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Coated wire chromium(III) ion-selective electrode based on azamacrocycles

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Abstract Tetraazacyclotetradecane, tetratosyltetraaza 12C4, and tritosyltriaza 9C3 have been explored as electroactive materials for preparing coated wire ion-selective electrodes (CWISEs) for Cr(III) ions. The best performance was observed for the membrane comprising electroactive material (tetratosyltetraaza 12C4), plasticizer (dibutyl phthalate), and poly(vinyl chloride) in the optimum ratio 5:60:35 (w/w). Linear Nernstian response for this electrode was obtained over the total Cr(III) concentration range of 1×10^{-1} to 1×10^{-7} M in 0.05 M NH_4NO_3 medium, with a slope of 20 ± 1 mV per decade change. The working pH range of the electrode was 1.8–5.5. Selectivity coefficients of some mono, divalent, and trivalent metal ions were determined. Analyses of electroplating bath solutions, chromating, and effluent samples have been carried out using this CWISE and the results are found to be comparable with those obtained by using conventional methods or by AAS.

Keywords Potentiometry · Coated wire ISE · Chromium(III) · Tritosyltriaza 9C3 · Tetratosyltetraaza 12C4 · Tetraazacyclotetradecane

Introduction

Ion-selective electrodes have been the subject of rapidly increasing interest over the past few years and their development has opened a large new field of potentiometry. A large number of ionophores, especially a wide variety of neutral macrocyclic polyethers, have been synthesized and

are being used to develop new sensors for fast, accurate, and selective determination of respective ions in environmental, industrial, and clinical samples [1]. Numerous types of ion-selective electrodes (ISEs) for alkali and alkaline earth metal ions based on crown ethers [2, 3, 4] have been prepared and studied. In contrast, only a few ion-selective electrodes for trivalent ions, namely, Au(III) [5], Bi(III) [6], Al(III) [7], Cr(III) [7, 8], Ce(III) [9], and La(III) [10], have been reported. Owing to the well-known fact that nitrogen- and sulfur-containing macrocycles show increased affinity towards transition metal ions than their oxygen-containing analogues [11], coated wire ion-selective electrodes (CWISEs) for Ag(I) ISE based on cyclam [12] and Cu(II) ISE based on dibenzodiaza 15C4 [13] have been fabricated. One of the important aspects of using CWISEs is that it not only needs a very small volume of sample, but also has other advantages such as simplicity of design, lower cost, mechanical flexibility (i.e., the electrode can be used at any angle), absence of internal solution, and the possibility of miniaturization and microfabrication [14, 15, 16]. Literature studies revealed that very little work has been done on the development of Cr(III) ISE for routine potentiometric analysis.

Experimental

Reagents

All metal salts, acids, tetrahydrofuran (THF), ethylenediaminetetraacetic acid disodium salt (EDTA), dibutyl phthalate, etc. were of analytical grade and were used as such. Calcium and magnesium perchlorates were prepared by general methods described elsewhere [17]. 1,4,8,11-Tetraazacyclotetradecane (cyclam), manganese nitrate, chromium(III) perchlorate, Iron(III) perchlorate, and PVC were purchased from Fluka and were used as such. 1,4,7-Tritosyl-1,4,7-triazacyclononane (tritosyltriaza 9C3), 1,4,7,10-tetratosyl-1,4,7,10-tetraazacyclododecane (tetratosyltetraaza 12C4) were synthesized by the Richman–Atkins method [18, 19]. All working solutions were prepared in doubly distilled deionized water and standardized by the recommended methods [20] wherever necessary.

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Preparation of membrane

The PVC membranes contained 5% w/w ionophore (cyclam/tetra-syltetraaza 12C4/tritosyltriaza 9C3), 33% PVC, and 62% plasticizer (dibutyl phthalate). A total of 0.3 g of these reagents was mixed in THF. A platinum wire was used as a substrate to coat the slurry, by dipping it several times in the slurry until a bead was formed. This bead thus prepared was allowed to dry in air for 24 h and then used as the Cr(III) ISE.

Storage of the membrane

The electrodes were kept under dry conditions in an airtight bottle when not in use. Before using, the electrode was conditioned by dipping it for 20 min in 1×10^{-3} M Cr(III) perchlorate in 0.05 M NH_4NO_3 solution. The slurry prepared for the bead preparation was stored in an airtight chamber when not in use. A fresh electrode was prepared by adding THF into the slurry and repeating the above procedure.

Apparatus and emf measurements

All solutions were prepared by using a digital single-pan balance (Mettler Toledo AB204, Switzerland). A Mettler Toledo DL53 (Switzerland) autotitrator with automatic temperature compensation (ATC) was used for the standardization of metal salt solutions. A CyberScan 2500 pH meter (Eutech Instruments, Singapore) having ± 0.1 mV accuracy with an SCE as reference electrode and KNO_3 salt bridge was used for potential measurements.

All measurements were carried out at 25°C with a cell of the type: $\text{Hg, Hg}_2\text{Cl}_2; \text{KCl (satd)}/\text{Cr(III) solution/ion-selective membrane (bead)}/\text{Pt wire}$.

