

Cr(III) Ion-Selective Membrane Sensor Based on 1,3-Diamino-2-Hydroxypropane-N,N,N',N'-Tetraacetic Acid

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A new greatly selective and sensitive PVC membrane sensor has been developed as a Cr(III) ion selective electrode, using an ionophore named 1,3-Diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid (DPTA). The sensor displays a linear dynamic range between 7.0×10^{-7} and 1.0×10^{-1} M, with a near Nernstian slope of 19.8 ± 0.3 mV per decade and a detection limit of 2.0×10^{-7} M. The best performance was obtained with a membrane composition of 32% poly(vinyl chloride), 57.5% nitrophenyl octyl ether, 3% sodium tetraphenyl borate and 7.5% DPTA. The potentiometric response of the proposed electrode is pH independent in the range of 2.5–6.8. The sensor possesses the advantages of short conditioning time, fast response time (<10 s) and, especially, good selectivity towards transition and heavy metal, and some mono, di, and trivalent cations. The electrode can be used for at least 10 weeks without any considerable divergence in the potentials. It was effectively used as an indicator electrode in the potentiometric titration of Cr(III) ions with EDTA and also in the Cr(III) determination in wastewaters of chromium electroplating industries.

Keywords: Potentiometry, Cr(III) Sensor, PVC, 1,3-Diamino-2-Hydroxypropane-N,N,N',N'-Tetraacetic Acid.

1. INTRODUCTION

Chromium exists in two states; Cr(VI) and hydrated chromium(III) species, despite the Cr trace amounts in the trivalent state. It is known to be an essential element in the human nutrition but its accumulation in the human body results in toxicity. Chromium is widely employed in various industries such as plating, tanning, paint, and pigment production as well as metallurgy, which possibly contaminates the environment.

Furthermore, chromium in hexavalent state is 100–1000 times more toxic than the other. Chromium(VI) is also reported as mutagenic and carcinogenic for the human body, leading to lung cancer, skin allergy and probably to asthma and renal diseases. As a result, finding an effective method for the chromium determination is of great importance.

Consequently, numerous analytical methods have been developed for its determination in different sample

matrices such as spectroscopic methods,^{1–5} chromatographic methods,^{6–8} and electrochemical methods.^{9–11} Although these methods present high selectivity and sensitivity, they tend to be complicated and expensive to apply. There are only a limited number of reports on the development of highly selective ionophores for chromium(III).^{12–25}

Recently, several electrodes have been reported for anions and metal ions.^{26–35} In this paper, the introduction of a simple and inexpensive method is reported. Particularly, a new Cr³⁺ ion-selective membrane electrode is employed with the help of 1,3-Diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid (DPTA) as a neutral ion carrier (Fig. 1).

2. EXPERIMENTAL DETAILS

2.1. Reagent

The Merck Co. was the provider for the reagent grades of dibutyl phthalate (DBP), nitrobenzene (NB), *ortho*-nitrophenyloctyl ether (NPOE), tetrahydrofuran

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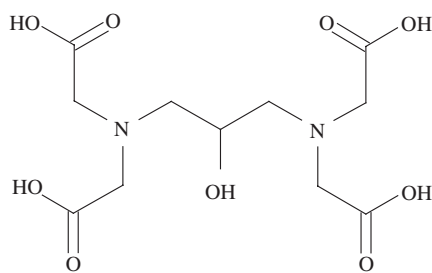


Fig. 1.

(THF), sodium tetraphenyl borate (NaTPB), and high relative molecular weight PVC. On the other hand, 1,3-Diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid was purchased from Fluka. However, all of them were used as received. The nitrate and the chloride salts of all cations (all from Merck and Aldrich) were of the highest available purity and used without any further purification, except for vacuum drying over P_2O_5 . Triply distilled de-ionized water was used for the experiments.

2.2. Electrode Preparation

Membrane solutions were prepared by thoroughly dissolving 7.5 mg of DPTA, 32 mg of powdered PVC, 57.5 mg of NPOE and 3 mg of NaTPB in 5 ml of fresh THF. The resulting clear mixture was evaporated slowly, until an oily concentrated mixture was obtained. A Pyrex tube (3–5 mm o.d. on top) was dipped into the mixture for about 5 s, so that a transparent membrane of about 0.3 mm in thickness was formed.^{32–41} The tube was removed from the mixture, kept at room temperature for 12 h and then filled with an internal solution (1.0×10^{-3} M $Cr(NO_3)_3$). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-2} M chromium nitrate solution. A silver/silver chloride electrode was used as an internal reference electrode.

