



Carbon nanotube composite coated platinum electrode for detection of Ga(III)

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ABSTRACT

This study demonstrates the application of composite multi-walled carbon nanotube (MWCNT) polyvinylchloride (MWNT-PVC) based on 7-(2-hydroxy-5-methoxybenzyl)-5,6,7,8,9,10-hexahydro-2H benzo [b][1,4,7,10,13] dioxatriaza cyclopentadecine-3,11(4H,12H)-dione ionophore for gallium sensor. The sensor shows a good Nernstian slope of 19.68 ± 0.40 mV/decade in a wide linear range concentration of 7.9×10^{-7} to 3.2×10^{-2} M of $\text{Ga}(\text{NO}_3)_3$. The detection limit of this electrode is 5.2×10^{-7} M of $\text{Ga}(\text{NO}_3)_3$. This proposed sensor is applicable in a pH range of 2.7–5.0. It has a short response time of about 10 s and has a good selectivity over nineteen various metal ions. The practical analytical utility of this electrode is demonstrated by measurement of Ga(III) in river water.

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1. Introduction

Ion-selective electrodes (ISEs) have found wide spread use for the direct determination of ionic species in complex samples [1]. The development of miniaturized and micro sized ISE probes continues to be a “hot” area of research. One way to reduce the size of conventional ISEs is to remove the internal reference solution. This approach has resulted in the development of coated wire electrodes (CWEs) and ion-selective field effect transistors (ISFETs). With regard to simple miniaturization of ISEs there is no doubt that the coated wire approach is an attractive one [2].

Carbon electrodes are widely used in electroanalysis because of their low background current, wide potential window, chemical inertness, low cost and suitability for various sensing and detections [3]. In recent years, the electrodes and detectors of most interest have been composites of insulating organic polymers filled with electrical conductors—for example carbon powders, ligands, and additives [4]. Several forms of carbon that are suitable for electroanalytical applications are available. Various forms of carbon or graphite with different polymers as binders were reported. Glassy carbon electrodes [5], carbon film electrode [6] and carbon–polyvinylchloride were used for analytical detections [7]. Although conductor–polymer composites were being increasingly used in electrochemistry, carbon–polyvinylchloride composites were rarely used, due to difficulties in electrode preparation. Our research group previously demonstrated that the

carbon–polyvinylchloride composite electrodes can be prepared easily on coated platinum wire electrode for analysis of Ag(I) [8], Pb(II) [9,10] and Al(III) [11].

The recent discovery of carbon nanotubes (CNTs), has attracted much attention because of their dimensions and structure sensitive properties [12]. The nanotubes consisted of up to several tens of graphitic shells (so called multi-walled carbon nanotubes, MWCNT) with adjacent shell separation of ~ 0.34 nm, diameters of ~ 1 nm and high length/diameter ratio. Carbon nanotubes have a novel structure, a narrow distribution size, highly accessible surface area, low resistance, and high stability. Multi-walled carbon nanotubes (MWCNTs) were first used to construct the electrode and to probe bioelectrochemical reactions [13]. Though MWCNTs have been used to response biomolecules, the electrochemical properties of MWCNTs are less studied so far [14]. To the best of our knowledge, only one carbon nanotube composite coated wire is reported in the literature which is for chromium ion [15].

Gallium is an indispensable rare metal in manufacture of electronic products. The average crustal abundance of the element is 16.9 ppm. In recent years, several techniques such as spectrophotometric [16], chromatography [17], electrothermal-AAS [18], ICP-AES [19], X-ray fluorescence spectrometry [20], graphite furnace-AAS [21], calorimetry [22], and polarography have been reported for the determination of gallium [23]. But these instrumental methods not only need a preliminary step for separation and preconcentration of gallium they are also expensive methods.

