Preparation of a new chromium(III) selective electrode based on 1-[(2-hydroxy ethyl) amino]-4-methyl-9H-thioxanthen-9-one as a neutral carrier

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ABSTRACT

A new chromium carbon paste electrode sensor based on a carbon paste electrode containing 1-[(2-hydroxy ethyl) amino]-4-methyl-9H-thioxanthen-9-one (AMTX) as new carrier has been prepared. The influence of carbon paste ingredients including sodium tetraphenylborate (NaTPB), ionophore, Nujol and graphite powder on the electrode response has been investigated. The best performance characteristics for the electrode was obtained with a carbon:NaTPB:Nujol:AMTX in the mass ratio of (400:1.43:57.2:3 mg) (86.65:0.31:12.39:0.65%). At the optimum value of all variables, the response of electrode is linear in range of 3.2×10^{-7} to 1.0×10^{-1} mol L^{-1} with a Nernstian slope of 20.51 mV decade^{-1} of Cr^{3+} ion concentration with detection limit of 1.6×10^{-7} mol L^{-1}. The electrode response is independent of pH in the range of 4.8–6.3, while the response time of the electrode was ∼8 s. The potentiometric selectivity coefficients of proposed chromium-selective electrode towards various interfering ions were determined by fixed interference method (FIM), separate solution method (SSM) and matched potential method (MPM).

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1. Introduction

Due to wide application of chromium compounds in modern industries, a large quantity of this element is being discharged into the environment. Chromium occurs in wastewaters in both trivalent Cr(III) and hexavalent Cr(VI) forms. The chromium toxicity depends critically on its oxidation state. While chromium (III) is considered essential for mammals for the maintenance of glucose, lipid and protein metabolism, chromium (VI) is known to be toxic for humans [1]. Therefore, development of accurate and reliable method for determination of chromium ion is very important [2–5].

Among the various applied analytical methods in this regard, ion-selective electrode as a simple method due to unique advantages such as speed and ease of electrode preparation and procedure, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity and low cost widely has been used for this purpose [6].

Due to urgent need for accurate and selective determination of trace amounts of Cr^{3+} ions in food and water samples many coordination compounds have been used as ionophores in the construction of chromium-selective electrodes (ISEs) [7–14] (Table 1). Some of these electrodes suffer from limitations such as poor detection limit [7,9,10], narrow working concentration range [9,10,13] and narrow useful pH range.

A selective agent (ionophore) mixed thoroughly with carbon powder and paraffin oil which are named chemically modified carbon paste electrodes (CMCPEs) are easy to construct and present a stable electrochemical response while their surface can be renewed by removing an outer layer of the paste by re-smoothing the electrode surface. They have lower resistance than that of ion-selective electrodes based on polymeric membranes although in both of them selectivity and operation mechanism may be attributed to the modifier materials incorporated in carbon paste. These electrodes are superior to polymeric membranes electrode in terms of lower ohmic resistance and producing very stable response [15].

The operation mechanism of chemically modified electrodes (CMEs) depends on the properties of the modifier materials used to import selectivity towards the target species [16–25].

Our survey through literature reveals that thioxantone (TX) derivatives have been used efficiently as good ion carriers for preparation of ion-selective.

Hear in, we applied 1-[(2-hydroxy ethyl) amino]-4-methyl-9H-thioxanthen-9-one (Scheme 1) with unique ability to form highly selective 2:1 (TX:Cr ion) complex with Cr^{3+} ion in a DMSO solvent for construction of chromium carbon paste electrode. The proposed electrode at optimum value of all effective variables has good characteristic performance without need to cut the dried membrane in the desired pieces and then glue it to one end of a Pyrex glass tube.

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Table 1
General performance characteristics of some chromium (III) ion sensors based on various organic ionophore.

