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Determination of Cr(III) ions in Different Water Samples Using Chromium(III)-sensor Based on N-[4-(dimethylamino) benzylidene]-6-nitro-1,3-benzothiazol-2-amine

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A novel ion-selective chemically modified carbon paste sensor (CMCPs) for Cr(III) ions based on N-[4-(dimethylamino)benzylidene]-6-nitro-1,3-benzothiazol-2-amine (DMBNA) as a new ionophore was prepared and optimized. The best performance was observed for the paste composition, including 50:37.5:12.5 (wt%) graphite:TCP:DMBNA. The electrode showed a good Nernstian slope of 19.9 ± 0.2 mVdecade^{-1} in a concentration range from 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} Cr(III) with detection limit of 2.8×10^{-7} mol L^{-1}. The fabricated sensor exhibited a fast response time (9 s) and could be used for about 16 weeks in the pH range of 2.0–7.0. The electrode showed good selectivity for Cr(III) ion towards wide variety of metal ions. The proposed sensor was applied for the determination of Cr(III) ion in different real water samples. The results obtained were compared well with those obtained using inductively coupled plasma atomic absorption spectrometry (ICP-AES).

Keywords: Chemically modified carbon paste sensor; Selectivity coefficients; Environmental samples; Mercury; N-[4-(dimethylamino)benzylidene]-6-nitro-1,3-benzothiazol-2-amine ionophore**.**

1. INTRODUCTION

Heavy metals are attracting more attention in environmental, toxicological, pharmaceutical and biomedical analysis [1-3]. Among those, the detection of chromium is of particular interest owing to the high toxicity of chromium (VI). In aqueous solution, the stable oxidation states of chromium are Cr(III) and Cr(VI). Cr(III) is considered less toxic than Cr(VI) and even essential to human health in trace concentration. However, higher concentration of Cr(III) can cause adverse effects because of its high capability of coordinating with various organic compounds, resulting in inhibiting some metallicenzyme systems [4-6]. The tolerance limit for aqueous effluent discharged into inland waters is 1.0 mg L^{-1} for total chromium (Cr(III) and Cr(VI)) and 0.10 mg L^{-1} for Cr(VI) [7-9].

Although sophisticated analytical techniques like atomic absorption spectroscopy (AAS), X-ray fluorescence (XRF), high performance liquid chromatography (HPLC) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) are generally employed for the trace level determination of metals, yet these techniques are disadvantageous in terms of cost of routine analysis and time consuming and tedious procedure of sample preparation [10-16]. On the other hand chemical sensors offer many advantages such as simple instrumentation, speed and ease of sample preparation, low cost of instrument as well as analysis, online monitoring, wide dynamic range, good selectivity and nondestructive analysis. Due to these advantages a number of ion selective electrodes have been reported in the recent past and the list is continuously growing. Recently ion-selective electrodes have been proved promising alternative as these provide fast response time, linear dynamic range, and non-destructive and ‘online’ analysis. Extensive efforts have made to develop a good sensitive sensor for chromium ion [17-25] using different neutral ionophores. However, reported sensors exhibit narrow working concentration range, non-Nernstian response and high response time [26-31] and showed significant interference from foreign ions [10-14,32]. In order to achieve wider applicability, these limitations need to be removed. An important requirement for the preparation of a selective ion sensor is that the electroactive material, which is used in the membranes, should exhibit high lipophilicity and strong affinity for a particular metal ion to be determined and poor affinity for others. Sensors comprising Schiff bases as electroactive ingredient have been reported to exhibit excellent selectivity for specific metal ions [10-14]. Schiff base ligands have been extensively studied in coordination chemistry mainly due to their facile syntheses, easily tunable steric, electronic properties and good solubility in common solvents. They are stable under a variety of oxidative and reductive conditions, and these imine ligands are boarder line between hard and soft Lewis bases. They are becoming increasingly important as biochemical, analytical and antimicrobial reagents. The use of Schiff base as neutral carriers have been reported as ion selective electrodes for determination of cations such as copper(II) [13,14], mercury(II) [33] , nickel(II) [24], silver(I) [3], lead(II) [2] and cobalt(II) [10].

The results presented in this paper show that the sensor developed for Cr(III) ion using chemically modified carbon paste sensor based on N-[4-(dimethylamino)benzylidene]-6-nitro-1,3-benzothiazol-2-amine (DMBNA) ionophore has a wide working concentration range, good Nernstian slope, low detection limit, high selectivity over a wide variety of other cations and wider pH range than previous papers [17-19]. The sensor has a fast response time and gives reproducible results.

