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Full Paper

Novel PVC Based Ion Selective Electrode for Cr(III) by using 8,11,14-Triaza-1,4-dioxo-5(6),6(17)-ditolylcycloseptadecane (TADODTSD) Ionophore

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Abstract- A potentiometric response of an ion-selective electrode with a new ionophore 8,11,14-triaza-1,4-dioxo-5(6),16(17)-ditolylcycloseptadecane (TADODTSD) toward Cr(III) ions was studied. The designed electrode showed a Nernstian behavior with a slope of 19.6±0.5mV/decade in a working concentration range of 1.0×10^{-8}-1.0×10^{-1} mol L^{-1} and a detection limit of 8.0×10^{-8} mol L^{-1}. A membrane composition made of PVC: DBP: ionophore (TADODTSD): NaTPB; 30%: 60%: 8%: 2 wt.% displays the best results. Response time was found to be 7 seconds and can be used for 120 days without showing any substantial deviation in potential. The proposed electrode exhibits selectivity for Cr(III) ions. The electrode worked well under laboratory conditions with its, potential response being constant over a pH range of 3.0-8.0. The electrode proposed in this work could be used to determine the presence of Cr(III) ion in wastewater and also an indicator electrode with EDTA.

Keywords- Potentiometric sensor; Selectivity coefficient; Membrane; Cr(III) ion; Detection limit

1. INTRODUCTION

It is well known that chromium is present in several food items like the one having high quantities of modest sugars in small amounts. The lack of chromium in humans is tenuous, but a regimen including high quantities of normal sugars raises chromium secretion in urine.

Contusion, gestation, and severe practice can also increase its secretion in urine. The standard staffing quotidian of chromium for sensible women extent from 20 to 25 micrograms, based on their age, increasing with lactation or gestation period. The Chromium element has been widely used in various industries such as in alloys, steel, coating, wood and dying industries. Chromium exists in (II) to (VI). The most oxidized state is Cr(VI). Cr(III) is essential for human body 50-200 µg per day [1,2], while Cr(VI) is known for its toxicity, it can damage the cell by penetrate in it. Chromium causes various diseases like ulceration, contact dermatitis, chronic bronchitis, liver, kidney damage & cancer. Potentiometric sensors (PS) are one of the most powerful sensing tools owing their ability to select various cations/anions based on their charge and size in clinical and environment analyses [3,4]. The dynamic response of the potentiometric sensor (PS) is produced by highly selective complexation of the target ion with ionophores spread on a poly (vinyl chloride) (PVC) matrix, it is based on the recent advance of host-guest chemistry, polymeric membrane for Cr(III) ion have been widely developed by the use of connected macrocyclic hosts as well as acyclic ligands [5]. The use of an ion-selective electrode potentiometric detection has many advantages like simple production, uncomplicated instrumentation, faster response, wide dynamic range, good selectivity, and low cost. Such electrodes are highly selective for certain ions. A variety of potential ion carriers has been working in the building of Cr(III) on selective electrode**s**. Though, most of these Cr(III) selective sensor suffers from the intrusive effect of such cations [6-8], such as Cd^{2+}, $Pb^{2+,}$ Zn^{2+}, Hg^{2+} and Ag^{+}. The current study is connected the usages of 8,11,14-triaza-1,4-dioxo-5(6),16(17)-ditolylcycloseptadecane (TADODTSD) as an ionophore for Cr (III) ions.

2. EXPERIMENTAL WORK

2.1. Instruments and the use reagents

Plasticizers: dibutylphthalate (DBP), n-benzyl acetate (NBA), dioctylphthalate (DOP), tributylphthalate (TBP), nitrobenzene (NB). Cation excluder: sodium tetrkis(p-chlorophenyl) borate (NaTpClPB). Solvent: tetrahydrofuran (THF). High molecular weight polymer: Polyvinyl chloride (PVC). The high-grade metallic salts (Merck, Aldrich) were used without any further decontamination except for vacuum drying over P4O10. Triply distilled water was just used. Potential analysis was studied with on potentiometer EQ-602(digital). Equiptronics (precision, 0.001V). The pH analysis was carried out on pH meter(digital) (Lab India pH Conmeter India).

