Carbon composite–PVC based membrane coated platinum electrode for chromium determination

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ABSTRACT

A new synthesized 1-(2-(1H-imidazole-1-yl)-1-(4-methoxyphenyl)ethylidene)-2-phenyl hydrazine has been used as an ionophore in carbon composite–PVC coated platinum electrode for fabrication of chromium(III)-selective sensor. The homogenization procedure of membrane mixture was performed by applying of the ultrasound in this respect. The sensor shows a good Nernstian slope of 19.62 ± 0.45 mV decade^{-1} in a wide linear range concentration of 8.4×10^{-8}–1.0×10^{-2} M and a detection limit of 6.8×10^{-8} M for $Cr(NO_3)_3$. The proposed electrode has a short response time of about 10 s and is reproducible and stable for a period of at least 2 months. The performance of the sensor is pH independent in the pH range of 3.3–5.9 and it also works well in partially non-aqueous medium. The electrode has good selectivity relative to variety of metal ions. The practical analytical utility of the electrode is demonstrated by measurement of Cr(III) quantitatively in multivitamin, mineral water and also as an indicator electrode in the potentiometric titration of chromium (III) against EDTA.

1. Introduction

The necessity of selective determination of heavy metal ions has increased during the last few decades due to the growing environmental problems. Among various heavy metals, the pollution by chromium ions is of considerable concern, as it is highly toxic and has used in many industries such as chrome plating, pigment manufacturing, refractory industries, leather tanning, wood treatment, and making steel and other alloys [1]. Chromium exists in Cr(III) and Cr(VI) oxidation states in aqueous solutions. The properties of these species are different. While chromium (III) is necessary for the living organisms especially for human, chromium (VI) is known to exhibit carcinogenic properties that attacks liver, kidney and lungs. Chromium is one of the essential trace elements in multivitamin with multimineral pharmaceutical formulations that contain only Cr^{3+} either in the form of chromium chloride (inorganic source) or organic source, so the detection of chromium(III) that exist in many biological and industry materials is important. Though sophisticated analytical techniques such as AAS, ICP-AES, X-ray fluorescence, HPLC and DPP have been employed for trace level determination. These methods in spite of their good sensitivities have disadvantageous in terms of cost and unsuitability for routine analysis [1,2].

Many intensive studies on the design and synthesis of highly selective ionophores for ion-selective electrodes (ISEs) have been reported and in spite of successful progresses in the design of highly selective ionophores for various metal ions, there are only a limited number of reports on the development of highly selective ionophores for chromium (III). In addition due to the vital importance of chromium (III) in many biological and industrial samples, the need for new selective and sensitive PVC-membrane electrodes is a challenging goal [3–16].

On the other hand the need for miniaturization has resulted in the development of coated wire electrodes (CWEs) [17] and the first report on these CWEs was published by Cattrall and Freiser [18]. Since then a variety have been reported [19,20]. In this study we have shown that carbon composite electrodes can be prepared easily as coatings on wire electrodes. Carbon-based materials have been used because of their many advantageous such as their low background current, low cost, high stability, and also their resistance to passivation [21]. Our group previously reported, for the first time, the use of a PVC–carbon composite on platinum wire as a CWE for analysis of Ag(I) and Pb(II). In comparison with most commercially available electrodes, these electrodes were readily prepared and had high selectivities with a low detection limits [22,23].

For extension to our previous studies in the present work a sensor is developed for Cr(III) ion using the newly synthesized 1-(2-(1H-imidazole-1-yl)-1-(4-methoxyphenyl)ethylidene)-2-phenylhydrazine as an ionophore in a carbon–PVC matrix,

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the obtained electrode has a wide concentration range $(8.4 \times 10^{-8} - 1.0 \times 10^{-2}\,M)$, good Nernstian slope, relatively long life time and a fast response time. In addition to the best of our knowledge this is the first report on CWE of Cr^{3+} that its membrane composes of carbon. The significance of using carbon is to improve sensitivity, stability and conductivity of the membrane. On the other hand use of ionophore is an important aspect of increasing the selectivity of this composition. Moreover, the proposed sensor has very good selectivity for Cr(III) ions over variety of the cations. This new design CWE not only is comparable with the most reported PVC based electrodes but also is a simple, accurate, sensitive, inexpensive, relatively rapid method and applicable for detection of Cr(III) in multivitamin, natural water and also partially non-aqueous medium.