2. EXPERIMENTAL

2.1. Apparatus

Laboratory potential measurements were performed using Jenway 3505 pH-meter. Silver-silver chloride double-junction reference electrode (Metrohm 6.0726.100) in conjugation with different ion selective electrodes was used. pH measurements were done using Thermo-Orion, model Orion 3 stars, USA. Prior to analysis, all glassware used were washed carefully with distilled water and dried in the oven before use.

2.2. Reagents and Chemicals

Analytical grade reagents are used in this study. Distillated water was used throughout all experiments. Chromium nitrate [$Cr(NO_3)_3.9H_2O$] was supplied from Aldrich. *o*-Nitrophenyloctylether (*o*-NPOE) was supplied from Fluka and N-[4-(dimethylamino)benzylidene]-6-nitro-1,3-benzothiazol-2-amine (DMBNA) was prepared according to the previously published method [34]. Graphite powder (synthetic 1–2 μm) was supplied from Aldrich and was used for the fabrication of different electrodes. Chloride salts of mercury, copper, magnesium, cadmium, nickel, calcium, potassium, cobalt, sodium, ferric and aluminum, in addition to bromide, iodide, sulphate and nitrate anions are used as interfering materials. Also, potassium chromate and potassium dichromate were used as source for Cr(VI).

2.2.1. Samples

Real water samples includes formation water (Amry deep (9), Western Desert, Agiba Petroleum Company (sample 1), Egypt), tab water (sample 2), river water samples (sample (3), Giza, Egypt) and cooling tower waters (EMISAL, Egyptian Mineral and Salts Company, Fayoum (sample 4), Egypt).

2.3. Procedures

2.3.1. Preparation of chemically modified carbon paste electrode

A 500 mg pure graphite powder and 2.5-15 mg of DMBNA ionophore are transferred to mortar and mixed well with plasticizer (0.2 mL of *o*-NPOE). The modified paste is filled in electrode body and kept in distillated water for 24 h before use [10-14,27-32,35,36]. A fresh surface was obtained by gently pushing the stainless-steel screw forward and polishing the new carbon-paste surface with filter paper to obtain a shiny new surface.

2.3.2. Preparation of ionophore

N-[4-(dimethylamino)benzylidene]-6-nitro-1,3-benzothiazol-2-amine (DMBNA) was prepared according to the previous reported method [34].

2.3.3. Calibration of the new CMCPE

The new CMCPE was calibrated by immersion in conjunction with a reference electrode in a 25-mL beaker containing 2.0 mL acetate buffer solution of pH 4. Then 10 ml aliquot of Cr(III) solution of concentration ranging from 1×10^{-6} to 1×10^{-1} mol L^{-1} was added with continuous stirring and the potential was recorded after stabilization to ±0.1 mV. A calibration graph was then constructed by plotting the recorded potentials as a function of -log [Cr(III)]. The resulting graph was used for subsequent determination of unknown Cr(III) concentration [10-14].

2.4. Determination of Cr(III) in spiked real water samples

About 5 ml of spiked real water samples were transferred to a 25 ml beaker and adjusted to pH 4 then content was estimated via potentiometric calibration using CMCPE as sensing electrodes. The method was repeated several times to check the accuracy and reproducibility of the proposed method [10-14].

3. RESULT AND DISCUSSION

3.1. Effect of ionophore content

For this purpose, six electrodes were prepared containing different amounts of the N-[4-(dimethylamino)benzylidene]-6-nitro-1,3-benzothiazol-2-amine (DMBNA) ionophore (2.5-15 mg). The results (Table 1) showed that on using paste of optimum compositions (electrode V), a slope of 19.90±0.57 mV $decade^{-1}$ over a relatively wide range of Cr(III) concentration from 2.8×10^{-7} to 1×10^{-1} mol L^{-1} was obtained, and the value of the correlation coefficient (r^2) was higher than that obtained with other paste [20]. Other pastes exhibit slopes of 12.50, 14.20, 15.95, 17.73 and 19.41 mV $decade^{-1}$ for Cr(III), but the linearity ranges of the calibration curves are shorter and the correlation coefficients are worse (0.975–0.998). In all subsequent studies, electrode (V) made of paste consisting of 12.5 mg ionophore was used. A typical calibration plot for the electrode is shown in Fig. 1. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 2.8 × 10^{-7} mol L^{-1}.