To check for Nernstian behavior, standard solutions of chromium perchlorate (1×10^{-1} to 1×10^{-7} M) in 0.05 M NH_4NO_3 , 0.05 M HNO_3 , and 0.05 M HClO_4 were prepared and the emfs were noted every 30 s over a period of 5 min or less until the emfs were stable to within ± 0.1 mV. The medium with 0.05 M NH_4NO_3 was found to give the best response and was maintained for the rest of the studies. To evaluate the response time, the electrode was dipped in a series of solutions having a tenfold difference in Cr(III) concentrations and the potentials were noted at 5-s intervals.

A GBC 906AA atomic absorption spectrophotometer with air-acetylene flame was used at 359.3 nm to analyze real samples.

Sample preparation

The synthetic trivalent chrome plating solutions, trivalent chromating solutions, and effluents from electroplating shops were diluted appropriately using 0.05 M NH_4NO_3 and pH was adjusted to between 2–5 by using HNO_3 whenever required. Hydroxylamine hydrochloride (10%) was used to reduce any Fe(III) to Fe(II) and Cr(VI) to Cr(III).

Results and discussions

Initially, an attempt was made to develop Cr(III) CWISE based on a Cr–cyclam complex as cyclam shows appreciable stability with chromium(III) ($\log K_s = 8.53$ in 90% (v/v) DMSO+water) [21]. For the first few days the electrode showed an excellent Nernstian response in the range 1×10^{-1} to 1×10^{-7} M in 0.05 M NH_4NO_3 medium, with a slope of 21 ± 2 mV per decade change. The response slowly started deteriorating, which could be due to the solubility of Cr–cyclam complex in water. Therefore, tetra-syltetraaza 12C4 and tritosyltriaza 9C3 were tried out as neu-

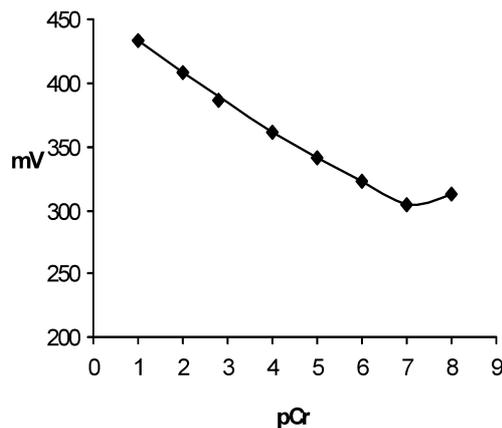


Fig. 1 Plot of potential versus log [Cr(III)]

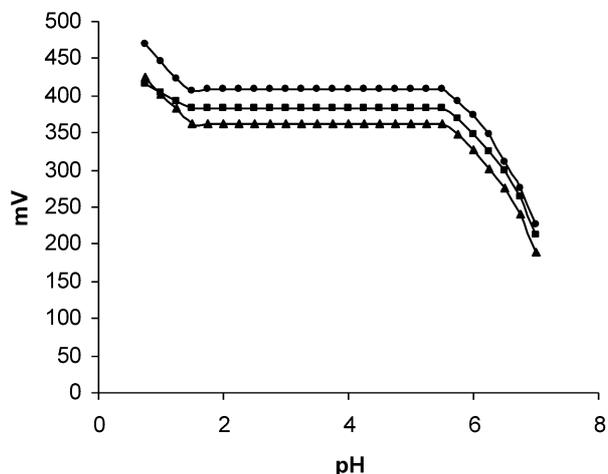


Fig. 2 Effect of pH on electrode potential at various concentrations of Cr(III): ● 1×10^{-2} M, ■ 1×10^{-3} M, ▲ 1×10^{-4} M

Table 1 Selectivity coefficients of Cr(III) ISE

Sr. no.	Interfering ion	Selectivity coefficient ($K_{Cr,M}$)
1	Li(I)	1.1×10^{-3}
2	K(I)	3.6×10^{-3}
3	Mg(II)	3.5×10^{-3}
4	Ca(II)	5.2×10^{-4}
5	Ba(II)	4.1×10^{-4}
6	Mn(II)	2.5×10^{-3}
7	Co(II)	6.8×10^{-3}
8	Ni(II)	1.2×10^{-2}
9	Cu(II)	2.3×10^{-3}
10	Zn(II)	6.8×10^{-3}
11	Cd(II)	1.0×10^{-3}
12	Pb(II)	1.1×10^{-3}
13	Hg(II)	6.9×10^{-3}
15	Fe(II)	1.8×10^{-2}
14	Fe(III)	7.6×10^{-1}
16	Al(III)	5.2×10^{-4}

tral carrier molecules for Cr(III). Wickstrom and others [22] found that aza-crown ethers with a *p*-toluene sulfonyl group attached to the nitrogen atom showed a better re-

Table 2 Results obtained by direct potentiometry of synthetic samples ($n=5$)