2. Experimental

2.1. Reagents and chemicals

Analytical-reagent grade dibutyl phthalate (DBP), dibutyl sebacate (DBS), diethyl sebacate (DES), and o-nitrophenyl octyl ether (o-NPOE) were obtained from Fluka. Poly(vinylchloride) (PVC), carbon powder and tetrahydrofuran (THF) were purchased from Merck. Chloride and nitrate salts of metal cations were provided from either Merck or Fluka and were used without further purification. All solutions were prepared from analytical reagents with triply distilled water.

2.2. Ionophore preparation

The used ionophores were, 2-imidazol-1-yl-1-(4-methoxyphenyl)-ethanone oxime (Ionophore I), 2-benzotriazol-1-yl-1-phenyl-ethanoneoxime (Ionophore II) and 1-(2-(1H-imidazole-1-yl)-1-(4-methoxyphenyl)ethylidene)-2-phenylhydrazine (Ionophore III) (Fig. 1). Typical procedures for the synthesis of these ionophores are in the literature [24].
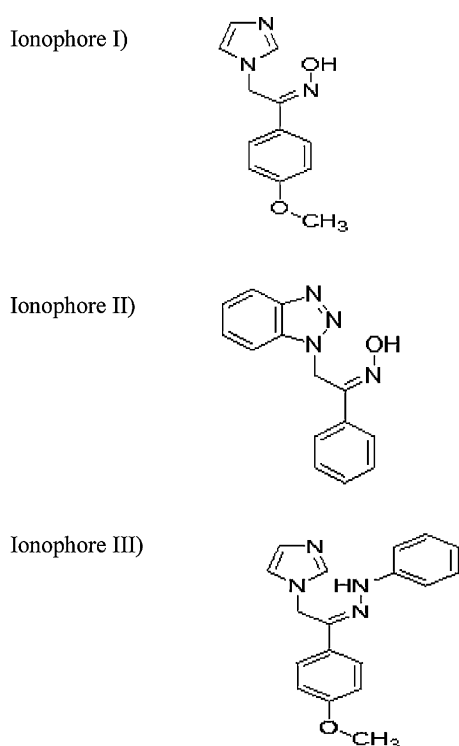
Characteristics of ionophores: The characteristics of ionophore I: IR (KBr): 1255, 1438, 1515, 1606, 2827, 2962, 3327 cm^{-1}. ^{1}H NMR (DMSO, 250 MHz): $\delta = 3.72$ (s, 3H, OCH$_3$), 5.28 (s, 2H, CH$_2$), 6.82 (s, 1H, C(5)-H, imidazole), 6.89 (d, $J = 8.8$ Hz, 2H, ArH), 7.03 (s, 1H, C(4)-H, imidazole), 7.53 (s, 1H, C(2)-H, imidazole), 7.70 (d, $J = 8.8$ Hz, 2H, ArH), 11.95 (s, 1H, OH, exchangeable with D$_2$O). ^{13}C NMR (DMSO, 62.5 MHz): $\delta = 49.27$, 55.00, 113.90, 119.49, 127.36, 128.26, 130.05, 137.53, 151.37, 159.95.