Ionophore	L.R.[a]	Slope[b]	D.L. (µM)	pH	R.T.[d]	Reference
DMAAB	1.66–0.01	19.5 ± 0.6	0.8	3.0–5.5	10	[7]
GBHA	3–0.01	19.8 ± 0.5	0.63	2.7–6.5	<20	[9]
NBDA	1–0.1	19.9 ± 0.3	0.7	3.0–6.6	<12	[10]
AHMTO	1–0.1	19.7 ± 0.3	0.58	2.7–6.6	<10	[11]
NDAE	0.089–0.1	19.8	0.056	2.0–7.0	10	[12]
NTETA	0.83–0.1	19.5	0.63	2–5.5	22	[12]
ATCA	7–0.1	19.0	7.0	3.5–6.5	10	[13]
TOT	4–0.1	20.0 ± 0.1	0.2	2.8–5.1	15	[14]

[c]Interference; DMAAB 4-dimethylaminoazobenzene. GBHA, Glyoxal bis(2-hydroxyanil). NBDA, N-(1-thien-2-ylethylidene)benzene-1,2-diamine (SNS). AHMTO, 4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one. NBAE, N-(acetoacetanilide)-1,2-diaminoethane. NTETA, N,N.-bis(acetoacetanilide)-triethylenetetraammine. ATCA, Aurin tricarboxylic acid modified silica. TOT, tri-o-thymotide.

[a] Linear range (µM-M).
[b] mV per decade concentration.
[d] Response time (s).

2. Experimental

2.1. Apparatus

All the potential and pH measurements were carried out with a pH/Ion meters model 691 (Metrohm). The UV–vis absorbance spectra were recorded on a PerkinElmer (Lambda 25) spectrophotometer with 1.0 cm glass cell.

2.2. Reagents and materials

All chemicals used were of analytical reagent-grade and doubly distilled water was used throughout. Graphite powder from Fluka (Buchs, Switzerland), sodium tetraphenylborate (NaTPB), dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) Dermasdat, Germany. Different surfactants including cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS), Triton X-100 and Triton X-114 were purchased from Merck, the analytical grade nitrate and chloride salts of all the cations were purchased from Merck and Aldrich without any further purification. High purity Nujol oil was purchased from Fluka (Buchs, Switzerland) and used as received. The stock solution of 0.5 M chromium (III) ion was prepared by dissolving appropriate amount of chromium (III) nitrate form Merck in 100 mL of doubly distilled water.

2.2.1. Synthesis of 1-[(2-hydroxyethyl)amino]-4-methyl-9H-thioxanthen-9-one

An excess amount of 2-aminoethanol (3 mmol) was added to a solution of 1-fluoro-4-methyl-9H-thioxanthen-9-one (1 mmol) in dimethyl formamid (DMF) and was heated in an oil bath at 120 °C for 10 h till the color of the reaction mixture changed from yellow to red. The progress of reaction was monitored by thin layer chromatography (TLC). The obtained red solution was cooled and a yellow resulted suspension was diluted with cool water. The solid was filtered and washed with water and then dried at room temperature. The schematic diagram of ligand synthesis was pointed in Fig. 1. The ligand information is pointed out as following.

mp = 179–181 °C; IR (KBr, cm^{-1}): 3458 (b), 1600 (s), 1510 (s), 1271 (s), 1226 (s), 1068 (s); 1H NMR (CDCl3, 250 MHz) δ 10.46 (1H, s), 8.43 (1H, d, J = 7.9), 7.47–7.43 (1H, m), 7.37–7.31 (2H, m), 7.18 (1H, d, J = 8.5), 6.56 (1H, d, J = 8.5), 3.90 (2H, t, J = 5.4), 3.41 (2H, t, J = 5.4), 2.35 (3H, s); 13C NMR (DMSO-d6, 62.9 MHz) δ 181.9, 152.0, 136.4, 135.9, 135.0, 132.1, 129.4, 128.5, 126.4, 125.7, 117.3, 111.6, 107.3 59.1, 44.8, 18.4; MS: m/z (%) 285 (20.6, M$^+$), 254 (100), 226 (11.9), 149 (14.6). Anal. calc. for C16H15NO2S (258.36): C, 67.34; H, 5.30. Found: C, 67.38; H, 5.33.

