Frontiers in Health Informatics
ISSN-Online: 2676-7104
2024; Vol 13: Issue 8

www.healthinformaticsjournal.com

Open Access

Novel PVC Based Ion Selective Electrode for Chromium(III) by using Macrocyclic Compound as Ionophore

Pratibha Singh* and Ramesh Chandra

Department of Chemistry, K.S. Saket P.G. College, Ayodhya, India

Corresponding Author: Pratibha Singh
Email: rameshckanojia@yahoo.com

Cite this paper as: Pratibha Singh* and Ramesh Chandra (2024) Novel PVC Based Ion Selective Electrode for Chromium(III) by using Macrocyclic Compound as Ionophore. *Frontiers in Health Informatics, 13*(8), 2024, 5809-5817

Abstract

A potentiometric response of an ion-selective electrode with a new macrocyclic based ionophore 1-amino-6-hydroxy-4-methyl-5,6-trimethylenehexahydropyrimidine-2-thione (AHMTHHPT) toward Cr(III) ions was studied. The designed electrode showed a Nernstian behavior with a slope of 19.6 ± 0.5 mV/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 (AHMTHHPT): 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 chromium(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; Thione.

Introduction: Chromium is commonly found in several dietary items, particularly those containing minor amounts of carbohydrates. The deficiency of chromium in humans is minimal, although a diet high in regular sugars increases chromium excretion in urine. Contusion, pregnancies, and intense exercise can also elevate its excretion in urine. The recommended daily intake of chromium for women ranges from 20 to 25 μg, depending on their age, and increases during lactation or pregnancy. The Chromium element is extensively utilized throughout multiple industries, including alloys, steel, coatings, wood, and dyeing sectors. Chromium exists in oxidation states ranging from (II) to (VI). The highest oxidation state is Cr(VI) and chromium(III) is vital for the human body, requiring 50-200 μg daily [1,2], whereas chromium(VI) is recognized for its toxicity, since it can infiltrate and destroy cells. Chromium induces numerous ailments, including ulceration, contact dermatitis, chronic bronchitis, and damage to the liver and kidneys, as well as cancer. Potentiometric sensors (PS) are highly effective sensing instruments due to their capability to selectively detect distinct cations and anions based on charge and size in clinical and environmental evaluations [3,4]. The dynamic response of the potentiometric sensor (PS) arises from the highly selective complexation of the target ion with ionophores embedded in a poly(vinyl chloride) (PVC) matrix, leveraging recent advancements in host-guest chemistry. Polymeric membranes for chromium(III) ions have been extensively developed through the utilization of interconnected macrocyclic hosts and acyclic ligands [5]. The utilization of an ion-selective electrode for potentiometric detection has numerous advantages, including straightforward fabrication, uncomplicated instrumentation, rapid response, extensive dynamic range, excellent selectivity, and cost-effectiveness. These electrodes have a strong selectivity for specific ions. A range of prospective ion carriers has been utilized in the construction of chromium(III) selective electrodes. However, many Cr(III) selective sensors are adversely affected by the interference of cations such as Cd^{2+}, Pb^{2+}, Zn^{2+}, Hg^{2+} and Ag^{+}. The present study examines the application of 1-amino-6-hydroxy-4-methyl-5,6-trimethylenehexahydropyrimi-dine-2-thione (AHMTHHPT) as an ionophore for chromium(III) ions.

Methods:

Materials: Plasticizers like 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 P_4O_{10}. Triple-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).

Synthesis of macrocylic ionophore: A 100 mL two-necked round-bottom flask was used to synthesize the ionophore by dissolving under acidic conditions, hydrazones of 4-(γ-oxoalkyl)thio-semicarbazides could be converted into new azamacrocyclic compounds as strong metal-binding chelators. However, the reaction of methyl-substituted β-isothiocyanatoketone with hydrazine afforded thiosemicarbazide ketone only as intermediate that spontaneously converted into its cyclic isomeric form, *viz*. 1-amino-6-hydroxy-4-methyl-5,6-trimethylenehexahydropyrimidine-2-thione. Melting point: 220 °C; yield: 75%.