The characteristics of ionophore II: IR (KBr): 1456, 1593, 1687, 2864, 3039, 3364 cm^{-1}. ^{1}H NMR (DMSO, 250 MHz): $\delta = 6.07$ (s, 2H, CH$_2$), 7.28–8.15 (m, 9H, ArH), 12.22 (s, 1H, OH, exchangeable with D$_2$O). ^{13}C NMR (DMSO, 62.5 MHz): $\delta = 54.08$, 119.04, 126.22, 127.30, 128.20, 128.32, 128.90, 129.10, 133.97, 134.22, 145.10, 150.65.

The characteristics of ionophore III: IR (KBr): 1249, 1573, 1604, 2916, 3100, 3224 cm^{-1}. ^{1}H NMR (DMSO, 250 MHz): $\delta = 3.76$ (s, 3H, OCH$_3$), 5.43 (s, 2H, CH$_2$), 7.73–6.83 (m, 12H, ArH, imidazole), 10.09 (s, 1H, NH, exchangeable with D$_2$O). ^{13}C NMR (DMSO, 250 MHz): $\delta = 44.70$, 60.30, 118.11, 119.07, 124.41, 124.68, 131.87, 133.71, 134.25, 134.78, 142.01, 142.37, 150.77, 164.35.

2.3. Membrane preparation

The schematic setup and general protocol for preparation of this sensing electrode used in this work was similar to our previous studies [10,25–27] except that this electrode was a carbon composite–PVC coated wire electrode with a chromium(III) selective ionophore. This cocktail mixture was prepared by weighing ionophore (5%); carbon powder (2.0%); DES (61.8%); PVC (31.2%). A total weight of the mixture (150 mg) was dissolved in 1.5 cm^3 of dry freshly distilled THF and the mixture was homogenized by use of ultrasound. Coating process of this carbon composite coated platinum wire 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 was formed by using the technique as our previous work [28–29]. The electrode was finally conditioned for 3 h in a 0.01 M of Cr(NO$_3$)$_3$ solution.

2.4. Apparatus and emf measurements

For obtaining the characteristics of the ionophores a FTIR-8300 spectrophotometer (Shimadzu, Japan) and Spectra A220 flame atomic absorption spectrophotometer (Varian, Germany) were used. ^{1}H NMR (250 MHz) and ^{13}C NMR (62.5 MHz) were run on a Bruker Avanced DPX-250 (Germany). All measurements of emf were made at 25 °C by using a Corning pH/mV meter (Model 125) with a saturated calomel electrode (SCE) as a reference electrode in a cell assembly as follows:

SCE//Cr^{3+}soln./membrane/Pt wire.

Activities were calculated in accordance with the Debye–Huckel procedure [30].

3. Results and discussion

3.1. Electrode response characteristics

A preliminary description potentiometric behavior based on composite carbon–PVC coated platinum electrodes for a wide variety of cations was obtained and the results are shown in Fig. 2. As this figure shows, among these cations the potential response of the chromium ion exhibited a better linear response characteristics to activity of Cr(III) ions within the concentration range of 8.4×10^{-8} to 1.0×10^{-2} M of Cr(NO$_3$)$_3$. Accordingly membrane components were optimized (Section 3.2) to give Nernstian response to chromium ion. The sensor with optimum composition showed a good Nernstian slope of

Ionophore I)

Ionophore II)

Ionophore III)

Fig. 1. Chemical structure of ionophores.

Table 1
Effect of ionophore on the electrode response.

Coating composition (%)				Slope (mV decade^{-1})	R^2	Concentration range (M)
No.	Plastisizer (DES)	PVC	C[a]	Ionophore[b]			
1	61.8	31.2	2.0	5.0 (I$_1$)	15.46	0.993	1.6×10^{-7}–1.5×10^{-3}
2	61.8	31.2	2.0	5.0 (I$_2$)	29.40	0.991	2.5×10^{-7}–1.0×10^{-2}
3	61.8	31.2	2.0	5.0 (I$_3$)	19.74	0.998	8.4×10^{-8}–1.0×10^{-2}