2.2. Synthesis of the ionophore

The ionophore [9] was synthesized by carried by dissolving methyl salicylaldehyde 5.32 mL (1.0 M) in 20 mL ethanol in a 100 mL two-neck round bottom flask. In this solution add

20 mL ethanolic solution of 1,2-dibromoethane 2.15 mL (0.5 M) with continuous stirring. The reaction mixture was heated for 3 hours at 65 °C and cooled up for 30 minutes at 35 °C, then 20 mL ethanolic solution of diethylenetriamine (0.5M, 2.14 mL) adding with continuous stirring. This reaction mixture was again warmed for 2 hours at 65 °C [9]. Keep it overnight, and a yellowish-white powder is obtained. Then washed with water and dry over P_4O_{10}. A compound of yellowish-white color was obtained (Figure 1), formed. Yield: 75%; Melting point 220 °C.

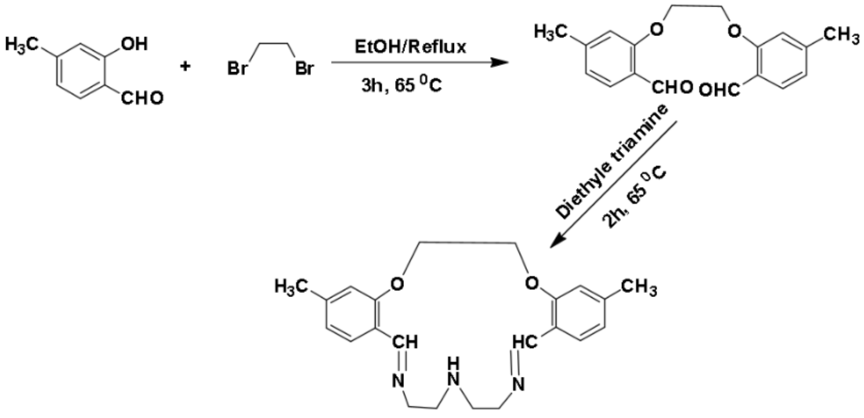


Figure 1. Scheme of ionophore synthesis

2.3. Analysis of CHN

Anal. Calcd. (%) for $C_{22}H_{27}N_3O_2$: C: 72.32; H: 7.39; N: 11.50; O: 8.76; Found: C: 72.22; H: 7.35; N: 11.62; O: 8.78.

2.4. Infra-red (IR) analysis

IR (KBr) (v/cm^{-1}): 1416: (C=N), 3460: (>N-H), 3045:(C-H aromatic), 1208: (H_2C-O), The peak due to carbonyl and amino group was absent in synthesize the compound.

2.5. NMR data

^1H NMR $CDCl_3$ (300MH$_Z$, 298K), δ=9.40 (s: 2H: HC=N), 4.34 (s:4H: C-O), 7.56 (t:2H: aromatic), 7.65 (d: 2H: aromatic), 7.57 (t: 2H: aromatic), 7.23 (d: 2H: aromatic).

2.6. Electrode preparation

8 mg of ionophore (TADODTSD) material was incapacitated with polyvinyl chloride (PVC) 30 mg in 10 mL tetrahydrofuran (THF). In this mixture 60 mg of dibutyl phthalate (DBP) was used as a plasticizer and 2 mg of NaTPB was added as an anion excluder. The resulting solution was sensibly cast into a glass dish of 2 cm width for slow evaporation to get a membrane of optimum performance.

2.7. EMF measurements

All emf measurements were recorded by a Corning ion analyzer 250-pH/mV meter at 25±0.5 ºC in the following cell assembly:

Ag-AgCl│internal solution (1×10^{-3} mol L^{-1} $CrCl_3$) PVC membrane│sample solution│Hg-Hg_2Cl_2, KCl (Saturated)

3. RESULTS AND DISCUSSION

3.1. Complexation study

The complex formation constant, K_f of the ionophore (TADODTSD) with different cations assessed in an acetonitrile solution, at 25±0.05 ºC, to get evidences about the stability and selectivity of the subsequent complexes. The analysis was done by fitting the molar conductance in mole ratio data with appropriate equations 1 and 2. The obtained results are shown in Table 1. It is clear, K_f of the Cr(III)-TADODTSD complex is higher than the other tested cations.