Up to now only two gallium selective electrodes [24], one optically based sensor [25] and novel sensitive voltammetric detection method for trace gallium(III) [26] are reported in literature. Although gallium is important for use in the semiconductor indus-

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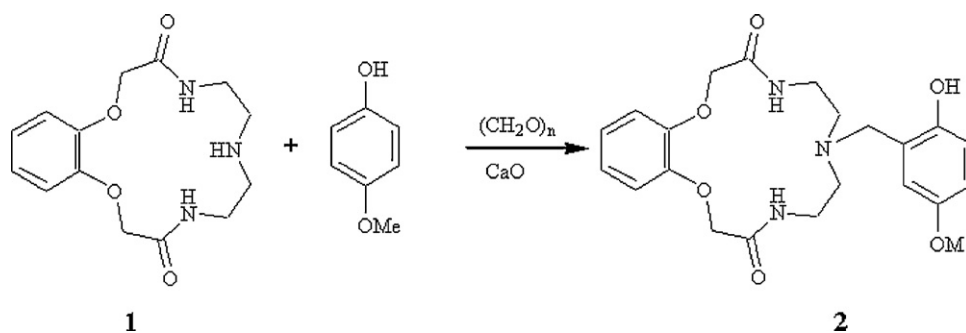


Fig. 1. Chemical structure of ionophore (2).

try, gallium particles and gallium compounds such as gallium arsenide have been identified as potential health hazards. Therefore, from an environmental point of view, the need for sensitive and reliable method for determining trace concentration of gallium has become apparent in various fields. Although there are many reports on the development of CWEs for metal ion determinations [8,9,14], there has been no report on the use of CWEs for gallium determination.

In an attempt to increase the sensitivity in the present work we applied composite electrode sensor based on MWCNT. This new composite which is coated on platinum wire has a good sensitive and selective characteristic. A wide concentration range (7.9×10^{-7} to 3.2×10^{-2} M) and low detection limit were (5.2×10^{-7} M) obtained for this proposed electrode. This new design is a simple, accurate, inexpensive and relatively rapid method for detection of Ga(III).

2. Experimental

2.1. Reagent and materials

Analytical reagent grade *o*-nitrophenyl octyl ether (*o*-NPOE), diethyl sebacate (DES), acetophenon (AP), dibutyl phthalate (DBP), dibutyl sebacate (DBS), multi-walled carbon nanotubes, (all from Fluka or Merck chemical companies) were used as received. Tetrahydrofuran (THF) was purchased from Riedel-deHaen. Reagent grade nitrate salts of all cations used (from Merck and Fluka) were of highest purity available and used without any future purification. Doubly distilled water was used throughout the experiment.

Fig. 1 shows structure of the ionophore which is used (7-(2-hydroxy-5-methoxybenzyl)-5,6,7,8,9,10-hexahydro-2H benzo[b][1,4,7,10,13] dioxatriaza cyclopentadecine-3,11(4H,12H)-dione (2)) in the proposed sensor.

2.2. Synthesis of Ionophore (2) [27,28]

Azacrown ether (1) (1 mmol), phenol (1.2 mmol), paraformaldehyde (1.2 mmol) and CaO (1.0 g) were thoroughly mixed. The resulting fine powder was transferred to a round-bottom flask and stirred in an oil bath at 100°C for 20–30 min. After cooling, acetone was added to the mixture and CaO was removed by filtration. Evaporation of the solvent under reduced pressure gave the crude products, which were purified by flash column chromatography (eluent: *n*-hexane/EtOAc 1/1). Compound (2) was obtained as a white powder in 75% yield. Mp 205.5°C . IR (KBr): 3410(s), 3254(br), 2955(m), 2818(m), 1684(vs), 1547(s), 1508(s), 1497(s), 1437(m), 1254(s), 1219(s), 1125(s), 1049(s), 754(s) cm^{-1} . ^1H NMR (CDCl_3): (2.74(t, 4H, $J=5.3$ Hz), 3.51(t, 4H, $J=5.3$ Hz), 3.70(s, 3H), 3.72(s, 2H), 4.49(s, 4H), 6.62–6.67(m, 3H), 6.89–7.06(m, 4H), 7.51(s, 2H), 7.97(s, 1H). ^{13}C NMR (CDCl_3): (35.8, 53.0, 55.6,

56.1, 68.4, 113.8, 114.6, 115.8, 116.4, 122.8, 123.0, 147.2, 149.7, 153.0, 167.9. MS m/z (%): 431(M^{+2} , 0.6), 430(M^{+1} , 4.7), 429(M^{+} , 11.6), 357(3.2), 294(6.1), 293(4.7), 292(12.5), 225(43.0), 167(19.2), 136(39.2), 85(59.9), 69(87.2), 56(100). Anal. Calcd for $\text{C}_{22}\text{H}_{27}\text{N}_3\text{O}_6$ (429.466): C, 61.53; H, 6.34; N, 9.78. Found: C, 61.69; H, 6.50; N, 9.61. UV(CHCl_3): λ_{max} (log ϵ) 247(3.22), 267(3.24), 302(3.35) nm.