[a] Carbon powder.
[b] Ligand (I$_1$: ionophore number I; I$_2$: Ionophore number II; I$_3$: Ionophore number III).
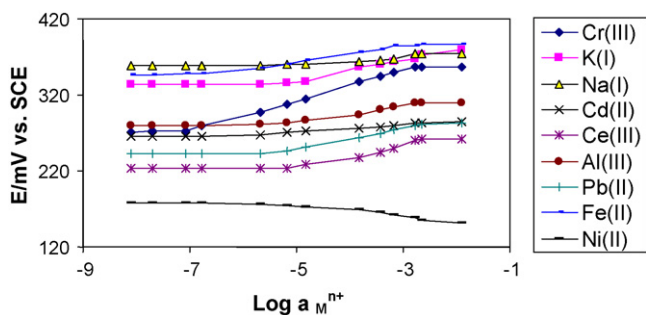
Fig. 2. The potential response of various cations on CWE.

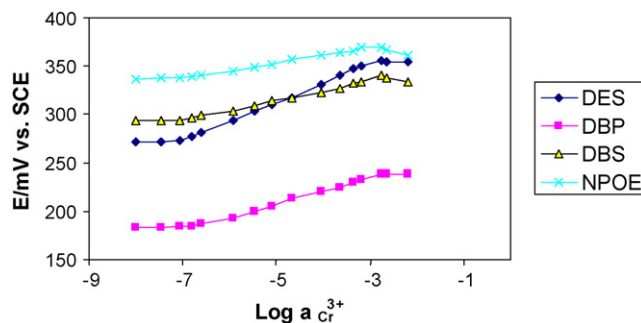**Fig. 3.** Investigation of several plastisizers in the composite electrode at optimized condition (electrodes No. 4, 5, 6, 7 in Table 2).

19.62 ± 0.45 mV decade^{-1} with a correlation coefficient of 0.998 ($n = 8$).

3.2. Optimization of membrane composition

Studies on the response characteristics of chromium ISEs based on ionophores I–III, show that ionophore number III has the best behavior than the others with a good Nernstian response over a wide linear concentration range (8.4×10^{-8}–1.0×10^{-2} M). The results are given in Table 1 (electrodes 1–3). By observing the results obtained in Table 1 ionophore No. III have used to fabricate chromium selective electrode. To obtain better response characteristics, several solvent mediators such as (o-NPOE, DES, DMS and DBP) were tested. The chromium ISE based on DES exhibits a better Nernstian slope (19.62 ± 0.45 mV decade^{-1}) than o-NPOE, DBP and DBS (with slopes of 8.37, 13.56 and 10.27 mV decade^{-1}, respectively) as it is shown in Fig. 3 and the results are given in Table 2 in a wide concentration range of 8.4×10^{-8}–1.0×10^{-2} M of Cr(NO$_3$)$_3$. Therefore, DES was chosen as plasticizer in the subsequent experiments.

The proposed sensor was examined by different compositions and the effect of these membrane compositions are given in Table 2. It is apparent from the table that the response of the elec-

trode coated with the composite containing no ligand (No. 11) has a super Nernstian slope of 24.85 mV decade^{-1} over a short range of concentration and that the electrode coated with the composite containing 0.0% carbon powder (No. 8) has a near Nernstian slope of 15.11 mV decade^{-1} in the concentration range of 4.3×10^{-7}–1.0×10^{-2} M. At the optimum composition of ionophore (5.0%), carbon powder (2.0%), DES (61.8%), and PVC (31.2%) the slope obtained was 19.62 ± 0.45 mV decade^{-1} in the concentration range of 8.4×10^{-8}–1.0×10^{-2} M (No. 7).

Performance of the carbon powder for increasing the sensitivity of the electrode was demonstrated by comparing the slope of electrodes No. 9 and 10 in Table 2. As this table shows an electrode with the optimum amount of ionophore but with less carbon than its optimum value (No. 9) has a sub-Nernstian slope and changing the composition of the electrode by increasing the amount of carbon to more than its optimum value (No. 10) a supper-Nernstian response was resulted.