2.3. EMF Measurements

The EMF measurements with the polymeric membrane were carried out with the following cell assemblies:

Ag–AgCl | internal solution, 1.0×10^{-3} M $Cr(NO_3)_3$ | PVC membrane | test solution | Hg–Hg₂Cl₂, KCl (satd.)

The activities were calculated according to the Debye-Hückel procedure.⁴²

3. RESULTS AND DISCUSSION

3.1. Stability of Various Complexes of DPTA-Metal Ions in Acetonitrile Solution

The complexes stability of DPTA and alkali, alkaline earth, transition, and heavy metal ions were evaluated with the help of the conductometric method in acetonitrile

Table I. The formation constants of the DPTA– M^{n+} complexes.

Cation	$\log K_f$	Cation	$\log K_f$
Cr^{3+}	5.97 ± 0.11	Na^+	<2
Ce^{3+}	4.26 ± 0.08	Cs^+	<2
La^{3+}	4.93 ± 0.15	Sr^{2+}	2.61 ± 0.18
Fe^{3+}	<2	Mg^{2+}	<2
Cd^{2+}	2.56 ± 0.18	Ca^{2+}	<2
Co^{2+}	<2	Ag^+	<2
Cu^{2+}	<2	Hg^{2+}	<2

solution at 25.0 ± 0.05 °C. As already mentioned, the stability constants of the resulting 1:1 complexes are determined by computer fitting of the Eqs. (3) and (4) to the molar conductance-mole ratio data, using a nonlinear least-squares program KINFIT.⁴³ The resultant formation constants are illustrated in Table I. Clearly, among the tested cations, the interaction between the DPTA with Cr^{3+} ion is much stronger than that with the other cations. Thus, it may act as a selective ion carrier in the construction of a Cr(III) membrane sensor.

3.2. Potential Response of the DPTA-Based Sensors to Various Ions

The existence of eleven donating atoms (two nitrogen and nine donating oxygen) in the DPTA structure was expected to increase both the stability and selectivity of its complexes with transition and heavy metal ions, rather than alkali and alkaline earth metal ions. Thus, in order to check the DPTA suitability as an ion carrier for different metal ions, it was used to prepare PVC membrane ion-selective electrodes in preliminary experiments for a wide variety of cations, including alkali, alkaline earth, transition, and heavy metal ions. The potential responses of the most sensitive ion-selective electrodes based on DPTA are shown in Figures 2(a) and (b). As it can be seen, only the Cr(III) ion displays a strong response (with a slope of 19.8 ± 0.3 mV per decade) to the DPTA-based membrane sensors in comparison with the other tested cations. Comparison between the reported data in Figure 2 and the ones in Table I revealed that there is a good correlation between the DPTA selectivity and its stability complexes.

3.3. The Membrane Composition Influence on the Potential Response of the DPTA-Based Cr(III) Sensor

The DPTA-PVC-based membrane sensor generated stable potential responses in aqueous solutions, containing chromium ions after conditioning for about 12 h in a 1.0×10^{-2} M chromium nitrate solution. Table II exhibits the data obtained with membranes having various ratios of different constituents. The potential responses of all membrane sensors were studied in a broad concentration range of chromium nitrate solution. Table II shows that

