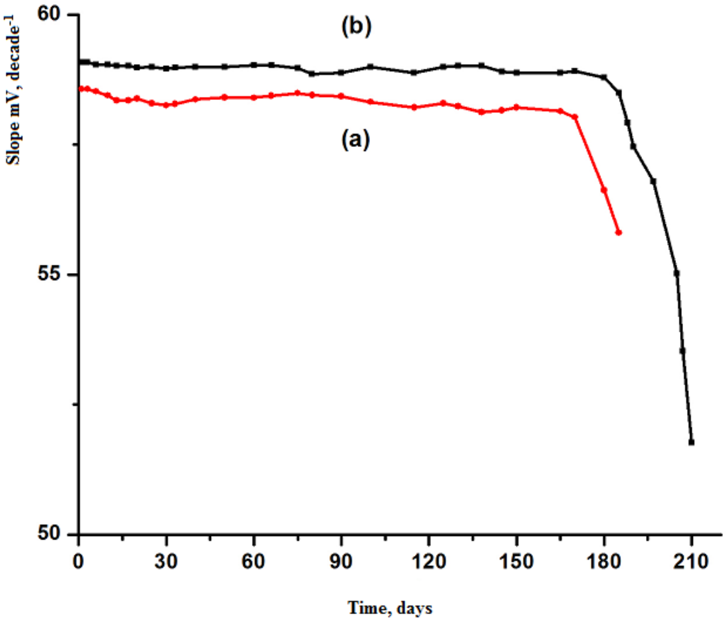

Figure 4. Life time of cyanide-screen-printed electrodes: (a) Electrode I and (b) Electrode II. T = 25 ºC, pH = 5.

The results were shown in Figure 5. As can be seen, the potential remained constant over a pH range of 3.0–8.0 and 3.0–9.0 for electrode (I) and electrode (II), respectively. However, the decreased potential of the electrodes at pH > 9.0 can be explained in terms of the increased interference from OH^- ions which may have a strong competing ligation reaction with cyanide ions for the central complex. On the other hand, at pH < 3.0, the electrodes showed an increased potential response, owing to the competition between the hydrogen ion and the target free cyanide. Potentiometric responses of sensors [63] based on metal phthalo-cyanines and iron(II)-bathophenanthroline were stable over the pH ranges 5 ± 7 and 5 ± 12, respectively. CPE electrode [64] had a better response at the pH of 10.0, and hence this pH value was chosen as the optimum pH for the system. The response of the electrode previously reported [65] was found to remain unchanged in the pH range of 8–12. It was clear from these data that the response of the reported electrodes in this study showed wider pH range than the other ones [63-65].

3.6. Effect of temperature

The electrode potential of 10^{-3} mol L^{-1} cyanide solutions was determined in 20, 30, 40 and 50 ºC in order to study the effect of temperature on the electrodes performance. The standard electrode potentials (E^{o}_{elec}) (obtained from the calibration plots as the intercepts at $p_{cyanide} = 0$) corresponding to each temperature is determined. The standard electrode potential (E^{o}_{elec}) at different temperatures was plotted versus (t - 25), where t is the temperature of the test solution (Figure 6) where the isothermal coefficient (dE^{o}/dT) of the electrodes can be determined. A straight-line plot was obtained according to the following [69]:

$$E^{o} = E^{o}_{(25)} + (dE^{o}/dt)\ (t-25)$$

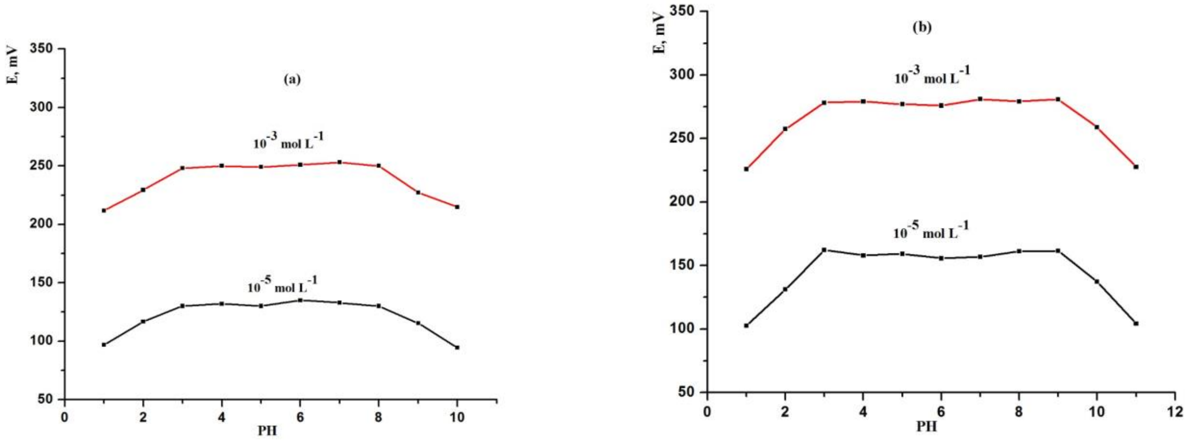

Figure 5. Effect of pH of test solutions on the performance characteristics of (a) electrode (I) and (b) electrode (II). T = 25 ºC.