From this table, it is clear that the detection limits and dynamic ranges for this CWE not only are influenced by carbon, but also depends on the amount of the ionophore. The results obtained in this study indicated that the electrodes based on both the 1-(2-(1*H*-imidazole-1-yl)-1-(4-methoxyphenyl)ethylidene)-2-

Table 2
Various membrane composition Pt electrode for Cr(III) detecting (using ionophore number III).

Coating composition (%)							Slope (mV decade^{-1})	R^2	Concentration range (M)
No.	o-NPOE	DES	DBP	DBS	PVC	C[a]	Ligand[b]			
4	61.8	–	–	–	31.2	2.0	5.0	8.37	0.989	2.5×10^{-7}–1.5×10^{-3}
5	–	–	61.8	–	31.2	2.0	5.0	13.56	0.996	1.6×10^{-7}–1.0×10^{-2}
6	–	–	–	61.8	31.2	2.0	5.0	10.27	0.993	8.4×10^{-8}–1.7×10^{-2}
7	–	61.8	–	–	31.2	2.0	5.0	19.74	0.998	8.4×10^{-8}–1.0×10^{-2}
8	–	63.5	–	–	31.5	–	5.0	15.11	0.996	4.3×10^{-7}–1.0×10^{-2}
9	–	62.7	–	–	31.3	1.0	5.0	16.95	0.996	1.0×10^{-7}–1.0×10^{-2}
10	–	61.5	–	–	30.5	3.0	5.0	23.04	0.997	8.4×10^{-8}–1.0×10^{-2}
11	–	65.5	–	–	32.5	2.0	–	24.85	0.991	7.0×10^{-6}–1.5×10^{-3}
12	–	61.4	–	–	30.6	2.0	6.0	17.43	0.998	1.0×10^{-7}–1.0×10^{-2}
13	–	62.5	–	–	31.5	2.0	4.0	21.54	0.996	2.5×10^{-7}–1.0×10^{-2}
14	–	62.2	–	–	31.3	2.0	4.5	20.73	0.997	1.0×10^{-7}–1.0×10^{-2}
15	–	60.7	–	–	30.3	3.0	6	22.48	0.997	1.0×10^{-7}–1.0×10^{-2}

[a] Carbon powder.
[b] Ionophore No. III (1-(2-(1*H*-imidazole-1-yl)-1-(4-methoxyphenyl)ethylidene)-2-phenyl hydrazine).
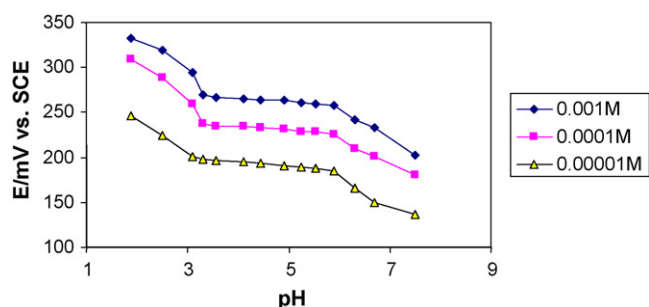
Fig. 4. pH effect on proposed composite electrode in three different concentrations of chromium ion in the pH range of 1.9–7.5.

phenyl hydrazine and the carbon powder show a high selectivity and sensitivity for chromium ions.

3.3. Effect of pH and water miscible solvent on electrode potential

The pH dependency of the membrane sensor was tested for 1.0×10^{-3}, 1.0×10^{-4} and 1.0×10^{-5} M chromium solutions over the pH range of 1.9–7.5 (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 3.3–5.7, 3.3–5.7 and 3.1–5.9 at concentration of 1.0×10^{-3}, 1.0×10^{-4} and 1.0×10^{-5} M of $Cr(NO_3)_3$, respectively. The observed potential increase at lower pH values could be due to the response of the electrode to H^+ ions. While, at higher pHs the formation of some hydroxyl complexes of Cr^{3+} ions may cause a decrease in potential responses.