Electrode preparation: The synthesized ionophore (AHMTHHPT, 8 mg) were mixed with 30 mg of polyvinyl chloride (PVC) in 10 mL of tetrahydrofuran (THF). In this formulation, 60 mg of dibutyl phthalate (DBP) served as a plasticizer, while 2 mg of sodium tetraphenylborate (NaTPB) was used as an anion excluder. The resultant solution was carefully poured into a glass dish with a width of 2 cm for gradual evaporation to obtain a membrane of optimal performance.

EMF measurements: All the emf measurements were recorded by a Corning ion analyzer 250-pH/mV meter at 27 ± 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)

Results: The stability and selectivity of the following complexes were determined by measuring the complex formation constant (K_f) of the ionophore (AHMTHHPT) with various cations in an acetonitrile solution at 25±0.05 ºC. Fitting the data from the molar conductance in mole ratio with the suitable equations 1 and 2 allowed for the analysis to be conducted. Table-1 displays the results that were collected. The Cr(III)-AHMTHHPT complex clearly has a greater K_f compared to the other cations that were examined.

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

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

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

where f is the activity coefficient of the species specified; $[ML^+]$ is the equilibrium molar concentration of complexes; $[M^+]$ is the free cation, and [L] is the free ligand. With the ligand at a diluted concentration, it is reasonable to assume that the activity coefficient, f(L), is one [10]. The activity coefficient in equation (2) is nullified because the Debye-Huckel limiting law of 1:1 electrolyte [11] is applied, which leads to the result that $f(M^+) \sim f(ML^+)$. The molar conductance-based expression for the formation constant can be given by the following [12–14].

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

$$L = C_L - \frac{\Lambda_M - \Lambda_{obs}}{\Lambda_M - \Lambda_{ML}} \qquad (4)$$

Both the cation's molar conductance (M) and the complex's molar conductance (ML) are measured in molar units. The C_L stands for the concentration of the ionophore (AHMTHHPT) introduced, C_M for the analytical concentration of the cation, and Λ_{obs} for the molar conductance of the solution during titration. Using a nonlinear least square algorithm known as KINFIT, the complex formation constants, K_f, and the molar conductance of complex, Λ_{obs}, were calculated [15]. The resulting 1:1 complex has logarithm of formation constants (log K_f) ranging from 1.08 to 1.89 for trivalent cations, and about two or less than 2 for monovalent and divalent cations. All elements except Cr(III) had a value of 5.68. As a result, AHMTHHPT is an appropriate ionophore for the production of a PVC membrane sensor that is ion-selective for Cr(III).

Potential responses: The ionophore (AHMTHHPT) was used to evaluate the potential responses of different ions; the results are displayed in Fig. 1. Because of its three nitrogen atoms and two oxygen atoms, this ionophore is anticipated to be a good fit for PVC membranes containing transition and heavy metal ions, which have a high charge density. Its near-Nernstian potential response for Cr(III) was uncovered by the responses (Table-2).

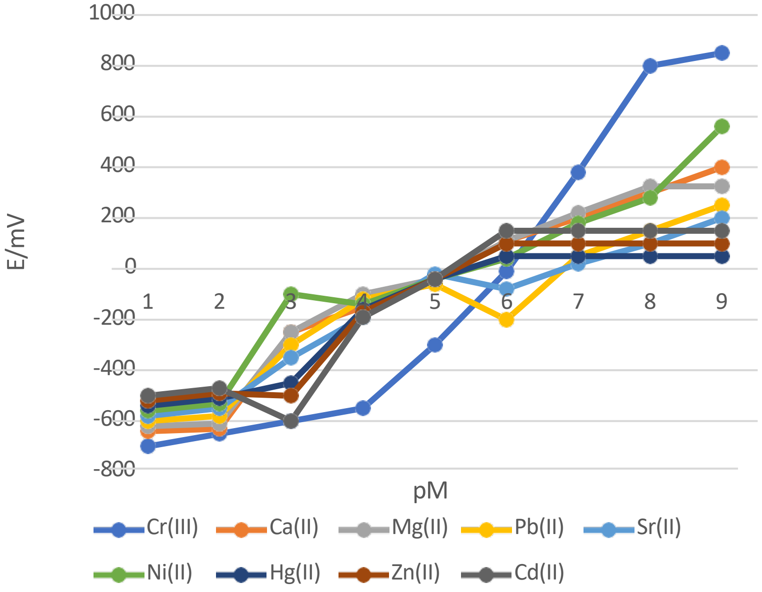

Fig. 1. Potentiometric responses of diverse metals ions of ionophore by membrane no. 4