The slope of the straight line obtained [E° = 22 + 1.052 (t – 25)] represented the isothermal coefficient of the electrodes. It amounted to 0.000398 and 0.000336 V/°C for electrode (I) and electrode (II), respectively. These data revealed good thermal stability of the electrodes within the permitted temperature range.

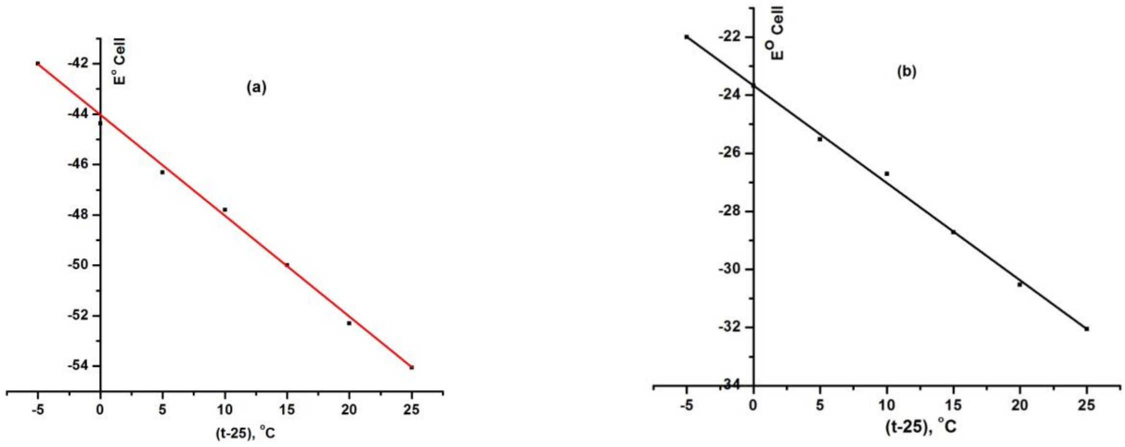

Figure 6. Effect of temperature on the performance of (a) electrode (I) and (b) electrode (II). pH = 5.

3.7. Effect of interfering ions on electrode performance

Selectivity is one of the most important feature of an ISEs which is measured in terms of selectivity coefficient. It defines the extent to which it may be used to estimate the particular ionic species in real samples. To be a good sensor, it is necessary for it to be selective over all the other ions likely to be present in actual samples along with the determined species [70]. To determine the selectivity of the sensors, the IUPAC recommended fixed interference method (FIM). It was described for determining the potentiometric selectivity coefficient values for these electrodes [71]. For this purpose, a fixed concentration of interfering ion (a_B = 1.0 × 10^{-3} mol L^{-1}) was added to the primary cyanide ion solutions ranging from 2.0 × 10^{-6} to 1.0 × 10^{-2} mol L^{-1} and the potentials were measured. The potential values obtained were plotted versus the activity of the cyanide ion. The linear portions of the potential response curve were extrapolated and the value of cyanide was obtained from the intersection point. Potentiometric selectivity coefficients were then calculated using the expression:

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

where a_A is the activity of the primary ion (cyanide) at the lower detection limit in the presence of interfering ion and Z_A and Z_B are the charge of the primary and interfering ions. The potentiometric selectivity coefficient values given in Table 2 indicated that the electrodes were highly selective to cyanide 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.

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

Interfering ions (B)	$-log\ K^{FIM}_{A,B}$ (a) Electrode (I)	$-log\ K^{FIM}_{A,B}$ (a) Electrode (II)

Cl^-	2.56	2.78
NO_3^-	3.37	3.59
I^-	2.31	2.52
Br^-	2.72	2.85
HCO_3^-	4.81	4.93
F^-	3.50	3.63
ClO_3^-	4.42	4.57
CH_3COO^-	4.60	4.64
HPO_4^{2-}	3.67	3.81
SO_4^{2-}	2.74	2.78
CO_3^{2-}	3.79	3.88
SO_3^{2-}	2.03	2.08
$C_2O_4^{2-}$	4.03	4.09
$S_2O_3^{2-}$	2.79	2.90
Hydrazine	5.01	5.13
Glycine	5.51	5.60
Formate	5.31	5.44
Tartrate	4.30	4.57
Citrate	5.12	5.38

[a] Selectivity coefficients found by fixed interference method.