The electrode response was also investigated in water miscible organic solvents such as methanol and ethanol. The potential of the electrode was found to be virtually constant up to 10% content of the methanol and 12.5% of ethanol which clearly suggested that electrodes can be applied to estimate the chromium ions in presence of the water miscible organic solvents without any interference. The results are given in Table 3. This feature is important in the cases that analytical sample is not completely soluble in water but it could be solved in partially water–alcohol mixture. On the other hand since the ionophore is soluble in ethanol and methanol these solvents were chosen to test the stability of the membrane toward these solvents.

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

The limit of detection (LOD) as defined by IUPAC is the interpolated point at which the two linear regions of a calibration curve intersect. The two linear regions are being the Nernstian portion and the non-Nernstian portion of the calibration plot. Obviously to calculate LOD, the equations for the two linear regions are set

equal to each other and the activity is solved for yielding LOD. The limit of detection, which is evaluated according to IUPAC recommendations [31] was 6.8×10^{-8} M of $Cr(NO_3)_3$. 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 19.24 ± 0.64 mV decade^{-1}.

In the repeatability study, the calibration curves of one electrode in five times were obtained during 10 days, the calibration curves had been taken every other day. The obtained average slope with its standard deviation was 19.62 ± 0.45 mV decade^{-1}.

The response time of the electrode was evaluated (according to IUPAC definition) by measuring the time required to achieve a 90% value of steady potential for a chromium solution. A response time of 10 s was obtained for this carbon–PVC membrane.

To investigate the life time of the electrode the calibration curves of chromium electrode at its optimized composition were periodically obtained for 2 months and the results exhibited that no significant drift was observed for this period of time.

3.5. Selectivity coefficients of chromium selective electrode

The influence of interfering ions on the response behavior of ISE has usually described in terms of selectivity coefficient. The experimental selectivity coefficients depend on the activity and the method of their determination. Different methods of selectivity determination have been reported in the literature. In the present study, the selectivity coefficients were determined using the matched potential method (MPM) [31,32]. This is recently recommended method by IUPAC [33] which can get rid of the limitations of the corresponding methods based on Nicolsky–Eisenmen equation for determining the potentiometric selectivity coefficient (including the fixed interference and the mixed solution methods) [34]. These limitations include non-Nernstian behavior of interfering ions and an inequality of the charges of the primary and interfering ions. According to the MPM, the selectivity coefficient is defined as the activity ratio of the primary ion (A) and the interfering ion (B) that gives the same potential change in a reference solution [31]. Thus, first the change in potential upon changing the primary ion activity is measured, and then the interfering ion would be added to an identical reference solution until the same potential change is obtained.

The selectivity coefficient, $K_{A.B}^{pot}$, is determined as:

$$K_{A.B}^{pot} = \frac{\Delta A}{a_B}$$

where $\Delta A = a_A' - a_A$, a_A is initial primary ion activity and a_A' the activity of A in the presence of interfering ion, a_B. It should be noted that the concentration of Cr^{3+} used as primary ion in this study was 5.0×10^{-5} M. The resulting selectivity coefficient values thus obtained for the proposed Cr^{3+} sensor are given in Table 4. As this tables shows all cations would not significantly affect the selectivity of the present chromium electrode.

3.6. Potentiometric titration

The sensor was used successfully for the end point determination in the potentiometric titration of 25.0 ml of 1.0×10^{-4} M Cr(III) solution with 1.0×10^{-2} M EDTA at pH 4.0–5.0. As it is seen, the titration plot obtained (Fig. 5) is not of a sigmoid shape due to response of the membrane towards Na^+ ions as available from disodium salt of EDTA. However, a sharp break point was observed which corresponds to the stoichiometry of Cr^{3+}–EDTA complex and therefore, the proposed sensor could be used as an indicator electrode for the potentiometric determination of Cr^{3+}.