Table 1. Effect of ionophore content on the performance characteristics of CMCP sensor.

No. of electrodes	Ion Pair Content (mg)	Concentration rang (mol L^{-1})	Slope (mV $decade^{-1}$)	Recovery %	Total potential change, mV
I	2.5	1.0×10^{-5}-1.0×10^{-1}	12.50±2.06	97.50	72
II	5.0	3.0×10^{-6}-1.0×10^{-1}	14.20±1.95	98.90	84
III	7.5	1.0×10^{-6}-1.0×10^{-1}	15.95±1.41	99.00	93
IV	10.0	1.0×10^{-6}-1.0×10^{-1}	17.73±1.03	99.25	105
V	12.5	2.8×10^{-7}-1.0×10^{-1}	19.90±0.57	99.80	116
VI	15.0	1.0×10^{-6}-1.0×10^{-1}	19.41±0.88	99.75	112

3.2. Effect of soaking time

Freshly prepared electrodes must be soaked in their respective Cr(III) solution to activate the surface of the paste to form an infinitesimally thin gel layer at which ion-pair processes occur. The preconditioning process requires different soaking intervals depending on the diffusion and equilibration at the interface, fast establishment of equilibrium is certainly a sufficient condition for fast potential response. The performance characteristics of the electrode were studied as a function of soaking time. For this purpose the electrode was soaked in a 1.0×10^{-3} mol L^{-1} Cr(III) solution and the slope of the calibration curve was measured at 5 min time intervals for 24 h at 25 ˚C. The optimum soaking time was found to be 15 min at pH 4.0 to prove more suitable measuring solution, which the slope of the calibration curve was 19.90±0.57 mV $decade^{-1}$, at 25˚C for electrode (V) the data is shown in Table 2. A soaking time longer than 2 h is not recommended as leaching, although very little, of the electroactive species into the bathing solution occurs. The electrode should be kept dry in an opaque closed vessel and stored in a refrigerator while not in use, in order to preserve the slope values and to extend the response properties for several months.

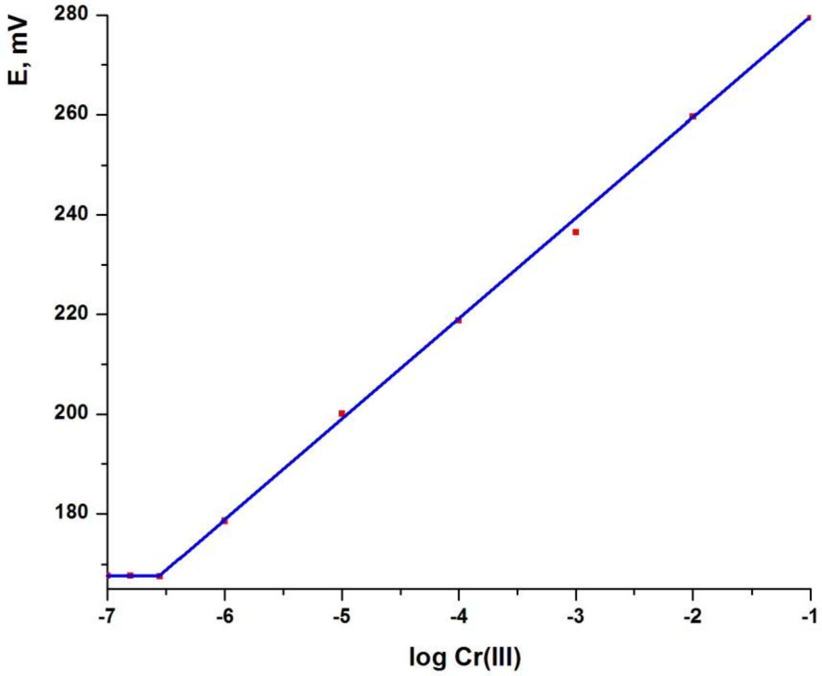

Figure 1. Calibration curve for Cr(III)-chemically modified carbon paste electrode

3.3. Response time of the electrode

The response time of CMCPE is also an important factor for any analytical application. The average response time was defined as the time required for the electrodes to reach a cell potential of 90% of the final equilibrium values after successive immersions in a series of solutions each having a

10-fold concentration difference. The response time of the electrode (V) was evaluated (according to IUPAC definition) by measuring the time required to achieve a 90% value of steady potential for a Cr(III) solution. A response time of 9 s was obtained for this electrode (Fig. 2) [17].