2.3. Pretreatment of MWNT

The pristine MWNT (OD = 10–30 nm, ID = 5–10 nm, length = 0.5–500 μm , 95+%) was purified before use. For this purpose, the MWNT was stirred in HNO_3 (2 M) for 24 h and then was filtered and washed several times with deionized water for complete removal of nitric acid. The resultant MWNT was dried in an oven at 80°C overnight.

2.4. Membrane preparation

General procedure used to prepare the membrane is similar to our previous works [8,29–33], except that this electrode was a MWNT composite PVC coated wire electrode with a gallium selective ionophore. This cocktail mixture was prepared by weighing (3%) ionophore; (3.5%) MWNT; (62.3%) DBS; and (31.2%) PVC. A total weight of 100 mg of the mixture was dissolved in 1.5 cm^3 of freshly dried distilled THF. Then it was placed in ultrasonic for 20 min. The coating process of this carbon composite electrode was performed by dipping Pt wire five times into this mixture. After coating, the membrane was air-dried for 12 h until a thin film as in our previous work [14] was formed. The electrode was finally conditioned for 3 h in a 10^{-3} M of $\text{Ga}(\text{NO}_3)_3$ solution.

2.5. Apparatus and emf measurements

A Metrohm pH meter (model 630) with an Ag/AgCl, KCl(sat,d) as a reference electrode was used for measuring the potential. All EMF measurements were carried out at 25°C with a cell assembly as follows:

Ag/AgCl, KCl(sat, d) // Gasolution/membrane/Ptwire

Activities were calculated according to the Debye–Hückel equation [34].

3. Results and discussion

3.1. Potentiometric behavior of the gallium (III) electrode

A preliminary description of potentiometric behavior based on composite MWNT-PVC coated wire electrodes were obtained for a wide variety of cations and the results are shown in Fig. 2. As this figure shows among these cations the potential response of the gallium ion exhibited a better linear responses to activity of Ga(III)

Table 1
Various membrane compositions Pt electrode for Ga(III) ion.

Coating composition (%)									Slope (mV/decade)	r^2	Concentration range(M)
no	o-NPOE	DBS	AP	DES	DBP	PVC	MWCNT ^a	ionophore ^b			
1	64.0	–	–	–	–	32.0	2.0	2.0	26.57	0.9929	7.9×10^{-7} to 3×10^{-3}
2	–	64.0	–	–	–	32.0	2.0	2.0	18.62	0.9942	7.9×10^{-7} to 3.2×10^{-2}
3	–	–	64.0	–	–	32.0	2.0	2.0	11.28	0.9902	8.1×10^{-6} to 5×10^{-4}
4	–	–	–	64.0	–	32.0	2.0	2.0	14.80	0.9961	6.9×10^{-7} to 3×10^{-4}
5	–	–	–	–	64.0	32.0	2.0	2.0	13.47	0.9919	7×10^{-7} to 3.6×10^{-3}
6	–	62.3	–	–	–	32.2	3.5	3.0	19.68	0.9948	7.9×10^{-7} to 3.2×10^{-2}
7	–	61.6	–	–	–	31.4	4.0	3.0	24.43	0.9904	5.8×10^{-7} to 3×10^{-2}
8	–	63.0	–	–	–	31.0	3.0	3.0	16.84	0.9939	7.9×10^{-7} to 3×10^{-3}
9	–	63.0	–	–	–	31.5	3.5	2.0	17.65	0.9947	6.2×10^{-7} to 3×10^{-2}
10	–	64.0	–	–	–	33.0	–	3.0	16.47	0.9649	7.9×10^{-7} to 3×10^{-3}
11	–	63.0	–	–	–	33.5	3.5	–	12.72	0.9852	3.9×10^{-6} to 3×10^{-3}

^a Multi-walled carbon nanotube.