Table 3
Performance of the electrode in binary water–alcohol system.

Percentage of alcohol (%v/v)	Potential (mV vs. SCE)	
	Methanol	Ethanol
0	278	275
5	278	275
10	278	275
12.5	282	275
15	285	277
20	285	280
25	288	279
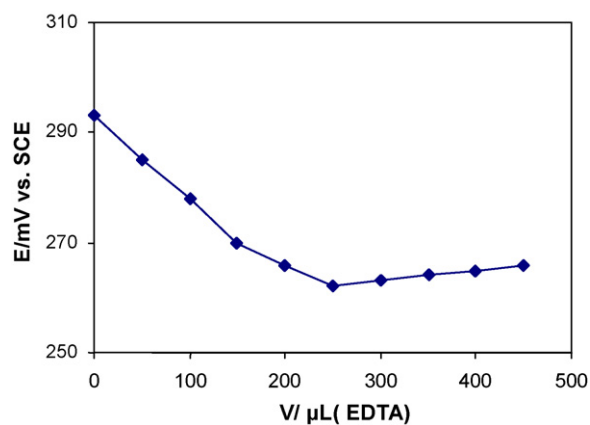
Fig. 5. Potentiometric titration curve of 25.0 ml 1×10^{-4} M of Cr(III) solution by 1×10^{-2} M EDTA at pH 4.0–5.0.

Table 4
Selectivity coefficients for various ions for Cr^{3+} ISE calculated by MPM.

Interfering ion	$K_{A,B}^{pot}$
Li^+	3.7×10^{-4}
Cu^{2+}	1.6×10^{-3}
Fe^{3+}	4.4×10^{-2}
Ga^{3+}	3.4×10^{-3}
Cd^{2+}	7.5×10^{-3}
Al^{3+}	1.1×10^{-2}
Pb^{2+}	6.1×10^{-3}
Ba^{2+}	6.7×10^{-3}
Co^{2+}	5.5×10^{-3}
Ni^{2+}	4.6×10^{-3}
Ce^{3+}	2.8×10^{-3}
Hg^{2+}	3.2×10^{-3}
Na^+	6.9×10^{-4}
Mg^{2+}	1.8×10^{-4}
Zn^{2+}	5.9×10^{-3}
Ca^{2+}	3.8×10^{-4}
Fe^{2+}	4.3×10^{-3}
K^+	2.1×10^{-4}
Ag^+	5.7×10^{-2}
La^{3+}	1.2×10^{-3}
Mn^{2+}	5.3×10^{-3}

3.7. Estimation of chromium (III) in multivitamin

In this case the purposed electrode was applied for determination of chromium in Bayer Health Care multivitamin. Three tablets of multivitamin were subjected to heating in a muffle furnace in silica crucible at about $600\,°C$ for 6–7 h; the ash was then dissolved in $10\,ml\,l^{-1}$ hydrochloric acid and diluted with 50 ml distillate water. This solution was used for Cr(III) determination by the proposed

Table 5
Investigation of real samples for this sensor.

Sample	Chromium content[a] ($\times 10^{-5}$ M)		
	Potentiometry with Pt/CWE	AAS method	Recovery %
Mineral water[b]	4.55 ± 0.22	4.71 ± 0.20	97
Multivitamin[c]	1.68 ± 0.25	1.83 ± 0.14	92

Components of Bayer HealthCare multivitamin (USA)	
Vitamin	2500 I.U.
Vitamin B1	1.5 mg
Vitamin B2	1.7 mg
Vitamin B6	2 mg
Vitamin B12	6 µg
Vitamin C	60 mg
Vitamin D	400 I.U.
Vitamin E	30 I.U.
Niacin	20 mg
Folic acid	400 µg
Biotin	50 µg
Pantothenic acid	10 mg
Potassium	99 mg
Copper	2 mg
Iodine	150 µg
Zinc	15 mg
Magnesium	100 mg
Calcium	100 mg
Chromium	120 µg
Molybdenum	75 µg
Selenium	70 µg
Manganese	2 mg

[a] Average of three determinations $\pm$ S.D.
[b] Sepidan mineral drinking water, Sepidan, Iran (Spiked with 1.0×10^{-3} M Cr^{3+}).
[c] Components of Bayer HealthCare multivitamin (USA).