Consequence of membrane composition: The sensitivity, selectivity, and linearity of ion-selective electrodes are influenced by the characteristics of the ion carrier and the membrane composition, as well as the type of solvent mediator and lipophilic additive employed. The plasticizers DBP, AP, and NBA used in membrane preparation indicate that DBP is the most effective, demonstrating a broad working concentration range and a near-Nernstian slope. Plasticizers regulate the dielectric constant of the membrane and the mobility of the ionophore. It also improves the membrane contact with Cr(III) ions.

The negatively charged lipophilic additives (specifically, the anionic component NaTPB) enhance the potentiometric performance of cation-selective electrodes by functioning as cation excluders. It is likely due not only to the reduction of ohmic resistance [19], but also to the enhancement of response behavior and selectivity [20]. Furthermore, at the membrane interface, the lipophilic additives can facilitate the exchange kinetics. The membrane composition with a percentage ratio of PVC: DBP: ionophore (TADODTSD): Additive (NaTPB) of 30: 60: 8: 2 exhibits optimal results (no. 4 in Table 2).

Table-2
Compositions of membrane ingredients

Membrane No.	Alignment of the membrane (wt.%)				
	Ionophore	Plasticizer	Poly(vinyl chloride)	Additive	Slope (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

pH range: By adding dilute HNO_3 or NaOH, the pH of the solution was changed from 1.0 to 10.0, and the membrane sensor's potential response was examined. It was found that the potential was expected to remain constant across a pH range of 3.0-8.0 for the solution. At high pH, the hydrolysis of Cr(III) ions caused a dramatic shift in potential, while at low pH, H^+ ions begin to interfere with the membrane's charge transfer process.

Response time and Lifetime of the sensor: Static response time is defined as the time it takes for the electrode assembly to achieve a stable voltage. In most cases, the PVC membrane electrode has a faster response time. Across all of the tested Cr(III) ion concentrations, the response time was 7 seconds, and the potential was stable for around 120 s. A Cr(III) membrane sensor has a 120-day life-span, according to the experiments. Throughout this time, the electrode was worn continuously for a long duration, one hour per day. The characteristics of the electrodes have not changed noticeably. Tabulated here are the findings. The slopes show a small but noticeable steady decline after 120 days, while the detection limit shows an increase. The components of the membrane may be leaking out into the solution, which could explain this. The majority of PVC membrane sensors have already shown this type of behavior. The current electrode also outperforms other published Cr(III) ion-selective sensors in terms of linear range, response time, and selectivity [21–28].

Selectivity coefficient: One of the most crucial features of a potentiometric ion-selective electrode is its selectivity coefficient, which reveals how well the membrane sensor responds to the target ion in comparison to other ions in the solution. Match potential method (MPM) [29,30] was used to study the potential response of the suggested Cr(III) ion-selective electrode. The selectivity coefficient, denoted as ΔA, is calculated by subtracting the interference ion, a_B, from the initial primary ion activity, a_A.