Table 1. Metal-Ligand (TADODTSD) formation constant values

Cations	**log K_f**
Pb(II)	1.69±0.08
Sr(II)	1.64±0.14
Cd(II)	1.58±0.17
Zn(II)	1.49±0.07
Cr(III)	5.68±0.05
Hg(II)	1.18±0.13
Ni(II)	1.88±0.14
Mg(II)	1.79±0.10
Ca(II)	1.82±0.19

$$M^+ + L \overset{K_f}{\leftrightarrows} ML^+ \tag{1}$$

$$K_f= [ML^+]/ [M^{+}] [L] \{f(ML^+)/f(M^{+}) f(L) \tag{2}$$

Ligand (TADODTSD) as a suitable ionophore in the fabrication of Cr(III) ion-selective membrane electrode.

$$K_f= [ML^+]/[M^+] [L]= (\Lambda_M-\Lambda_{obs})/ (\Lambda_{obs}-\Lambda_{ML}) (L) \tag{3}$$

$$L=C_L-(\Lambda_M-\Lambda_{obs})/ (\Lambda_M-\Lambda_{ML}) \tag{4}$$

Where $[ML^+]$, $[M^+]$, [L] and f represent the equilibrium molar concentration of complexes, free cation, free ligand, and the activity coefficient of the species indicated, respectively. Under the dilute condition the activity coefficient of the unchanged ligand, f(L) can be reasonably assumed as unity [10]. The use of Deby-Huckel limiting law of 1:1 electrolyte [11] lead to the conclusion that f (M^+) ~ f (ML^+), so the activity coefficient in equation (2) is canceled out. Thus, the formation constant in terms of the molar conductance can be expressed as described [12-14]. $\wedge_M$ and $\wedge_{ML}$ are the molar conductance of the cation without ligand and the complex. $\wedge_{obs}$ is the molar conductance of the solution during titration, C_L is the concentration of the ionophore (TADODTSD) added, and C_M the analytical concentration of the cation. The complex formation constants, K_f, and the molar conductance of complex, $\wedge_{obs}$, were obtained using a nonlinear least square program called KINFIT [15]. The logarithm of the formation constants (log K_f) of the resulting 1:1 complex for mono and divalent cations were approximately two or less than 2, and for trivalent cations, they were in the range of 1.08-1.89. Except for Cr(III) the obtained value was 5.68 Thus, (TADODTSD) is a suitable ionophore for making a Cr(III) ion-selective PVC membrane sensor.

3.2. Potential responses

The potential responses of various ions were estimated by using the ionophore 8,11,14-triaza-1,4-dioxo-5(6),16(17)-ditolylcycloseptadecane (TADODTSD), responses are shown in (Figure 2). This ionophore contains three-nitrogen atoms and two-oxygen atoms and hence likely to act as an appropriate ionophore for some transition and heavy metal ions (with high charge density) in PVC membranes. The potential responses revealed that it is close to-Nernstian potential response for Cr(III).

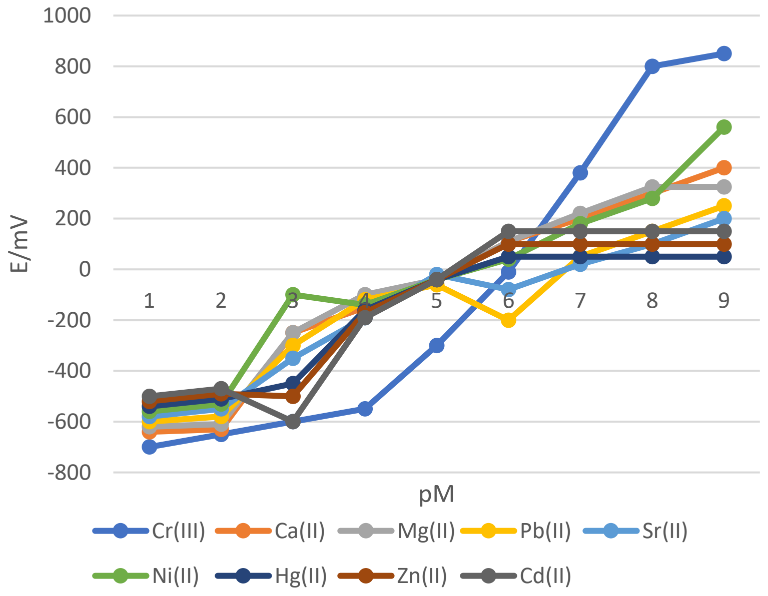


Figure 2. Potentiometric responses of diverse metal ion of ionophore (TADODTSD) by membrane no. 4