2.3. Electrode preparation and potential measurements

Unmodified carbon paste was prepared by hand mixing of 86.7% (w/w) of reagent-grade graphite powder and 13.3% (w/w) of Nujol oil with a mortar and pestle. A modified paste was maxid the roughy according to optimum value of ingredients (graphite, Nujol, NaTPB and ligand in the ratio) pastes were packed into 5.0 mL polyethylene syringes, which electrical contact of the paste (2.5 mm diameter) was established via inserting a thin copper wire thorough flank. The surplus of paste was cut out with a glass rod and the exposed-end polished on a paper until the surface showed shiny appearance.

2.4. Cell potential measurements

The Cell potential measurements of proposed carbon paste electrode were carried out with the following cell assemblies: MCPE |sample solution| reference electrode [28]. All the potential observations were made relative to a double junction Ag/AgCl electrode with a pH/mV meter. The performance of the electrodes was investigated by measuring the cell potential of chromium nitrate solutions in the concentration range of 1×10^{-1} to 1×10^{-7} M by serial dilution. Each solution was stirred and the potential reading was recorded when it became stable and then plotted as a logarithmic function of Cr^{3+} ion concentration.

2.5. Spectrophotometric titrations

Standard stock solutions of ligands (1.0×10^{-3} M) and metal ions (1.0×10^{-3} M) and 0.05 M tetraethyl ammonium perchlorate (TEAP) for investigation of the effect of structure by spectrophotometric methods were prepared by dissolving exactly weighed (with an accuracy of 0.0001 g) pure solid compounds in 25.0 mL volumetric flasks and diluted up to mark with dimethyl sulfoxide (DMSO) as stock solution. Working solutions were prepared by appropriate dilution of the stock solutions. Titration of the ligand solution (3.8×10^{-5} M, 2.6 mL) was carried out by the addition of microliter amounts of a concentrated standard solution of the metal ion in solvent (1.0×10^{-3} M) using a pre-calibrated microsyringe [29,30].

2.6. Pre-treatment of real sample

2.6.1. Tea and coffee

1 g of the sample was placed in a beaker and 10 mL of HNO$_3$ and 4 mL of HClO$_4$ were added, followed by digestion on a hot plate until the organic residue was completely oxidized. The solution was finally diluted to 100 mL after filtering it through a filter paper (Whatman No. 1) [9,12].
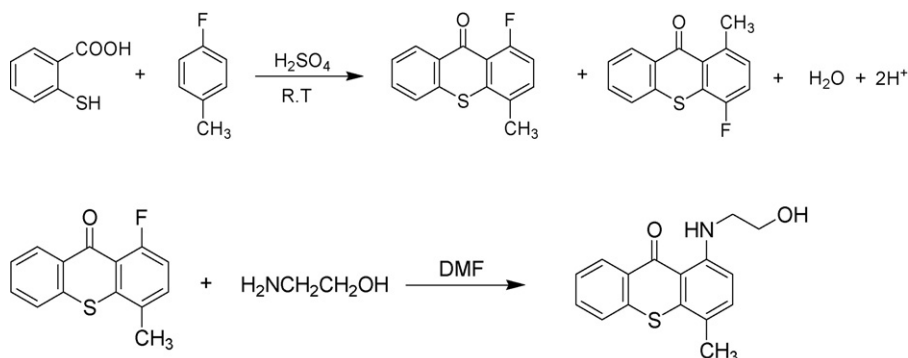
Fig. 1. Schematic of ligand preparation.

2.6.2. Tap water and waste petroleum water samples

The water samples were acidified with 0.1 M HNO_3 or KOH to adjust stable pH at 5.5 [9].

3. Result and discussion

It is well established that the selective interaction of given analyte ion and a lipophilic carrier incorporated in the membrane or carbon paste are essential to design a new ion-selective electrode. The existence of donating hydroxy group in carrier molecule was expected to increase both the stability and selectivity of its complexes with Cr^{3+} ion over other metal ions. It is known that the thioxantone ligands form very stable complexes with some of transition metal ions. However, little is known about their complex formation constants and stoichiometric ratio with metal ions for their sufficient application in analytical chemistry.