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

Ionophore	Working conc. range (mol L^{-1})	Detection limit (mol L^{-1})	Slope (mV/decade)	pH range	Lifetime	Response time	Ref.
4-Amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one	1.0×10^{-6} to 1.0×10^{-1}	5.8×10^{-7}	19.7 ± 0.3	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}	7.0×10^{-7}	19.9 ± 0.3	3.0–6.6	56 days	< 12 s	[22]
Glyoxalbis(2-hydroxyanil)	3.0×10^{-6} to 1.0×10^{-2}	6.3×10^{-7}	19.89 ± 0.5	2.7-6.5	90 days	< 20 s	[23]
Tri-*o*-thymotide	4.0×10^{-6} to 1.0×10^{-1}	2.0×10^{-7}	20.0 ± 0.1	2.8–5.1	150 days	15 s	[24]
p-(4-Acetanilidazo)-calix[4]arene	9.8×10^{-7} to 1.0×10^{-1}	7.3×10^{-7}	19.8 ± 0.2	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}	9.8×10^{-8}	19.8 ± 0.2	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}	2.0×10^{-7}	19.8 ± 0.3	2.5–6.8	70 days	< 10 s	[27]
Chitosan	1.0×10^{-6} to 1.0×10^{-1}	1.32×10^{-8}	58.5	4.0-6.0	120 days	10 s	[28]
8,11,14-Triaza-1,4-dioxo-5(6),6(17)-ditolylcyclosepta-decane	1.0×10^{-8} to 1.0×10^{-1}	8.0×10^{-8}	19.6 ± 0.5	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) $\left(K_{Cr^{3+}}^{Pot}\right)$

Interfering ion (B)	Selectivity coefficient $\left(K_{Cr^{3+}}^{Pot}\right)$
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}

Analytical applications: The developed Cr(III) ion-selective electrode demonstrated effective performance in controlled laboratory settings. The sensor demonstrated effective performance as an indicator electrode during the titration of chromium(III) with EDTA. Fig. 2 clearly demonstrates that this electrode is capable of quantitatively assessing the concentration of Cr(III) ions. The findings from the suggested Cr(III) sensor, along with the data gathered through atomic absorption spectrometry (AAS), are compiled in Table-5. An acceptable correlation was established between the outcomes achieved by the proposed sensor and those obtained through atomic absorption spectroscopy (AAS).

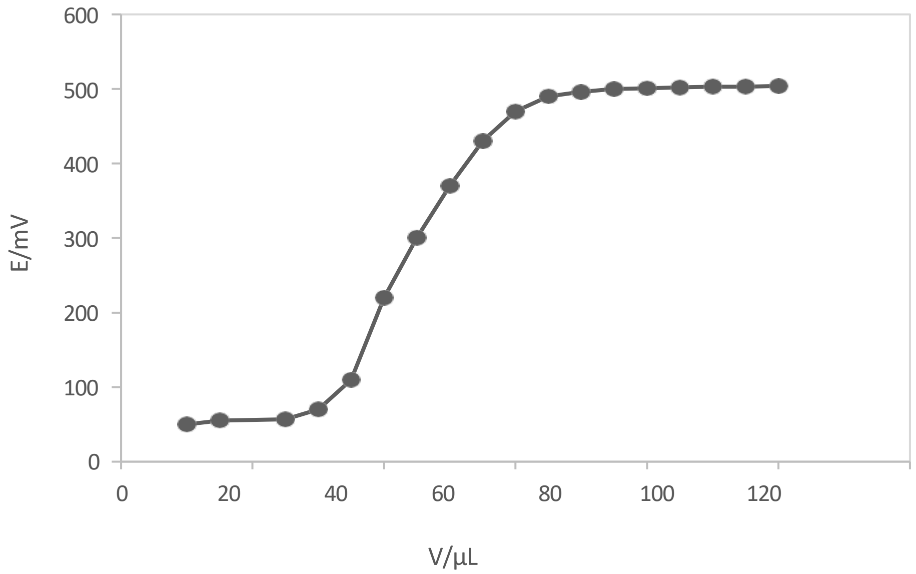

Fig. 2. Potentiometric titration curve of 50 mL solution of Cr(III) ion 1.0×10^{-2} mol L^{-1} with 1.0×10^{-2} mol L^{-1} EDTA solution

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}

Conclusion: This research demonstrated that the potentiometric sensor utilizing ionophore 1-amino-6-hydroxy-4-methyl-5,6-trimethylenehexahydropyrimidine-2-thione (AHMTHHPT) can effectively work as a highly selective electrode for chromium(III). The ionophore is capable of creating a selective and stable complex with Cr(III) ions, making it suitable for the determination of Cr(III) ions in the presence of various interfering ions. The relevant pH range, minimal detection threshold, and selectivity factors of the suggested sensor position it as a more advanced tool in comparison to alternative techniques for assessing Cr(III) ion levels. This membrane electrode exhibits a rapid potential response and excellent selectivity for Cr(III) ions. This method is applicable for assessing the concentration of Cr(III) ions in environmental and wastewater samples.