^b 7-(2-hydroxy-5-methoxybenzyl)-5,6,7,8,9,10-hexahydro-2H benzo[b][1,4,7,10,13] dioxatriaza cyclopentadecine-3,11(4H,12H)-dione.

ions within the concentration range of 7.9×10^{-7} to 3.2×10^{-2} M of $\text{Ga}(\text{NO}_3)_3$ while other cations did not show a Nernstian slop. This will illustrate that the interaction of ionophore is more stronger with gallium than with other cations.

The sensor with optimum composition shows also a good Nernstian slope of 19.68 ± 0.40 mV/decade with a correlation coefficient of 0.9946 ($n = 8$).

3.2. Optimization of membrane composition

Some important features of PVC composite such as the properties and amounts of the plasticizer are investigated as one of the significant influences on sensitivity and selectivity of this MWNT composite. For this purpose several solvent mediators such as o-NPOE, AP, DES, DBP, DBS were tested as potential plasticizers for preparing the membrane. The gallium ion selective electrode based on DBS exhibits a better Nernstian slope (18.62 ± 0.40 mV/decade) than o-NPOE, AP, DES, DBP (with slopes of 26.57, 11.28, 14.80, 13.47 mV/decade, respectively) as it is shown in Fig. 3 and are given in Table 1. Therefore, DBS was chosen as plasticizer in the rest of experiments.

The proposed sensor was examined by different compositions and the effects of these membrane compositions are given in Table 1. This table shows the responses of the MWNT-PVC composite electrodes with no ligand (no. 11) that exhibits a sub-Nernstian slope of 12.72 mV/decade in a shorter range of concentration (3.9×10^{-6} to 3×10^{-3} M) than optimized condition. While at the optimum composition of (3%) ionophore, (3.5%) MWNT, (62.3%) DBS, (31.2%) PVC, the obtained slope was 19.68 mV/decade in concentration range of 7.9×10^{-7} to 3.2×10^{-2} M. Table 1 also shows that an electrode at constant optimum percentage of the ligand

but with higher amount of MWNT than its optimum percentage (no. 7) the electrode show a super Nernstian (24.43 mV/decade). Decreasing the amount of MWNT to lower than of its optimum value (no. 8) the electrode response exhibits a sub-Nernstian (16.84 mV/decade). Changing the composition of the electrode by reducing the amount of ionophore to lower than its optimum value (No.9), results in a nearly Nernstian response. In this work introduction of CNTs into polymer matrix improves the electric conductivity as well as the mechanical properties of the original polymer matrix. From results (Table 1) it is clear that the detection limits and dynamic concentration ranges for this MWNT-PVC composite not only influenced by CNT percentages composition, but also it depends on the amount of ligand presents in the membrane. Results indicate that the use of nanoforms as reinforcement of organic polymers (polyvinylchlorides) has opened the possibility of developing novel ultra-strong and conductive nanocomposites. The results obtained in this study also indicate that the electrodes show a high selectivity and sensitivity for gallium ions and the main reason is due to applying of MWNTs with a good ionophore for Ga(III) in this new composition. Careful investigation of Table 1 reveals that the main factor affecting the adsorption of Ga(III) is ionophore. Because this factor characterizes the selectivity of the electrode, and without the ionophore, this electrode will response to any cation. On the other hand, electrode response characteristics would be more influenced in the absence of ionophore

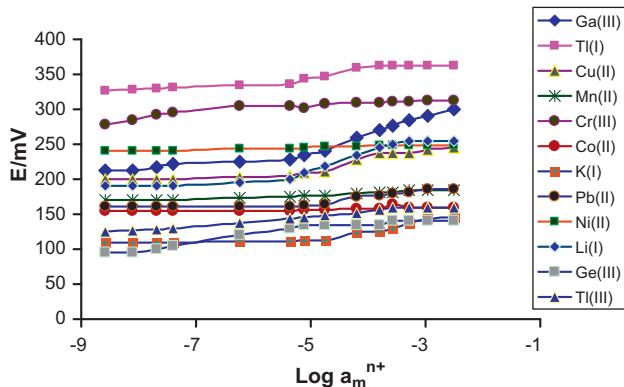


Fig. 2. Comparing various ions with MWNT composite electrode for Ga(III).