Cr(III) membrane sensor as an indicator electrode using the standard addition method and the results are summarized in Table 5. As Table 5 shows the results were comparable with the values obtained by AAS method.

3.8. Determination of chromium in mineral water

The proposed electrode was applied in measurements of Cr(III) in spiked solution. For this reason Sepidan mineral water was used as matrix without any preliminary pre-treatment except the pH of the mineral water was adjusted to 5.0 using HNO_3. The results are shown in Table 5. The results were compared with the data obtained from atomic absorption spectrometry (AAS) (Table 5). As can be seen from Table 5, the results obtained show satisfactory agreement with those obtained by AAS method.

Table 6
Comparing of various reported chromium ISE with the present work.

Ionophore	Concentration range (M)	Slope (mV decade^{-1})	Detection limit (M)	Type	Response time (s)	Ref.
4-Amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one	1.0×10^{-6}–1.0×10^{-1}	19.7 ± 0.3	5.8×10^{-7}	IS-ISE	10	[16]
Glyoxal bis(2-hydroxyanil)	3.0×10^{-6}–1.0×10^{-2}	19.8 ± 0.5	6.3×10^{-7}	IS-ISE	<20	[12]
4-Dimethyl amino benzene	1.6×10^{-6}–1.0×10^{-2}	19.5 ± 0.6	8.0×10^{-7}	IS-ISE	10	[10]
Aurin TCA	7.0×10^{-6}–1.0×10^{-1}	19.0	7.0×10^{-6}	IS-ISE	10	[13]
Tri-o-thymodite	4.0×10^{-6}–1.0×10^{-1}	20.0 ± 0.1	2.0×10^{-7}	IS-ISE	15	[15]
Tetraazacyclohexadecamacrocycle	1.0×10^{-6}–1.0×10^{-1}	19.5	–	IS-ISE	18	[14]
Schiff bases, N-(acetoacetanilide)-1,2-diaminoethane	8.9×10^{-8}–1.0×10^{-1}	19.5	5.6×10^{-8}	IS-ISE	10	[1]
1-(2-(1H-Imidazole-1-yl)-1-(4-methoxyphenyl)ethylidene)-2-phenyl hydrazine	8.4×10^{-8}–1.0×10^{-2}	19.62 ± 0.45	6.8×10^{-8}	CWE	10	This Work

3.9. Comparison of the proposed electrode with other chromium electrodes

The characteristic responses of this and other chromium-selective electrodes are listed in Table 6. When the data are compared it is apparent that this electrode is comparable to previously reported electrodes in most cases. Furthermore in contrast to most of previous electrodes which are internal solution-ion selective electrodes (IS-ISEs) type, this one is CWE which can be miniaturized and be easily used in small sample volumes.

4. Conclusions

In conclusion, the use of carbon–PVC composite coated platinum electrode allows the electrochemical detection by potentiometric method. Results show that the proposed electrode was successfully used for chromium detection in concentration range of 8.4×10^{-8}–1.0×10^{-2} M with a good selectivity and a fast response time of 10 s. The sensor works well in a pH range of 3.3–5.9, and can be successfully employed for the estimation of Cr^{3+} in real samples. This electrode in most cases is comparable over the previously reported chromium-selective electrodes and to the best of our knowledge this is the first CWE of Cr^{3+} that use of carbon to improve sensitivity, stability and conductivity. Finally this electrode not only can be used in aqueous media, but also is applicable for determination of chromium ion in binary water–alcohol system.

Acknowledgements

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