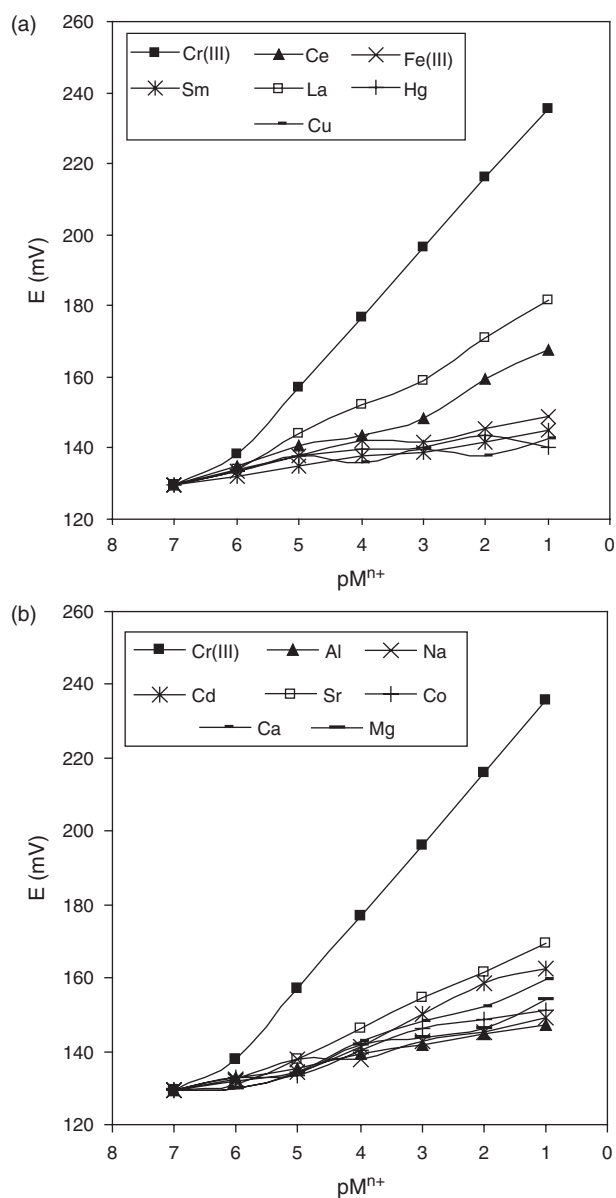


Fig. 2. Potential responses of different ion-selective electrodes based on DPTA.

the total potentiometric electrode response towards Cr(III) ions is dependent on the DPTA concentration, incorporated within the membrane. From Table II, it is evident that the increase of the DPTA amount in the membranes (nos. 6 and 7) up to 7.5% resulted in greater slopes. A maximum slope of 19.8 ± 0.3 mV per decade of chromium concentration was observed for the membrane no. 6 with 7.5% of DPTA. Since the plasticizer nature influences the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands,⁴⁴ it was expected to play a key role in the determination of the selectivity, working concentration range and response time of the membrane electrode. Among the three different solvent mediators (NPOE, DBP, and NB), NPOE demonstrated the best sensitivity in the construction of the Cr(III) membrane sensor.

It is well established that the presence of lipophilic anions in cation-selective membrane electrodes diminishes the ohmic resistance, enhances the response behavior and selectivity and increases the sensitivity of the membrane electrodes.⁴⁵ Obviously from Table II, the sensor slope in the absence of NaTPB is lower than the expected Nernstian value (membranes nos. 1–5). Nevertheless, the addition of 3% NaTPB will increase the sensitivity of the electrode response considerably, so that the membrane electrode demonstrates a Nernstian behavior (membrane no. 6). However, the membrane sensor with a composition of 32% PVC, 57.5% NPOE, 3% NaTPB, and 7.5% DPTAD exhibits the best performance.

3.4. Slope and Detection Limit

As it can be observed from Figure 3, the developed sensor exhibits a Nernstian response slope of $(19.8 \pm 0.3$ mV/decade) across a broad concentration range of 7.0×10^{-7} – 1×10^{-1} M. The detection limit, defined as the Cr(III) concentration obtained after the extrapolation of the linear region of the standard plot to the baseline potential, was 2.0×10^{-7} M. The optimum electrode response was obtained after its conditioning in a 1.0×10^{-2} M chromium nitrate for 24 h. The standard deviation for ten replicate measurements was ± 0.5 mV.

Table II. The composition of the membrane ingredients.

Electrode no.	Composition (wt%)				Slope (mV/decade)	Concentration range (M)
	PVC	Plasticizer	NaTPB	DPTA		
1	32	NPOE, 65	0	3	4.3 ± 0.4	1.0×10^{-4} – 1.0×10^{-1}
2	32	NPOE, 63	0	5	9.2 ± 0.5	1.0×10^{-5} – 1.0×10^{-1}
3	32	NPOE, 62	0	6	11.5 ± 0.3	1.0×10^{-5} – 1.0×10^{-1}
4	32	NPOE, 61	0	7	13.7 ± 0.4	1.0×10^{-6} – 1.0×10^{-1}
5	32	NPOE, 60	0	8	12.1 ± 0.6	1.0×10^{-6} – 1.0×10^{-1}
6	32	NPOE, 57.5	3	7.5	19.8 ± 0.3	7.0×10^{-7} – 1.0×10^{-1}
7	32	NPOE, 56.5	4	7.5	18.2 ± 0.5	1.0×10^{-6} – 1.0×10^{-1}
8	32	NB, 57.5	3	7.5	18.4 ± 0.3	1.0×10^{-6} – 1.0×10^{-1}
9	32	DBP, 57.5	3	7.5	17.7 ± 0.4	1.0×10^{-6} – 1.0×10^{-1}