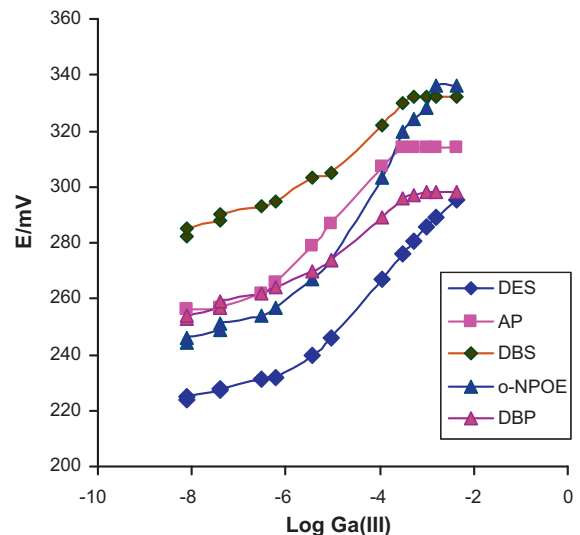


Fig. 3. Investigation of several plasticizers on the response of the proposed Ga-selective electrode (electrodes nos. 1–5) in Table 1.

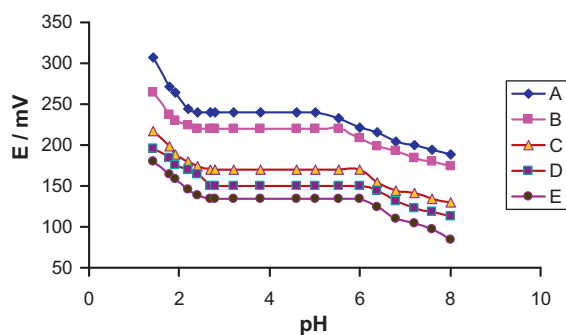


Fig. 4. pH effect on proposed composite electrode in (A) 1.0×10^{-6} M, (B) 1.0×10^{-5} M, (C) 1.0×10^{-4} M, (D) 1.0×10^{-3} M, (E) 1.0×10^{-2} M of Ga(III) ion in the pH range of 1.6–8.

(Table 1, no. 11) than when there is no carbon (Table 1, no. 10).

3.3. pH effect

The pH response profile of the proposed electrode for 1.0×10^{-6} , 1.0×10^{-5} , 1.0×10^{-4} , 1.0×10^{-3} and 1.0×10^{-2} M gallium solutions were investigated over the pH range of 1.6–8 (using HNO_3 or NaOH solutions for adjusting the pH) and the results are depicted in Fig. 4. The potential responses remained constant over the pH ranges of 2.4–5, and 2.4–5.5 at concentration of 1.0×10^{-2} and 1.0×10^{-3} mol L⁻¹, 2.7–6.0 for 1.0×10^{-4} to 1.0×10^{-6} of $\text{Ga}(\text{NO}_3)_3$, respectively. Drift observed at low pH values could be due to the response of the electrode to H^+ ions whereas at high pH values the formation of hydroxyl complexes of Ga^{3+} ions may cause a decrease in potential value.

Table 2

Selectivity coefficients for some common cations by match potential method.

Interference	$\log K^{\text{pot}}$
Co^{2+}	-2.30
Ni^{2+}	-2.88
Zn^{2+}	-2.96
Ca^{2+}	-2.40
Pb^{2+}	-1.69
Li^+	-3.52
Na^+	-3.20
Ag^+	-2.68
Cd^{2+}	-3.26
Ba^{2+}	-2.05
Cu^{2+}	-2.87
Mg^{2+}	-2.92
Cs^+	-3.06
K^+	-3.25
La^{3+}	-2.16
Cr^{3+}	-2.24
Mn^{2+}	-2.25
Tl^+	-2.36

Table 3

Results of gallium(III) ion determination in spiked samples by the proposed electrode.