Table 2. Compositions of membrane ingredients

Membrane no.	**Alignment of the membrane (wt %)**				
	Ionophore	**Plasticizer**	**Poly(vinyl chloride)**	**Additive**	**Slope in (mV/decade)**
1	--	73 DBP	27	-	2.4±0.8
2	3	70 DBP	27	-	7.5±0.2
3	5	63 DBP	27	5	14.3±0.5
4	8	60 DBP	30	2	19.4±0.5
5	9	59 DBP	27	5	16.3±0.7
6	8	60 AP	27	5	15.7±0.4
7	7	59 NBA	27	7	12.3±0.6
8	6	61 NBA	27	6	8.9 ±0.4

3.3. Consequence of membrane composition

The sensitivity, selectivity, and linearity of ion selective electrodes are affected by the nature of the ion carrier as well as the membrane composition [16], the nature of the solvent mediator and the lipophilic additive used [17,18]. The plasticizers including DBP, AP and NBA for the preparation of membrane displayed that plasticizer DBP accomplishes best as it exhibits the extensive working concentration range and near-Nernstian slope. Plasticizers control both the dielectric constant of the membrane and the mobility of the ionophore. It also enhances the membrane interface with Cr(III) ions. The negatively charged lipophilic additives (i.e., anion part NaTPB) improve the potentiometric behavior (as a cation excluder) of composed cation-selective electrodes. It is probable not only by dropping the ohmic resistance [19], but it enhancing response behavior and selectivity [20]. Additionally, at the sample membrane interface, the lipophilic additives can catalyze the exchange kinetics. It displayed that the composition of the membrane as PVC: DBP: ionophore (TADODTSD): Additive (NaTPB) percentage ratio of 30: 60: 8: 2 shows the best results (no. 4 in Table 2).

3.4. pH range

The pH of the solution was adjusted from 1.0-10.0 by adding dilute HNO_3 or NaOH and the potential response of the membrane sensor was tested. The potential was to be found constant for the solution having a pH range of 3.0-8.0 (Figure 3), at high pH a sharp change in potential was observed, probably because of the hydrolysis of Cr(III) ions, at a lower pH value H^+ ions start contributing to the charge transport process of the membrane thereby causing interference.

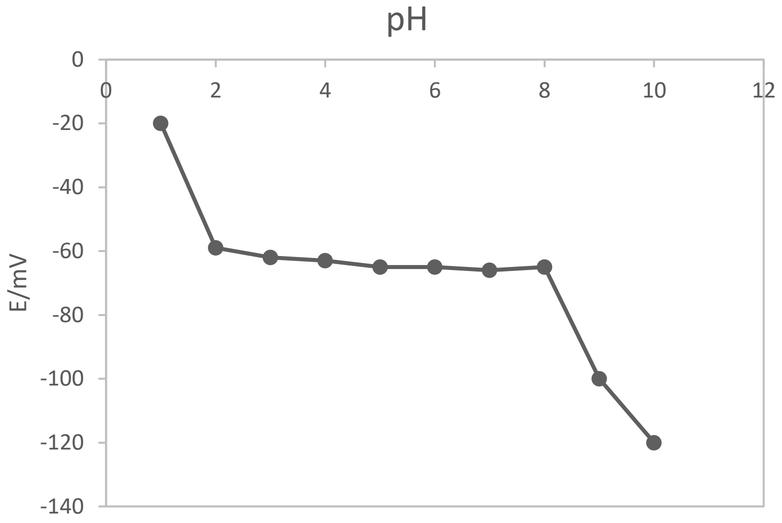


Figure 3. pH effect on the test solution of 1.0×10^{-4} mol L^{-1} of Cr(III) ions by TADODTSD ionophore

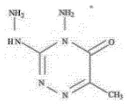
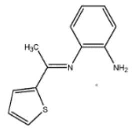
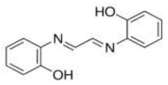
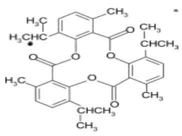
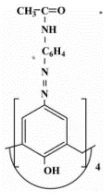
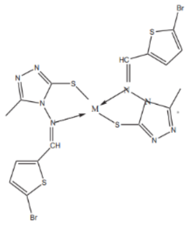
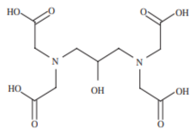
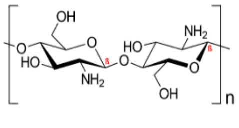
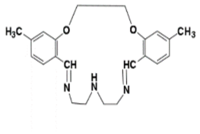
3. 5. Response time and Lifetime of the sensor