Therefore, in preliminary experiments in order to obtain a clue about the stability and selectivity of the resulting complexes, the complexation of carrier with Cr^{3+} ion was investigated spectrophotometrically. The respective titration curve and mole ratio plot for complexation of proposed carrier with Cr^{3+} ions in DMSO were depicted in Fig. 2. In titration procedure the various increments of titrant Cr^{3+} were added to 2.6 mL of AMTX and the corresponding spectra for each addition after equilibrium have been recorded. As it is obvious from the figure, while Cr^{3+} ion possesses negligible absorption in 262–460 nm spectral regions, AMTX shows two distinct absorption maximums at 450 nm and 334 nm. The observed spectral shifts in coincide to substantial increase in absorbance after the contact of the carrier solution with the chromium ion solution suggest the preferred coordination of this ion to the carrier. Kinfit program was used for analyzing the absorbance at maximum wavelength after each addition (various mole ratios) for obtaining the stoichiometry and stability constant of AMTX complexes with Cr^{3+} ion. The calculated stability constants for the binary Cr-AMTX system is ML_2 with cumulative stability constant of Log β_2 = 11.0 ± 0.2. The high stability constant for complexation makes it suitable for preparation of new Cr^{3+} ion-selective electrode.

In a set of primary experiments, carrier was used as carrier for construction of carbon paste electrodes for numerous common mono-, di- and tri-valent metal ions. It was observed clearly that the carbon paste electrode responds to Cr^{3+} ion in a wide concentration range with a near-Nernstian slope while the other anions present a poor response. This phenomenon can be attributed to the higher ionophore selectivity and its fast exchange kinetics towards Cr^{3+} ion with respect to other ions.

The cell potential responses obtained for all other cation-selective electrodes were much lower than that predicted by the Nernest equation.

In order to improve the response property of electrode, the carbon paste composition must be optimized. It is seen from Table 2

that the blank membranes (carbon and Nujol) or carbon paste containing additives and Nujol show very poor response to Cr^{3+} ion with a very small slope and short linear range. Addition of ionophore to this mixture (carbon paste containing other ingredients) shows an increase in slope and working concentration range that indicate the utility and suitability of proposed carrier for preparation of Cr^{3+} ion-selective electrode.

The electrodes with no carrier (blank membrane containing carbon, nujol and NaTPB) in comparison to blank membranes without additive (only carbon and Nujol) has better characteristics performances but still in comparison slope is sub-Nernstian (12.01 mV decade^{-1}) and the concentration range is short (1.0×10^{-6} to 0.05 mol L^{-1}) and displayed insignificant selectivity and sensitivity towards Cr^{3+} ions. Addition of ionophore to the
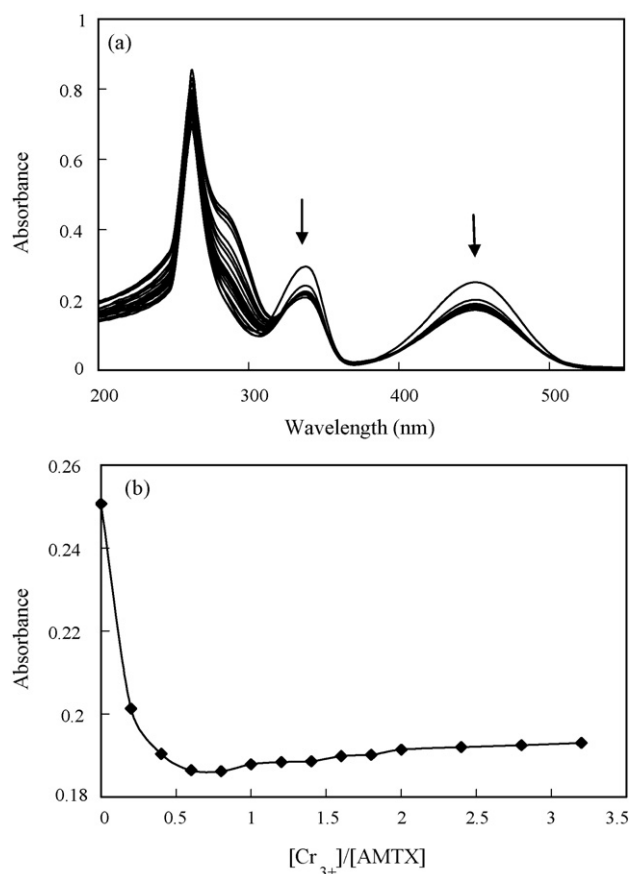