Sample	Ga(III) added (μM)	Ga(III) found (μM)	Recovery (%)
Water	0	Not detected	–
1	10	9.3	93.0
	50	49.2	98.4
Water	0	Not detected	–
2	30	29.4	98.0
	100	99.6	99.6

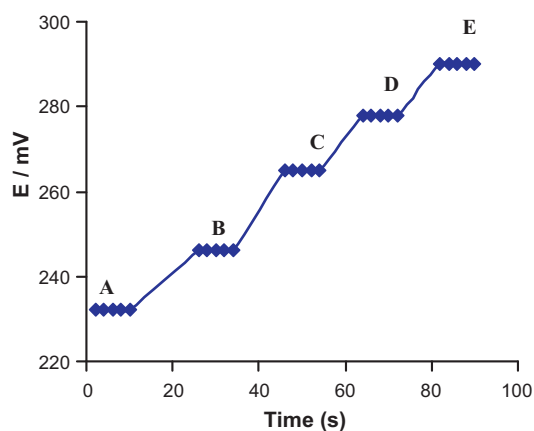


Fig. 5. Dynamic response time of the proposed electrode for step changes in the concentration of Ga^{3+} (M): (A) 1.0×10^{-6} , (B) 1.0×10^{-5} , (C) 1.0×10^{-4} , (D) 1.0×10^{-3} , (E) 1.0×10^{-2} .

3.4. Detection limit, reproducibility, repeatability response time and life time of the gallium electrode

The limit of detection, which is evaluated according to IUPAC recommendations was 3.2×10^{-7} M of $\text{Ga}(\text{NO}_3)_3$. The reproducibility was investigated by preparing seven similar electrodes at optimum membrane composition then the slope of each electrode was determined and the average slope with standard deviation was 19.78 ± 0.5 mV/decade.

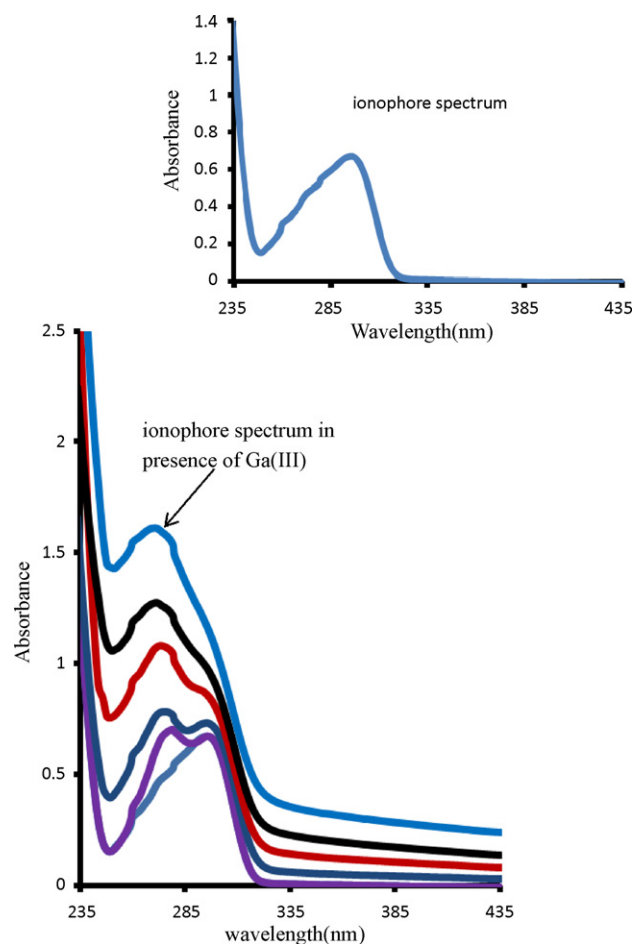


Fig. 6. Spectra of ionophore in absence and presence of different concentrations of Ga(III).

Table 4
Comparison of the proposed electrode with other methods.