The amount of time takes the electrode assembly to reach a steady potential is assumed as static response time. The response time of the PVC membrane electrode is normally less. The response time was measured for the different concentration ranges of Cr(III) ions and it was 7 seconds and the potential remained constant for about 120 s. The experimental results show that the lifetime of Cr(III) membrane sensor is 120 days. During this period, the electrode was in daily use over an extended period of time (1 h per day). There are no significant changes in the electrode features. The results are presented in Table 3. After 120 days, a minor gradual decrease and increase in the slopes and detection limit, respectively, can be seen. This may be to the leaking of the membrane ingredients from the membrane to the solution. This kind of behavior has been already reported for most PVC membrane sensors. Furthermore, the linear range, response time, and selectivity of the present electrode are superior to those previously reported Cr(III) ion-selective sensors [21-28].

3.6. Selectivity coefficient

The selectivity coefficients are perhaps the most important characteristics of a potentiometric ion-selective electrode since they show the relative response of the membrane sensor for the target ion over other ions, present in the solution. Here, the potential response of the proposed Cr(III) ion-selective electrode was studied by the match potential method (MPM) [29,30]. The selectivity coefficient is determined as: $\Delta A = {}'a_A - a_A$, where, a_A is the initial primary ion activity and $'a_A$ is the activity of A in the presence of interfering ion, a_B.

Table 3. Comparison of the proposed Cr(III)-selective electrode with some of the existing sensors

Ionophore	**Structure**	**Working concentration range**	**Detection limit**	**Slope**	**pH range**	**Lifet ime**	**Response time**	**Ref.**
4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one		1.0×10^{-6} to 1.0×10^{-1} mol L $^{-1}$	5.8×10^{-7} mol L $^{-1}$	19.7±0.3 mV/decade	2.7–6.6	90 days	<10 s	[21]
N-(1-thien-2-ylethylidene)benzene-1,2-diamine		1.0×10^{-6} to 1.0×10^{-1} mol L $^{-1}$	7.0×10^{-7} mol L $^{-1}$	19.9±0.3 mV/ decade	3.0–6.6	56 days	<12 s	[22]
Glyoxalbis(2-hydroxyanil)		3.0×10^{-6}- 1.0×10^{-2} mol L $^{-1}$	6.3×10^{-7} mol L $^{-1}$	19.89±0.5 mV/ decade	2.7-6.5	90 days	<20 s	[23]
tri-o-thymotide		4.0×10^{-6} to 1.0×10^{-1} mol L $^{-1}$	2.0×10^{-7} mol L $^{-1}$	20.0±0.1 mV/decade	2.8–5.1	150 days	15 s	[24]
p-(4-Acetanilidazo)calix[4]arene		9.8×10^{-7}- 1.0×10^{-1} mol L $^{-1}$	7.3×10^{-7} mol L $^{-1}$	19.8±0.2 mV/decade	2.8-5.7	84 days	< 14 s	[25]
4-(5-bromothiophen-2-carboxylidene amino)-3-methyl-5- mercapto-s-triazole		2.0×10^{-7} to 1.0×10^{-1} mol L $^{-1}$	9.8×10^{-8} mol L $^{-1}$	19.8±0.2 mV/decade	2.2–5.0	90 days	10–15 s	[26]
1,3-Diamino-2-Hydroxypropane-N,N,N′,N′-Tetraacetic Acid		7.0×10^{-7} and 1.0×10^{-1} mol L $^{-1}$	2.0×10^{-7} mol L $^{-1}$	19.8±0.3 mV/decade	2.5–6.8	70 days	<10 s	[27]
Chitosan		1.0×10^{-6}- 1.0×10^{-1} mol L $^{-1}$	1.32×10^{-8} mol L $^{-1}$	58.5 mV/decade	4.0-6.0	120 days	10 s	[28]
8,11,14-triaza-1,4-dioxo-5(6), 6(17)-ditolylcycloseptadecane		1.0×10^{-8}– 1.0×10^{-1} mol L $^{-1}$	8.0×10^{-8} mol L $^{-1}$	19.6±0.5 mV/decade	3.0-8.0	120 days	7 s	This work

As is seen, in Table 4 for all diverse the selectivity coefficients are in the range 1.7×10^{-3} to 8.2×10^{-4} M indicating that they do not disturb the functioning of the Cr(III) sensor.