3.8. Analytical applications

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

Samples	[cyanide] (µg L^{-1})									
	(Electrode I)				(Electrode II)			GC-MS		
	Added	Found	R.S.D (%)	Recovery (%)	Found	R.S.D (%)	Recovery (%)	Found	R.S.D (%)	Recovery (%)
1	3.0	2.95	1.084	98.33	2.98	0.208	99.33	2.94	1.836	98.00
	3.5	3.48	0.863	99.43	3.49	0.089	99.71	3.46	1.368	98.86
2	3.0	2.96	1.057	98.67	2.97	0.319	99.00	2.95	1.621	98.33
	3.5	3.47	0.681	99.14	3.48	0.174	99.43	3.45	1.417	98.57

3	2.0	1.97	1.074	98.50	1.99	0.121	99.50	1.96	1.799	98.00
	2.5	2.45	1.205	98.00	2.48	0.179	99.20	2.44	1.938	97.60
4	3.0	2.98	0.370	99.33	2.99	0.104	99.67	2.97	0.734	99.00
	3.5	3.48	0.321	99.43	3.49	0.087	99.71	3.47	0.361	99.14

The proposed electrodes (I and II) were also successfully applied to the direct determination of cyanide ions in different real spiked water samples. Different spiked real water samples were prepared by adding aliquots of cyanide solution into power station, cooling tower and tap water and the amount of spiked cyanide in samples was directly determined as shown in Table 3. As seen the recovery (n = 5) of cyanide ion at various concentrations is quantitative.

3.9. Comparison with other cyanide electrodes

A comparison with other cyanide ion-selective electrodes based on various ionophores reported in the literatures was made [63-66].

Table 4. Comparison between the proposed electrodes (I and II) and the previously reported ISEs.

References	Slope (mV decade^{-1})	Response time (s)	pH	Life time (months)	Linear range (mol L^{-1})	DL (mol L^{-1})
Proposed electrode (I)	58.57	13	3.0 – 8.0	<6	5.0×10^{-6}- 1.0×10^{-2}	5.0×10^{-6}
Proposed electrode (II)	59.09	9	3.0 - 9.0	<7	2.0×10^{-6}- 1.0×10^{-2}	2.0×10^{-6}
[63]	59.1	10	5.1 - 7.1	<2	3.0×10^{-5} –1.0×10^{-2}	8.1×10^{-6}
[63]	54.7	10	5.1 – 6.5	<2	1.0×10^{-5} – 1.0×10^{-2}	5.0×10^{-6}
[63]	55.0	20	5.5 – 12.0	<3	1.0×10^{-5} – 1.0×10^{-2}	5.3×10^{-6}
[64]	60.0	5 min	10.0-11.0	-	1.5×10^{-5} – 1.0×10^{-2}	9.0×10^{-6}
[65]	59.8	< 2 min	8.0 - 12.0	3	2.1×10^{-8} – 1.0×10^{-1}	1.3×10^{-8}
[66]	59.0	< 5 min	3.0-9.0	<7	3.1×10^{-5} – 1.0×10^{-2}	5.8×10^{-6}

Table 4 lists a comparative study between the reported method using electrodes (I and II) and the main analytical characters of some cyanide ion-selective electrodes previously reported with regard to the linear range, response time, detection limit, lifetime, slope and pH range. The proposed electrodes based on ruthenium(II)hexafluorophosphate complexes (ionophores A and B) exhibited superior performance characteristics in many respects than those previously reported ionophores, such as limit of detection (5.0×10^{-6} and 2.0×10^{-6} mol L^{-1} for electrode (I) and electrode (II), respectively) and potentiometric selectivity over other interferring ions. Meanwhile, relatively cheap and easily preparative method for electrodes (I and II) indicated the ease to use the proposed electrodes widely in the future.

4. CONCLUSIONS

Ionophores (A and B)-screen-printed electrodes offer variable techniques for the determination of cyanide ion in pure solutions and water samples. In addition, these electrodes showed a very good selectivity to cyanide ion in the presence of many inorganic anions. Results of high precision and accuracy and without interference by most common ions were obtained. A comparison with other electrochemical methods [63-66] indicated better selectivity of the present sensors especially in the presence of Cl^-, NO_3^-, SO_4^{2-}, $S_2O_3^{2-}$ ions. Ease of fabrication, short response time, and wide pH working range are additional characteristics over the previously reported data.

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