Fig. 2. UV-visible spectra for titration of AMTX (3.8×10^{-5} mol L^{-1}) with Cr^{3+} ion (1.00×10^{-3} mol L^{-1}) in DMSO (T = 25 °C and I = 0.05 mol L^{-1}) (a) and The molar ratio plot in λ_{max} = 450 nm (b).

Table 2
Response performance of the chromium (III) ion-selective electrode, conditions various carbon paste composition.

No.	Carbon powder[a]	Ligand[a]	NaTPB[a]	Nujol[a]	L.R.[b]	D.L.[c]	Slope[d]
1	500	3.0	2.15	128.7	5.01–0.1	3.16	18.82
2	500	5.0	2.15	128.7	10–0.1	5.01	25.22
3	500	7.0	2.15	128.7	15.85–0.1	10.0	24.55
4	500	9.0	2.15	128.7	5.01–0.1	3.16	23.01
5	500	3.0	0.72	128.7	2.5–0.025	1.0	24.29
6	500	3.0	1.79	128.7	5.01–0.1	2.51	29.88
7	500	3.0	2.87	128.7	15.85–0.1	10.0	23.23
8	400	3.0	1.43	28.6	10–0.1	5.01	16.27
9	400	3.0	1.43	57.2	0.32–0.1	0.16	20.51
10	400	3.0	1.43	85.8	5.01–0.1	3.16	27.74
11	400	3.0	1.43	114.4	7.94–0.50	5.01	30.56
12	400	3.0	–	57.2	1.0–0.05	0.63	12.01
13	400	–	1.43	57.2	2.52–0.1	1.58	35.19
14	400	–	–	57.2	100–0.025	50.0	22.01

[a] mg.
[b] Linear range (μM-M).
[c] Detection limit (μM).
[d] Slope (mV per decade concentration).

electrode containing the carbon, Nujol and NaTPB leads to improvement in electrode performance. The amount of modifier in the paste usually must have enough active sites in modified paste to bind analyte ions.

It is well known that some important features of the carbon paste electrode such as the nature and the amount of the additive and ionophore and the Nujol/carbon ratio significantly influence the sensitivity and the selectivity of the ion-selective electrodes.

Different carbon paste compositions were prepared by varying the concentration of the carriers, the nature and amount of additive and carbon and Nujol amount. The influence of these parameters on the response characteristics of the electrodes was investigated in Cr^{3+} ion concentrations in the range 1×10^{-7} to 0.1 M. The amount of carrier was changed while the ratios of carbon/Nujol and NaTPB/carrier concentrations were the same for all of the electrodes. The working range and sensitivity of the electrode response were improved by increasing the concentration of carrier up to 3 mg (Table 2). Further addition of the carrier concentration worsened the electrode response most probably due to saturation or non-uniformity of the membrane or due to the decreasing the conductance of the electrode material with increasing the percentage of the modifier. Electrodes with less than 3 mg of modifier shows super Nernstian slopes, of which this response may be attributed to pure carbon paste electrode. This percentage was chosen as the optimum amount of ligand for preparation of Cr^{3+} ion carbon paste electrode.

The optimization of perm-selectivity of electrode is known to be highly dependent on the incorporation of additional compounds [33]. It is well understood that addition of lipophilic negatively charged additives for cation-selective electrode improves the potentiometric behavior of electrode by reducing the ohmic resistance and improving the response behavior and selectivity, especially, when the extraction capability of the carrier is poor [34].

The influence of the type and concentration of the additives were also investigated by incorporating MTOACl or NaTPB into the carbon paste electrodes. The potentiometric response of the proposed electrode was greatly improved in the presence of the lipophilic anionic additive, NaTPB, compared to the membranes with no additive at all, while no response was observed when the cationic additive (MTOACl) incorporated into the carbon paste. The effect of NaTPB concentration in the membranes was investigated at several additive/carrier mole ratios. The electrode with NaTPB/carrier mole ratio of 40%, showed a nice near-Nernstian response to Cr^{3+} ion concentration in a wide linear range.