Method	Concentration range (M)	Life time (day)	pH range	Response time	Ref.
IS-ISE ^a	1.45×10^{-6} to 0.1	100	4.0–10.0	12 s	41
Optode	5×10^{-6} to 8.3×10^{-5}	–	3.5	10–15 min	42
Coated wire electrode	7.9×10^{-7} to 3.2×10^{-2}	40	2.4–5.6	10 s	This work

^a Internal solution-ion selective electrode.

For the repeatability study, the calibration curves of one electrode were obtained five times during 10 days. The calibration curves were taken every other day. The average slope with standard deviation obtained was 19.46 ± 0.41 mV/decade.

The dynamic response time of the sensor was measured by changing the concentration of Ga(III) from 1.0×10^{-6} to 1.0×10^{-2} M. The resulting data depicted in Fig. 5, which shows that the time needed to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of Ga^{3+} ions (each having a tenfold difference in concentration) was 16 s for Ga^{3+} concentrations lower than 10×10^{-4} M and was 10 s for concentrations higher than 1.0×10^{-4} M.

To investigate the life time of the electrode of the calibration curves of gallium electrode at its optimized composition were periodically obtained for 40 days, and the results exhibited that no significant drift could be observed for this period of time.

3.5. Potentiometric selectivity coefficient of gallium electrode

Probably one of the most important characteristics cation selective electrodes is its relative response to other ions present in solution, which is expressed in terms of selectivity coefficients. The selectivity coefficients of the proposed electrode were evaluated by the match potential method (MPM) [35]. This method has two advantageous [36]. The first one is that when ions of unequal charges are involved, the MPM is recommended, as it gives practical $K_{A,B}$ values. Secondly, when interfering ions and/or the primary ion do not satisfy the Nernstian condition, the matched potential method is also recommended, even if the charges of the primary and interfering ions are equal. According to this method, the potentiometric selectivity coefficient is defined as the activity ratio of primary and interfering ions that give the same potential change under identical conditions. At first, a known activity (a'_A) of the primary ion solution is added into reference solution that contained a fixed activity (a_A) of primary ions, and the corresponding potential change (ΔE) is recorded. Next, a solution of interfering ion (B) is added to the reference solution until the same potential change (ΔE) is recorded. According to this method, the selectivity coefficient ($K_{A,B}$) is defined as:

$$K_{A,B} = \frac{a'_A - a_A}{a_B}$$

It should be noted that the concentration of Ga^{3+} used as primary ion in this study was 3.0×10^{-3} M. The resulting selectivity coefficient values thus obtained for the proposed Ga^{3+} sensor are given in Table 2. As this table shows, all cations would not affect the selectivity of the present gallium electrode.

3.6. Determination of Ga^{3+} in natural water

To test the practical applicability of the present sensor, some natural water samples (river water) spiked with different amounts of gallium ion were analyzed and the concentrations of gallium ion

were measured by the proposed electrode (Table 3). As the result show in this table this electrode has a reasonable recovery for the spiked samples.

3.7. Comparison of the proposed electrode with other methods

The characteristic responses of this and other methods for determination of gallium are listed in Table 4. When the data are compared it is apparent that this electrode is superior to previously reported electrodes in most cases.

3.8. Spectroscopic studies

For investigation of interaction between ionophore and Ga(III), spectra of ionophore in absence and presence of different concentrations of Ga(III) in acetonitrile were recorded. As illustrated in Fig. 6, when the concentration of Ga(III) is increased, not only absorbance increase but also blue shift is observed in this spectrum. These results demonstrate that there is an interaction between ionophore and Ga(III).

4. Conclusion

In conclusion, based on the results obtained in the present work the use of MWNT-PVC composite coated platinum electrode allows the electrochemical detection of gallium ion by potentiometric method. Results showed this proposed electrode can be successfully used for gallium detection in concentration range of 7.9×10^{-7} to 3.2×10^{-2} M of $\text{Ga}(\text{NO}_3)_3$. The present sensor contain the advantageous of, simple operation, long-term stability, low cost, fast response time and low detection limit. Comparing this electrode with previously reported gallium selective electrodes, it shows that not only it is simpler (with no internal solution or reference electrode), applying MWNT in the membrane composition made this sensor to be reasonably superior in most important electrode response characteristics.

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