Table 2. Effect of soaking time on calibration of CMCPE (electrode V)

Electrode	Time of soaking	Concentration rang (mol L^{-1})	Slope (mV decade^{-1})	Recovery %	Total potential change, mV
V	5 min	5.1×10^{-7}-1.0×10^{-1}	19.35±1.03	99.50	110
	10 min	2.8×10^{-7}-1.0×10^{-1}	19.60±0.97	99.72	113
	15 min	2.8×10^{-7}-1.0×10^{-1}	19.90±0.57	99.80	116
	20 min	1.0×10^{-6}-1.0×10^{-1}	18.73±1.56	99.00	109
	30 min	1.0×10^{-6}-1.0×10^{-1}	18.50±1.72	98.24	107
	1 h	6.3×10^{-6}-1.0×10^{-1}	17.53±1.74	97.65	103
	2 h	1.0×10^{-5}-1.0×10^{-1}	16.75±2.25	96.97	96

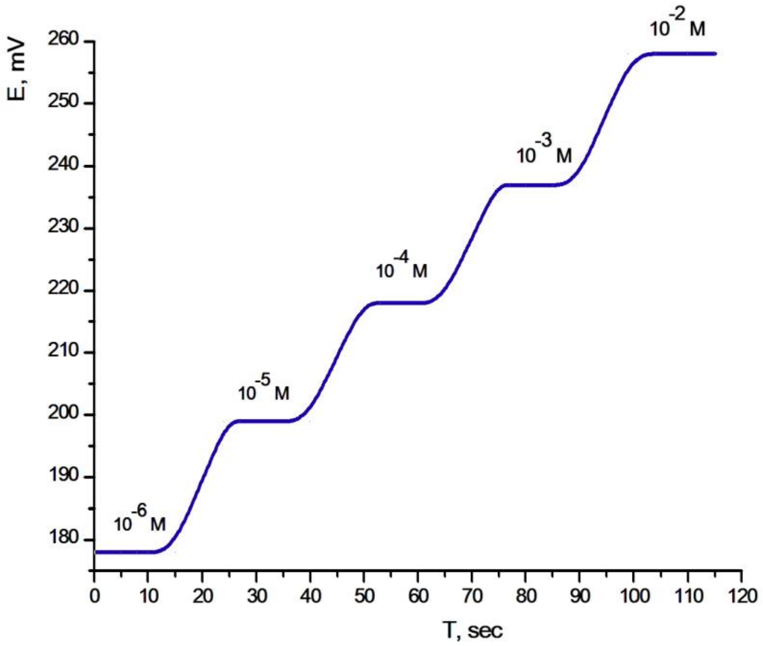

Figure 2. Dynamic response time of CMCPE (electrode V).

3.4. Lifetime of the electrode

The lifetime of the proposed Cr(III) sensor (electrode V) was evaluated for a period of 16 weeks, during which the sensor was used three hours per day. The obtained results showed that the proposed sensor (V) can be used for at least 13 weeks. After this time, a slight gradual decrease in the slope from 19.90 to 18.55 mV decade^{-1} is observed (Fig. 3).

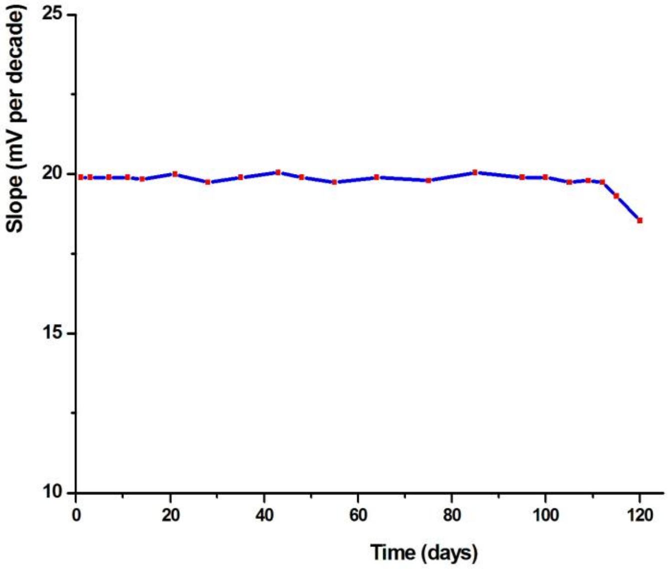

Figure 3. Life time of the Cr(III) CMCPE (electrode V).