The electrode with the composition of 86.65% (w/w) carbon powder 12.39% (w/w) Nujol, 0.31% (w/w) NaTPB and 0.65% (w/w)

AMTX displays a Nernstian behavior. On the basis of the above discussions, it seems that ionophore acts as neutral carrier. The data given in Table 2 revealed that in the absence of a proper additive, the sensitivity of the sensor is low. However, the presence of 0.31% (w/w) NaTBP (40% mole ratio) as a suitable additive will improve the sensitivity of the Cr^{3+} ion sensor considerably.

A liquid for use as pasting in a carbon paste electrode should fulfill certain conditions such as sufficiently chemically inert, insulating, non-volatile, water immiscible and to form paste mixtures of fine consistency [35]. The potentiometric response of electrodes prepared at fixed value of all variables and different amounts of Nujol to graphite has been investigated (Table 2). It was observed that for carbon paste with a graphite powder/Nujol oil weight ratio of 6.99 Nernstian behavior the over a wide concentration range of 3.2×10^{-7} to 1.0×10^{-1} M with slope of 20.51 was obtained. The detection limits were determined conventionally from the intersection of the two extrapolated segments of the calibration graph was 1.6×10^{-7} M.

3.1. Effect of pH on electrode response

The influence of pH on the performance of the proposed electrode was investigated in the pH range of 4.0–7.8 for 1.0×10^{-2} and 1.0×10^{-1} mol L^{-1} Cr^{3+} ion solution and the respective results are shown in Fig. 3. The pH of the test solution was adjusted by addition of HNO_3/NaOH. The response of electrode is independent of the solution pH in the range of 4.6–6.3. However, outside this range (pH < 4.6) the response seems ascribable to the competitive
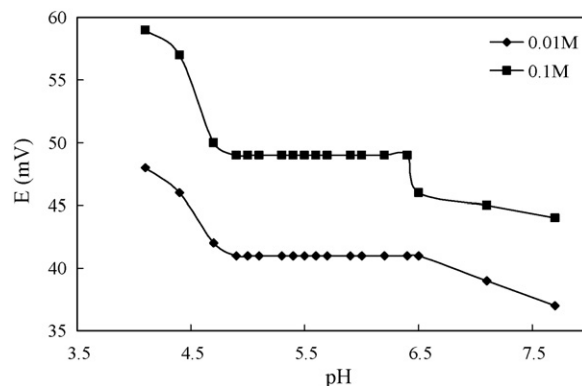
Fig. 3. Effect of pH of the test solution on the potential response of the Cr^{3+} ion-selective electrode.

Table 3
Selectivity coefficients of the chromium (III) ion carbon paste electrodes.

Ion	−Log MPM	−Log FIM	−Log SSM
Co^{2+}	1.35	–	0.15
Al^{3+}	–	0.80	
Ni^{2+}	2.17	–	0.11
Sr^{2+}	1.14	–	0.17
Zn^{2+}	2.17	–	0.80
Na^+	2.65	–	3.0
K^+	1.84	–	2.87
Mg^{2+}	1.87	–	0.17
Ba^{2+}	1.10	–	0.06
Ce^{3+}	–	1.60	–
La^{3+}	–	2.10	–

binding of proton to the carrier in addition to Cr^{3+} ion at the surface of the electrode, while the diminished potential at pH > 6.3 is to formation of chromium hydroxide in sample solution. In this working pH range, the trivalent chromium will exist as $CrOH_2^{3+}$ and the response of the electrode in this pH range is due to this ion.