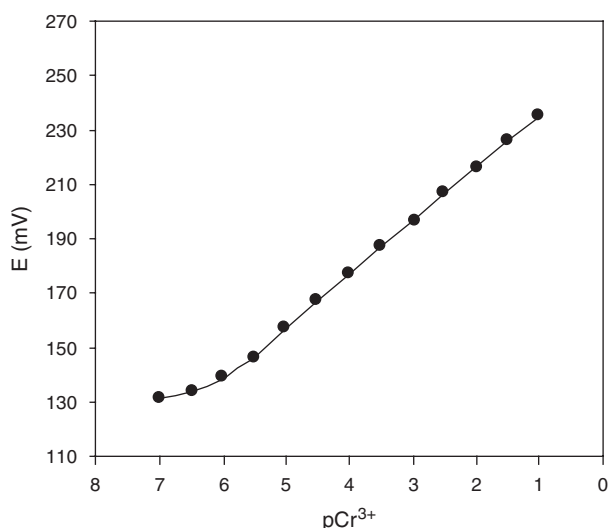


Fig. 3. Calibration curve of the DPTA-based iron electrode (membrane no. 6).

3.5. The pH Effect

The pH dependence on the membrane electrode was tested for the pH values from 1.5 up to 8.0 at a certain chromium ion concentration (1.0×10^{-3} M). The potential was found to stay fairly constant in the pH range of 2.5–6.8 (Fig. 4) (adjusted with HCl or NaOH). Beyond this range, a gradual drift in the potential was observed. The observed decreased potential drift at higher pH values could be due to the formation of some Cr(III) hydroxyl complexes in solution. At lower pH values, the potentials increased, indicating that the membrane sensor responds to hydrogen ions.

3.6. Dynamic Response Time

For analytical applications, dynamic response time is a significant parameter for any sensor. The dynamic response

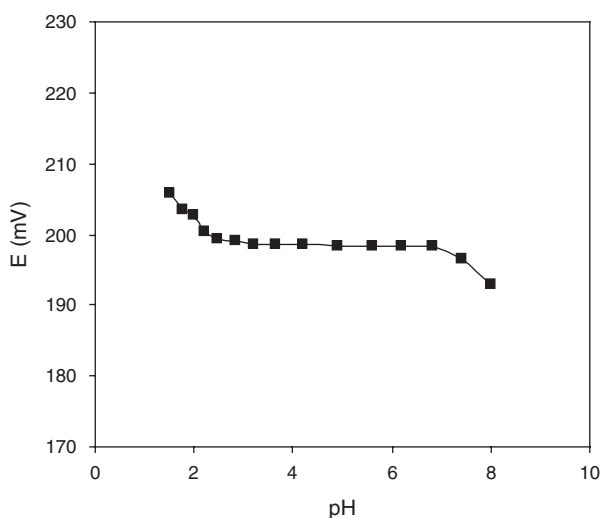


Fig. 4. The pH effect of the test solution (1.0×10^{-3} M) on the potential response of the chromium sensor (membrane no. 6).

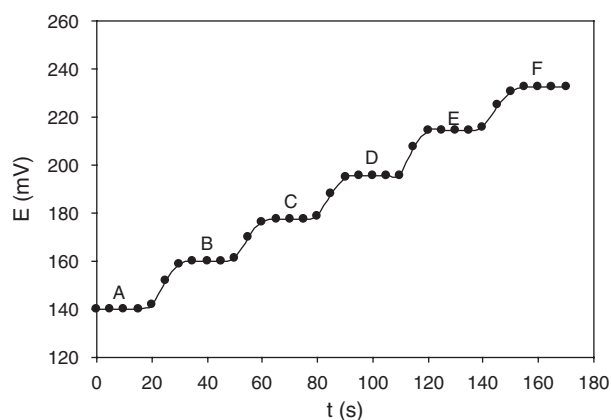


Fig. 5. Dynamic response time of the chromium electrode (membrane no. 6) for step changes in the Cr^{3+} concentration: (A) 1.0×10^{-6} M, (B) 1.0×10^{-5} M, (C) 1.0×10^{-4} M, (D) 1.0×10^{-3} M, (E) 1.0×10^{-2} M, (F) 1.0×10^{-1} M.

time of the membrane was measured at various concentrations (1.0×10^{-6} to 1.0×10^{-1} M) of the test solutions. The corresponding results are illustrated in Figure 5, where it can be evidently observed that within 10 s reasonably fast and stable potentials were achieved.