3.5. Effect of pH on the response of the electrode

The effect of pH on the response of the electrode was respectively investigated in two Cr(III) concentrations (1.0× 10^{-3} and 1.0× 10^{-5} mol L^{-1}) over a pH range of 1.0–9.0, where the pH was adjusted with dilute nitric acid and sodium hydroxide solutions. As shown in Fig. 4, the potential does not change apparently at pH range 2.0–7.0, which can be used as the working pH range of the proposed electrode. While, outside this range, the potential changed significantly. The increase of potential below pH 2.0 may be ascribed to the competitive binding of protons to the ligand on the electrode surface. The decrease of potential above pH 7.0 can be attributed to the formation of hydroxyl complexes of Cr(III) ions which diminished its ability to combine with the carrier [37].

3.6. Effect of temperature

Calibration graphs (electrode potential (E_{elec}) versus p[Cr(III)]) were constructed at different test solution temperatures (10- 65 ^{o}C). For the determination of the isothermal coefficient (dE^0/dt) of the electrode, the standard electrode potentials (E^o) against normal hydrogen electrode, at the different temperatures were obtained from the calibration graphs as the intercepts at p[Cr(III)] = 0 (after subtracting the values of the standard electrode potential of the silver-silver chloride double-junction reference electrode at these temperatures) and plotted versus (t-25), where t was the temperature of the test solution in °C (Fig. 5). A straight-line plot is obtained according to Antropov’s equation [10-14,26,28-31]:

$$E^0 = E^0_{(25)} + (dE^0/dt)(t-25)$$

where $E^0_{(25)}$ is the standard electrode potential at 25 °C. The slope of the straight-line obtained represents the isothermal coefficient of the electrode which is found to be 0.00527 V/°C. The value of the obtained isothermal coefficient of the electrode indicates that the electrode has a fairly high thermal stability within the investigated temperature range. The fabricated electrode was found to be usable up to 60 °C without noticeable deviation from the Nernstian behaviour.

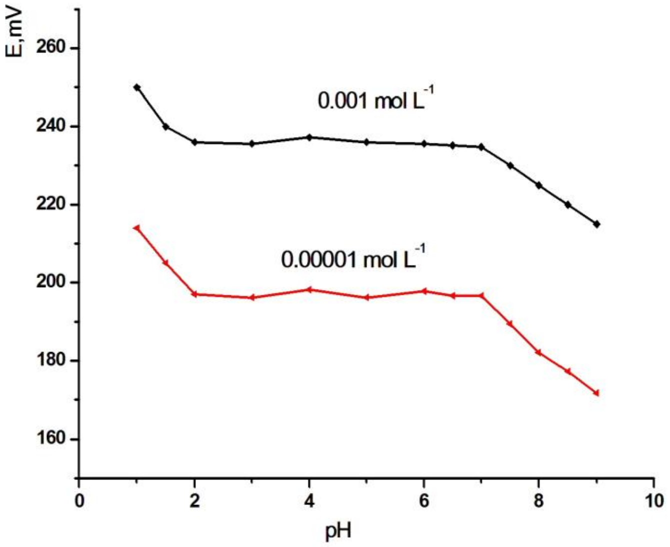

Figure 4. Effect of pH on the performance characteristics of electrode V.

3.7. Selectivity coefficients

The selectivity coefficient of the electrode (V) for various metal ions was evaluated by using both the fixed interference (FIM) [10-13] and the matched potential (MPM) [10-13] methods. In the FIM, the selectivity coefficient was determined from the potential measurements of solutions containing a fixed constant activity of the interfering ion (1.0×10^{-3} mol L^{-1}), a_B, and titration with varying activity of the primary ion. The selectivity coefficient is calculated from the following equation:

$$K_{AB} = \frac{a_A}{(a_B)^{Z_A/Z_B}}$$

where a_A is the activity of the primary ion (Cr(III)) at the lower detection limit in the presence of interfering ion and Z_A and Z_B are the charge of ions. In the matched potential method, at first a known activity (a_A') of the primary solution is added to a reference solution that contains fixed activity (a_A) of primary ion and the potential change is recorded. Secondly, solutions of interfering ions (a_B) are added to the primary ion solution until the same potential change is observed. The change in potential produced at the constant back-ground of the primary ion must be the same in both cases. The selectivity coefficient $K^{Pot}_{Cr(III),\, M^{n+}}$ is calculated by the equation:

$$K_{AB} = \frac{a'_A - a_{AB}}{a_B}$$

In the present studies $a_{Cr(III)}$ and $a'_{Cr(III)}$ was kept at 1.0×10^{-6} and 1.0×10^{-5} mol L^{-1} Cr(III) and a_B was experimentally determined. Matched potential method has an advantage of removing limitations imposed by Nicolsky–Eisenman equation while calculating selectivity coefficient by other methods (for example FIM). These limitations include non-Nernstian behavior of interfering ion and problem of inequality of charges of primary and interfering ions. The resulting potentiometric selectivity coefficients values are shown in Table 3. For all diverse ions, the selectivity coefficient's of the electrode (V) are in the order of 9.98×10^{-3} or smaller, indicating they would not significantly disturb the function of the Cr(III) selective sensor. The effect of interference of Cr(VI) is investigated and the selectivity coefficient was calculated using both FIM and MPM methods (Table 3). The results show that Cr(VI) does not interfere with Cr(III) which means that the electrode (V) can detect the Cr(III) savely [21].

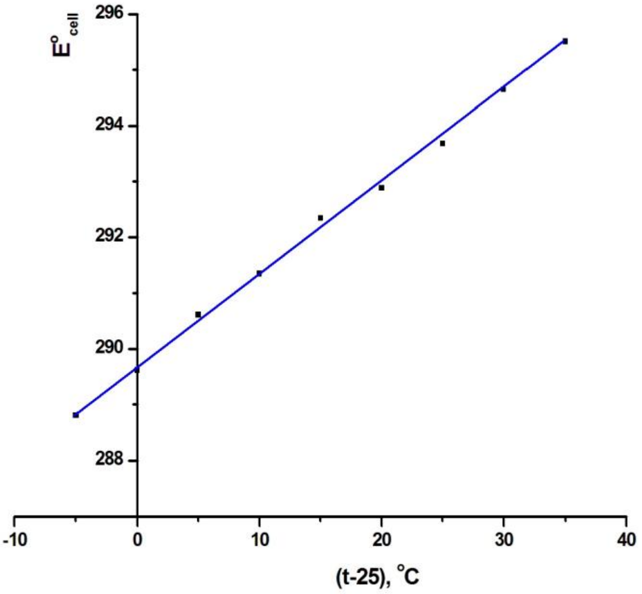

Figure 5. Effect of temperature on the performance of electrode V.

Table 3. Potentiometric selectivity coefficients of some interfering ions using electrode V.

Interfering ions	$K_{A,B}^{MPM}$	$K_{A,B}^{FIM}$	Interfering ions	$K_{A,B}^{MPM}$	$K_{A,B}^{FIM}$
Mg^{2+}	5.76×10^{-5}	7.08×10^{-5}	Ag^{+}	9.36×10^{-3}	9.98×10^{-3}
Zn^{2+}	4.38×10^{-4}	8.52×10^{-4}	Li^{+}	7.03×10^{-4}	8.20×10^{-4}
Hg^{2+}	6.75×10^{-3}	7.99×10^{-3}	Na^{+}	5.51×10^{-4}	7.62×10^{-4}
Cd^{2+}	7.23×10^{-4}	9.08×10^{-4}	NH_4^{+}	5.17×10^{-3}	7.77×10^{-3}
Pb^{2+}	2.85×10^{-4}	4.98×10^{-4}	Cl^{-}	7.43×10^{-4}	7.99×10^{-4}
Fe^{3+}	7.04×10^{-3}	8.66×10^{-3}	SO_4^{-2}	7.48×10^{-4}	8.52×10^{-4}
Al^{3+}	6.73×10^{-3}	8.21×10^{-3}	NO_3^{-}	4.75×10^{-4}	3.05×10^{-5}
I^{-}	3.71×10^{-3}	5.56×10^{-3}	Br^{-}	8.09×10^{-4}	9.16×10^{-4}
Cr(VI)	2.69×10^{-3}	2.88×10^{-3}			

3.8. Analytical application

The new chromium selective sensor (electrode V) was successfully applied to obtain recoveries of chromium in different samples. For sampling and the preparation of these samples, first, the pHs of real samples were adjusted to pH 4, and then the samples were filtered using 0.2 mm pore-size, polycarbonate membrane filters. The analysis was performed by the standard addition technique. The results are given in Table 4. The sensor was also successfully applied for the determination of Cr(III) spiked in a synthesized Cr(III)-polluted water sample [synthesized by: 5×10^{-4} mol L^{-1} Cr(III); 5×10^{-3} mol L^{-1} Co(II), Mg(II), Zn(II) and Cu(II); 1×10^{-3} mol L^{-1} Na(I), Ca(II) and Mg(II)]. The results are given in Table 4. Accordingly, the obtained results are comparable with those obtained by ICP-AES. Thus the sensor provides a good alternative for the determination of Cr(III) in real samples.