3.2. Selectivity

The influence of interfering ions on the response behavior of ion-selective electrode has usually been described in terms of selectivity coefficient. In the present study, the selectivity coefficient was determined using the matched potential method (MPM) [36,37], fixed interference method (FIM) and separation solution method (SSM). The first method has an advantage of removing limitations imposed by Nicolsky–Eisenman equation while calculating selectivity coefficient by other methods. These limitations include non-Nernstian behavior of interfering ion and problem of inequality of charges of primary and interfering ions. The selectivity of the electrode (at optimum value of all variables) towards Cr^{3+} ion is reasonable with respect to most of the cations. In the case of trivalent cations (Fe^{3+}, La^{3+}, Ce^{3+} and Eu^{3+}), the logarithmic of selectivity coefficients is relatively small (in the range of −0.8 to −2.1). The obtained selectivity coefficients indicate that the disturbance produced by these cations in the performance function of the proposed Cr^{3+} ion electrode is negligible (Table 3).

3.3. Response property of electrode

It is well known that the dynamic response time of an electrode is one of the most important factors in its evaluation. Dynamic response time of an ion-selective electrode is defined as the length of time between the instant at which the ISE and a reference electrode are brought into contact with a sample solution and the first instant at which the cell gives a constant potential. The response time is measured by changing the concentration of test solution successively from 1.0×10^{-3} to 1.0×10^{-1} M and each time the cell potential is measured. The results depicted in Fig. 4 show that the time needed to reach a potential within ±1 mV of the final equilibrium value after successive immersion of a series of Cr^{3+} ions (each having a tenfold difference in concentration) is 8 s. This indicates, fast exchange kinetics of complexation–decomplexation of Cr^{3+} ions ionophore at the test solution membrane interface. To evaluate the reversibility of the sensor, a similar procedure in the opposite direction was adopted. The measurements have been performed in the sequence of high-to-low (0.1–1.0×10^{-5} mol L^{-1}) sample concentrations and the results showed that the potentiometric response of the sensor was reversible; although the time needed to reach equilibrium values was longer than that of low-to-high sample concentrations.

The electrode surface should be renewed when the Cr^{3+} ion solution is changed from higher to lower concentration to remove
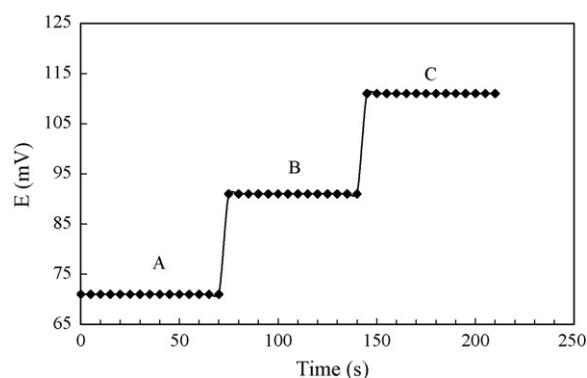
Fig. 4. Dynamic response time of chromium carbon paste electrode based on AMTX for step changes in concentration of Cr^{3+}; (A) 1.0×10^{-3} M; (B) 1.0×10^{-2} M; (C) 1.0×10^{-1} M.

its residual which still be adsorbed on the surface of carbon paste electrode. The small change in characteristics performances of proposed electrode (evaluated by repeated calibration of the electrode in Cr^{3+} ion solutions in linear range of electrode) indicates the repeatability and stability of electrode response. To evaluate the reproducibility of cell potential response of the cell assembly alternating measurements were performed in 1×10^{-5} and 1×10^{-3} M of Cr^{3+} ion solution and the procedure was repeated five times. The standard deviation of 10 replicate measurements at 1.0×10^{-5} and 1.0×10^{-3} M Cr^{3+} ion concentrations were lower than ±1.0 and it was observed that response is stable and electrode could be regenerated efficiently, while its preparation is very simple and fast. The electrode surface should be renewed when the copper solution is changed from higher to lower concentration to remove residual Cr^{3+} ion which still be adsorbed on the surface of carbon paste electrode, this process will improve reproducibility.