Table 4. Selectivity coefficient value for Cr(III) selective electrode as calculated by match potential method (K_{Cr3+}^{Pot})

Interfering ion (B)	**Selectivity coefficient** (K_{Cr3+}^{Pot})
Pb(II)	1.7×10^{-3}
Sr(II)	1.8×10^{-3}
Cd(II)	8.1×10^{-4}
Zn(II)	7.3×10^{-4}
Hg(II)	4.3×10^{-4}
Ni(II)	7.9×10^{-3}
Mg(II)	3.5×10^{-3}
Ca(II)	8.2×10^{-4}

3.7. Analytical applications

The proposed Cr(III) ion-selective electrode was found to work well under laboratory conditions. The sensor was used successfully as an indicator electrode in the titration of Cr(III) with EDTA. From Figure 4 it is evident that this electrode could be used to quantitatively measure Cr(III) ion concentration. The results obtained by the proposed Cr(III) sensor, together with those obtained by atomic absorption spectrometry(AAS), are summarized in Table 5. A satisfactory agreement was found between the results obtained by the proposed sensor and those by atomic absorption spectroscopy (AAS).

Table 5. Determination of Cr (III) ions in wastewater samples

Sample No.	**Cr (III)found (M)**	
	Proposed Electrode	**AAS**
Waste water sample 1	1.232×10^{-4}	1.254×10^{-4}
Waste water sample 2	6.537×10^{-4}	6.375×10^{-4}
Waste water sample 3	1.536×10^{-3}	1.642×10^{-3}
Waste water sample 4	4.369×10^{-3}	4.272×10^{-3}

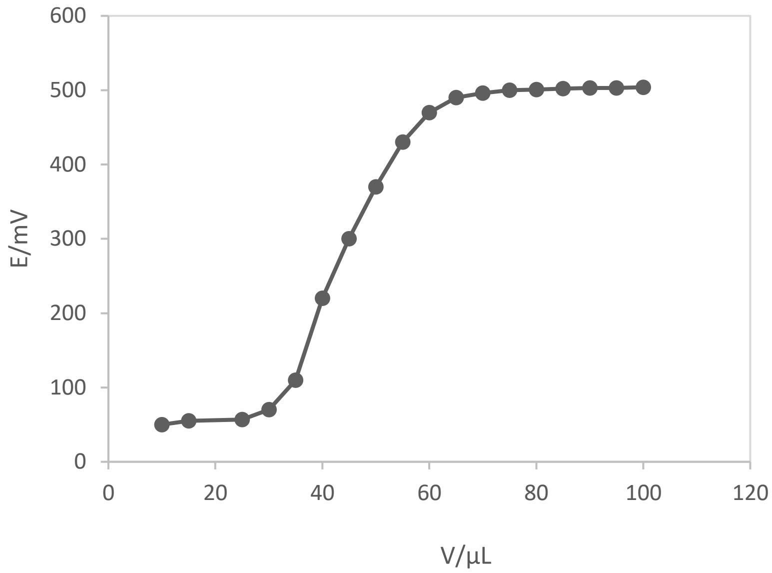


Figure 4. Potentiometric titration curve of 50 mL solution of Cr(III) ion 1.0×10^{-2} mol L^{-1} with 1.0×10^{-2} mol L^{-1} EDTA solution

4. CONCLUSION

The results obtained from this study confirmed that the proposed potentiometric sensor based on ionophore 8,11,14-triaza-1,4-dioxo-5(6),16(17)-ditolylcycloseptadecane (TADODTSD) can successfully act as an excellent Cr(III) selective electrode. The ionophore can form a selective and stable complex with Cr(III) ions and thus can be used for the determination of Cr(III) ions in presence of various interfering ions. The applicable pH range, lower detection limit, and selectivity coefficients of the proposed sensor make it a superior device as compared to other methods used for the determination of Cr(III) ion. This membrane electrode has a fast potential response and high selectivity toward Cr(III) ions. It can be used for the analysis of Cr(III) ion content of environmental and wastewater samples.

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