3.7. Sensor Lifetime

For the evaluation of the stability and the lifetime of the recommended membrane sensor, two electrodes were tested for a 10 week period. During this period, the electrodes were in daily use over an extended time period (one hour per day). A slight gradual slope decrease (from 19.8 to 17.9 mV/decade) was observed. This phenomenon is usual in these plasticized PVC membrane electrodes, most probably arising from the slight leaching of the membrane components.

3.8. Potentiometric Selectivity

The selectivity behavior is obviously one of the most important characteristics of an ion-selective electrode, determining the feasibility of a reliable measurement in the target sample. To investigate the membrane electrode selectivity, its potential response was monitored in the presence of various interfering foreign cations using the matched potential method (MPM).⁴⁶ The MPM was recommended by IUPAC in 1995.⁴⁷ The procedure was expected to report selectivity coefficients analytically relevant for practical applications.

According to the MPM, the selectivity coefficient is defined as the activity (concentration) ratio of the primary ion and the interfering ion, which gives the same potential change in a reference solution.⁴⁸ Thus, the potential change should be measured upon changing the primary ion activity. Then, the interfering ion would be added to an

Table III. Selectivity coefficients of various interfering ions.

Interfering ion (B)	Selectivity coefficient ($K_{Cr,B}$)
La ³⁺	-2.12
Ce ³⁺	-2.58
Sm ³⁺	-3.46
Fe ³⁺	-3.30
Al ³⁺	-3.31
Co ²⁺	-3.17
Cd ²⁺	-2.65
Cu ²⁺	-4.00
Hg ²⁺	-3.33
Na ⁺	-3.33
Sr ²⁺	-2.52
Ca ²⁺	-3.05
Mg ²⁺	-3.24

identical reference solution until the same potential change would be obtained. The matched potential method selectivity coefficient, K^{MPM} , is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K^{MPM} = a_A/a_B$.

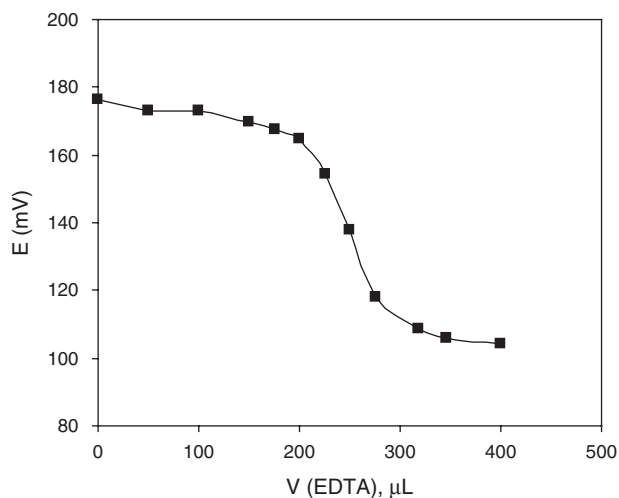
The resulting potentiometric selectivity coefficients values are given in Table III. Clearly, the selectivity coefficients for mono and divalent metal ions (Na⁺, Co²⁺, Cu²⁺, Cd²⁺, Hg²⁺, Mg²⁺, Sr²⁺, and Ca²⁺) are in the range of 4.7×10^{-4} and 1.0×10^{-4} – 3.0×10^{-3} , respectively. For the trivalent ions (Fe³⁺, Al³⁺, Sm³⁺, La³⁺, and Ce³⁺), the selectivity coefficients are in the range of 7.5×10^{-3} or smaller. These results revealed that common metal ions can not disturb the function of the chromium sensor.

3.9. Comparison of the Developed and the Previous Cr(III) Sensors

Table IV compared the linearity range, detection limit and selectivity coefficients of the suggested sensor with the best previously reported Cr(III) sensors. It is evident that

Table IV. Comparison of selectivity coefficients, linearity range and detection limit of the proposed Cr(III) sensor and the previously reported Cr(III) ion-selective electrodes.