References

1. K. Tohda, D. Dragoe, M. Shibata, and Y. Umezawa, Anal. Sci. 17 (2001) 733.
2. T. Bereznai, and J. Radioanal. Chem. 9 (1971) 81.
3. R.E. Kirk, and D.F. Othmer, Encyclopedia of Chem. Tech. 19 (1982) 836.
4. H. Fashui, H. Zhenggui, and Z. Guiwen, Biol. Trace Element Res. 75 (2000) 205.
5. W. Yongxing, W. Xiaorong, and H. Zichun, Bull. Environ. Contamin. Toxicol. 64 (2000) 611.
6. A. Hrdlicka, J. Havel, C. Moreno, and M. Valiete, Anal. Sci. 7 (1991) 925.
7. H. Aohan, and J. J. Wilson. Accounts of Chemical Research 55 (2022) 904.
8. D.H. Cornell, Pure Appl. Chem.65 (1993) 2453.
9. S. Chandra, and D.R. Singh, J. Saudi. Chem. Soc. 14 (2010) 55.
10. S.F. Marsh, Anal. Chem. 39 (1967) 641.
11. T. Ito, and C. Goto, J. Trace. Microprobe Tech. 19 (2001) 601.
12. M. Uppal, and G. Singh, J. Adv. Electrochem. 2 (2016) 103.
13. G.M. Mockler, G.W. Chaffey, E. Sinn, and H. Wong, Inorg. Chem. 11 (1972) 1308.

14. K.M. Tawarah, and S.A. Mizyed, J. Solution Chem. 18 (1989) 387.
15. C.W. Outhwaite, J. Chem, Phys. 50 (1969) 2277.
16. V.K. Gupta, M. Al Khyat, A.K. Minocha, and P. Kumar, Anal. Chim. Acta 532 (2005) 153.
17. R. Eugster, U.F. Spichiger, and W. Simon, Anal. Chem. 65 (1993) 689.
18. T. Rosatzin, E. Bakker, K. Suzuki, and W. Simon, Anal. Chim. Acta 280 (1993) 197.
19. E. Bakker, Electroanalysis 9 (1997) 7.
20. E. Bakker, E. Pretsch, and P. Buhlmann, Anal. Chem. 72 (2000) 1127.
21. H. A. G. Zamani, G. Rajabzadeh, and M. R. Ganjali, Sens. Actuators B 119 (2006) 41.
22. M. R. Ganjali, P. Norouzi, F. Faridbod, M. Ghorbani and M. Adib, Anal. Chim. Acta 569 (2006) 35.
23. M. B. Gholivand, and F. Sharifpour, Talanta 60 (2003)707.
24. V. K. Gupta, A. K. Jain, P. Kumar, S. Agarwal, and G. Maheshwari, Sens. Actuators B 113 (2006) 182.
25. P. Kumar, and Y. B. Shim, Bull. Korean Chem. Soc. 12 (2008) 2471.
26. P. Kumar, and H.K. Sharma, Electrochim. Acta 87 (2013) 925.
27. H. A. Zamani, M. R. Ganjali, M. R. Abedi, and P. Norouzi, Sensor Lett. 5(2007) 1.
28. S. Khalil, A.E. El-Beltagy, M.E.A. El-Sayed, A.A. Abdel Fattah1, Y.F.M. Kishk, and S.S. Alharth, Int. J. Electrochem. Sci. 16 (2021) 1.
29. V.K. Gupta, and P. Kumar, Anal. Chim. Acta 389 (1999) 205.
30. M. Javanbakht, A. Shabani Kia, M. Darvich, M.R. Ganjali, and M. Shamsipur, Anal. Chim. Acta 400 (2000) 75.