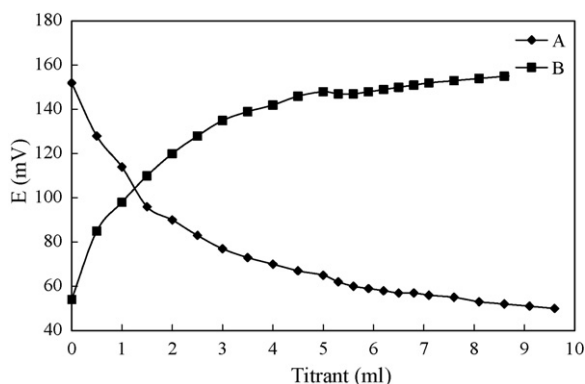### 3.4. Effect of surfactant on electrode response

The presence of surfactants leads to bleeding of the ionophore from the carbon paste to the aqueous phase that leads to significant decrease in the lifetime of electrode. On the other hand both ionic and nonionic surfactants can interact with the carbon paste ingredient or metal ions in the solution. The performance of the electrode assembly has observed in solutions contaminated with various amount of different surfactants including CTAB, SDS, Triton X-100 and Triton X-114. It was observed that the electrode response will be worsened in the presence of CTAB, Triton X-100 and SDS. The electrode response do not disturb up to 0.5 (w/v%) of Triton X-114 but at higher amount the electrode response will be destroyed.

3.5. Determination of Cr^{3+} ion in real samples

To assess the applicability of the electrode to real samples an attempt was made to determine Cr^{3+} ion concentration in synthetic sample and drinking water which was collected by a routine technique and treated by acidification with HNO_3 and then pH was adjusted to about 5.0. The sample was analyzed in five replicates using the electrode. The electrode also has been successfully applied for the determination of Cr^{3+} ion in tea sample, coffee sample and a petroleum waste water sample which was treated according to Section 2 after pH adjustments and the recovery were examined by standard addition method (Table 4). The results show the applicability of proposed electrode for accurate and precise determination of chromium (III) ion in various real samples with complicated matrix.

Table 4
Application of the proposed chromium(III) ion carbon paste electrode for determination of Cr^{3+} ion in various real samples.

Sample	Added (mM)	Found (mM)	RSD (%)	Recovery (%)
Pure drinking water	0	–	–	–
	0.500	0.508	3.9	101.6
	10.00	10.13	3.1	101.1
Distilled water spiked with Al^{3+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Ba^{2+}, Sr^{2+} (all 0.5 mM)	0.5	0.509	4.4	101.8
Coffee	0	0.0076	3.8	–
	0.01	0.0180	3.3	104.0
Tea leaves	0	0.0075	3.9	–
	0.01	0.0171	3.5	96.0
Tap water	0	0.0006	4.1	–
	0.01	0.0109	3.6	103.0
Petroleum waste water	0	0.0014	3.8	–
	0.01	0.0117	3.3	103.0

Fig. 5. Potentiometric titration curve of 50 mL of a 1.0×10^{-2} M Cr $^{3+}$ ion solution with 1.0×10^{-1} M EDTA (A) and 50 mL of a 1.0×10^{-2} M EDTA solution with 1.0×10^{-1} M Cr $^{3+}$ ion (B) at pH 4.8 using the proposed sensor as an indicator electrode.

The proposed electrode was also successfully used as an indicator electrode in conjunction with an Ag/AgCl reference electrode for the potentiometric titration of EDTA solutions with Cr^{3+} ion and vice versa. The potentiometric titration curve of the 50 mL of a 1.0×10^{-2} M Cr^{3+} ion solution with 1.0×10^{-1} M EDTA and 50 mL of a 1.0×10^{-2} M EDTA solution with 1.0×10^{-1} M Cr^{3+} ion at pH of 5.0 is presented in Fig. 5. As it can be seen, the equivalent points accurately with reasonable results can be obtained by extrapolating two linear segments.

4. Conclusion

A new chemically modified chromium carbon paste electrode (CMCPE) based on new carrier with simple preparation has fast response. The new carrier undoubtedly represents one of the most convenient materials for the preparation of modified Cr^{3+} ion carbon paste electrode. The electrode has wider working concentration range (3.2×10^{-7} to 1.0×10^{-1} mol L^{-1}, low detection limit (1.6×10^{-7}) and low response time (8 s). A comparison of the proposed sensor with reported sensors (Table 1) shows that the proposed sensor is better than most reported sensors in terms of working concentration range, detection limit and response time.

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