	Ref. [18]	Ref. [21]	Ref. [23]	Ref. [24]	Ref. [25]	This work
Linearity range (M)	1.7×10^{-6} – 1.0×10^{-1}	3.0×10^{-6} – 1.0×10^{-2}	1.6×10^{-6} – 1.0×10^{-1}	1.0×10^{-6} – 1.0×10^{-1}	4.0×10^{-6} – 1.0×10^{-1}	7.0×10^{-7} – 1.0×10^{-1}
Detection limit (M)	—	6.3×10^{-7}	—	5.8×10^{-7}	2.0×10^{-7}	2.0×10^{-7}
Selectivity coefficients	FIM	MPM	MPM	MPM	FIM	MPM
La ³⁺	—	—	-4.57	—	-2.60	-2.12
Ce ³⁺	—	-2.62	—	—	-2.72	-2.58
Sm ³⁺	—	—	—	—	—	-3.46
Fe ³⁺	-3.18	—	-3.65	-3.25	-1.34	-3.30
Al ³⁺	-3.20	-2.96	-3.15	-1.42	-2.44	-3.31
Co ²⁺	-1.75	-2.16	—	-1.92	-3.15	-3.17
Cd ²⁺	-2.01	—	-2.17	-0.66	-3.02	-2.65
Cu ²⁺	-2.05	-2.02	-1.57	-1.15	-3.00	-4.00
Hg ²⁺	-1.75	—	-2.15	—	-3.21	-3.33
Na ⁺	-0.91	-2.48	-0.76	-0.66	-3.39	-3.33
Sr ²⁺	-2.43	-2.38	-1.12	-2.01	-3.34	-2.52
Ca ²⁺	-1.87	-2.44	-1.85	-1.96	-3.37	-3.05
Mg ²⁺	-2.10	-2.21	-1.62	—	-1.33	-3.24

**Fig. 6.** Potentiometric titration curve of 25.0 ml 1.0×10^{-4} M solution of Cr³⁺ with 1.0×10^{-2} M of EDTA.

the newly developed sensor is superior to the formerly reported chromium sensors in terms of selectivity, detection limit and dynamic concentration range.

3.10. Analytical Applications

The Cr(III) membrane sensor was found to work well under laboratory conditions. It was successfully used as an indicator electrode in the titration of a 1.0×10^{-4} M Cr(III) solution with a 1.0×10^{-2} M EDTA solution. The resulting titration curve is shown in Figure 6. As it is seen, the Cr³⁺ amount in solution can be determined by this certain sensor.

The electrode was also successfully applied to the direct chromium(III) determination in wastewater of chromium electroplating industries. 10.0 ml of each sample was taken and diluted with 10.0 ml of buffer acetic acid/sodium acetate (pH 8.0) and distilled water in a 100.0 ml flask.

Table V. Cr(III) determination in four industrial wastewater samples using AAS and direct potentiometry with the DPTA-based sensor.

Sample no.	ISE (ppm)	AAS (ppm)
1	4.26 ^a ± 0.10	4.15 ^a ± 0.12
2	0.97 ± 0.04	0.74 ± 0.03
3	2.63 ± 0.14	2.56 ± 0.07
4	1.34 ± 0.05	1.31 ± 0.04

^aResults are based on three measurements.

Then, the potential of the resulting solutions was measured and with the help of the calibration curve, the Cr(III) concentration was determined. The results were compared with the data obtained from atomic absorption spectrometry (AAS) (Table IV). According to the reported data in Table IV, there is a satisfactory agreement between the results of the recommended sensor and the ones of the AAS technique.

4. CONCLUSION

The use of the 1,3-Diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid (DPTA) with NPOE as plasticizer shows the best response characteristics with Nernstian behavior over the concentration range of 1.0×10^{-6} – 1.0×10^{-1} M Cr³⁺ and a fast response time of 10 s. The sensor works well in a pH range of 2.5–6.8 and it can be successfully employed for the Cr³⁺ estimation in real samples. Eventually, it is concluded that the proposed sensor is superior to the existing sensors in terms of response time as well as lifetime. For actual analysis, the developed sensor is comparable with the other sensors regarding parameters such as slope, pH range, concentration range, and selectivity.

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