Table 4. Potentiometric determination of Cr(III) in spiked real water samples using electrode V.

Sample No.	Cr(III) add	[Cr(III)] (mg/L) found		SD		RSD (%)	
		CMCPE	ICP	CMCPE	ICP	CMCPE	ICP
1	0.50	0.501	0.488	0.05	0.09	0.43	1.00
2	0.45	0.457	0.449	0.01	0.04	0.26	1.10
3	0.50	0.492	0.480	0.07	0.09	0.56	1.09
4	0.65	0.651	0.649	0.14	0.15	1.00	1.45
Synthesized Cr(III)-polluted water	1.5×10^{-4}	6.52×10^{-4}	6.5×10^{-4}	0.14	0.38	1.01	1.25
	2.5×10^{-4}	7.54×10^{-4}	7.51×10^{-4}	0.21	0.63	1.10	1.55

3.9. Comparison of the proposed electrode (V) with literature precedents

For comparative study, the linear range, detection limit, slope, response time and pH range of the previously reported chromium [17-24] ion selective electrodes are listed in Table 5 against the proposed electrode (V). It is clearly evident from this table that the proposed electrode based on DMBNA sensing material is superior to those reported in terms of its wide concentration range, lower detection limit and improved selectivity with respect to the various interfering ions. Most of these Cr(III)-selective electrodes suffer considerable interference from various cations. However, these cations do not interfere in the monitoring of Cr(III) ions using the proposed electrode, because all of them show low values of selectivity coefficients. The results also indicate that the proposed electrode has fast response time in comparison to other reported electrodes. In addition, this method offers several distinct advantages such as simplicity, cheapness and rapidness. Overall, this electrode is more useful in analytical applications.

Table 5. Comparing some of the Cr(III)-CMCPE characteristics with some of the previously reported Cr(III)-ISEs.

References	Slope (mV decade^{-1})	Response time (s)	pH	Life time (months)	Linear range (mol L^{-1})	DL (mol L^{-1})
Proposed electrode	19.90	9	2.0 – 7.0	4	1.0×10^{-6} – 1.0×10^{-1}	2.8×10^{-7}
17	19.60	10	3.2 - 6.3	2	1.0×10^{-6} –1.0×10^{-1}	5.3×10^{-7}
18	19.70	10	2.7 – 6.6	3	1.0×10^{-6} –1.0×10^{-1}	5.8×10^{-7}
19	19.80	>10	2.2–5.0	3	2.0×10^{-7} –1.0×10^{-1}	2.0×10^{-7}
20	20.00	15	4.5 - 6.5	5	4.0×10^{-6} –1.0×10^{-1}	2.0×10^{-7}
21	19.80	< 20	2.6 - 6.5	3	3.0×10^{-6} –1.0×10^{-2}	6.3×10^{-7}
22	19.50	10	3.0 – 5.5	3	1.66×10^{-6} –1.0×10^{-2}	8.0×10^{-7}
23	19.80	20	1.7-6.5	-	1.0×10^{-7} – 1.0×10^{-2}	6.3×10^{-7}
24	19.00	10	3.5 – 6.5	5	7.0×10^{-6} –1.0×10^{-1}	1.0×10^{-6}

4. CONCLUSIONS

The CMCP electrode, prepared with DMBNA under optimal CMCPE ingredients, revealed a Nernstian response over a wide chromium activity range (from 2.8×10^{-7} to 1.0×10^{-1} mol L^{-1}), lower detection limit 2.8×10^{-7} mol L^{-1} and fast response time 9 s. This sensor also shows selectivity towards Cr(III) over a number of mono-, bi- and trivalent cations, which generally shows interference in some of the reported electrodes. The electrode was used as an indicator electrode for direct potentiometric determination of chromium ion in water and real samples.

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