Sr. No.	Composition	Observed content of Cr(III)
1	0.0010 M Cr(ClO ₄) ₃ +0.01 M NaNO ₃ +0.01 M Co(NO ₃) ₂ +0.01 M Pb(NO ₃) ₂	0.00117±0.00006 M
2	0.0010 M Cr(ClO ₄) ₃ +0.01 M Mg(ClO ₄) ₂ +0.01 M Cu(NO ₃) ₂ +0.01 M KNO ₃	0.00123±0.00009 M
3	0.0010 M Cr(ClO ₄) ₃ +0.01 M NaNO ₃ +0.01 M Cd(NO ₃) ₂ +0.01 M Mn(NO ₃) ₂	0.00112±0.00005 M
4	0.0010 M Cr(ClO ₄) ₃ +0.01 M Hg(NO ₃) ₂ +0.01 M Ni(NO ₃) ₂ +0.01 M Zn(NO ₃) ₂	0.00091±0.00009 M
5	0.0010 M Cr(ClO ₄) ₃ +0.01 M KNO ₃ +0.01 M Fe(ClO ₄) ₃	0.00782±0.00041 M
6	0.0010 M Cr(ClO ₄) ₃ +0.01 M KNO ₃ +0.01 M Fe(ClO ₄) ₃ +10% NH ₂ OH·HCl	0.00121±0.00002 M
7	7.400 g L ⁻¹ Cr(III) (as CrCl ₃)+63 g L ⁻¹ H ₃ BO ₄ +260 mg L ⁻¹ thiourea+1.0 mL TritonX 100 diluted to 1 L	7.322±0.012 g L ⁻¹
8	0.003 M CrCl ₃ +0.006 M sodium thiocyanate+0.003 M aspartic acid+60 g L ⁻¹ H ₃ BO ₄ +60 g L ⁻¹ NaCl	0.00274±0.00003 M
9	0.05 mg L ⁻¹ Cr(III) (as CrCl ₃)+0.01 M KNO ₃ +0.01 M Fe(ClO ₄) ₃ +10% NH ₂ OH·HCl	0.055±0.005 mg L ⁻¹

sponse among all the other side arms attached when used as an ionophoric material for ISEs. Srivastava et al. had used tritosyltriaza 9C3 and tetratosyltetraaza 12C4 for the development of chemically modified electrodes [23]. However, membranes with tritosyltriaza 9C3 gave erratic responses, probably because of its large side groups relative to its small cavity size. Tetratosyltetraaza 12C4 ($\log K_s=8.06$ in 90% (v/v) DMSO+water) [21] gave good results over a long period of time and this electrode was used for all further studies.

Nernstian slope and response time

The plot of the difference of the emf between the working CWISE and the reference calomel electrode against the logarithm of the concentration of the Cr(III) (in 0.05 M NH₄NO₃) shows that the electrode gives a linear Nernstian response from 1×10^{-1} to 1×10^{-7} M with a slope value 22 ± 2 in the first week, but the value changed to 20 ± 1 mV per decade change in concentration from the second week onwards (Fig. 1). The detection limit observed was $6 \times 10^{-8} \pm 1.1 \times 10^{-8}$ M. The wide working range with a response time of 15 s in the region 1×10^{-1} M– 1×10^{-4} M and 20 s in the lower range up to 1×10^{-7} M was found to be better than or comparable to those observed earlier [7, 8].

Effect of pH

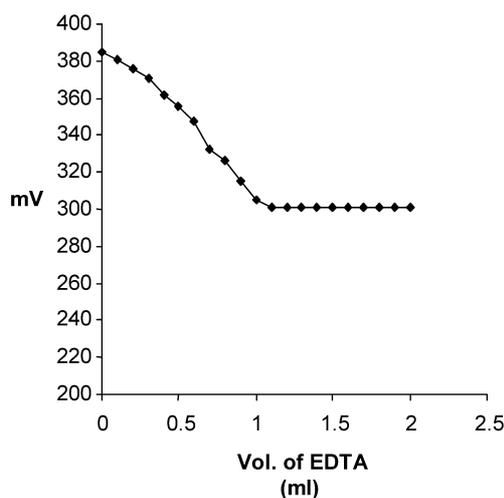
To study the effect of pH on the electrode response, the electrode potentials were measured over a pH range of 1.0–7.0 for 1×10^{-2} , 1×10^{-3} , and 1×10^{-4} M Cr(III) solutions. The potential was found to be independent of the change in pH in the range 1.8–5.5 (Fig. 2). The electrode has a wide lower working range of pH relative to those reported earlier [7, 8, 24].

Interferences by ions

The selectivity of the electrode for chromium(III) ions in the presence of other cations was studied by the mixed solution method [25] by using a fixed concentration of in-

Table 3 Results obtained by direct potentiometry of real samples ($n=5$ for all)

Samples	ISE method (ppm)	Titrimetric method (ppm)	AAS method (ppm)
Chromating solutions			
1.	1,060±0.5	1,040±0.8	–
2.	7,010±0.4	6,970±0.5	–
Effluent samples			
1.	520±0.4	–	521±0.3
2.	360±0.3	–	362±0.3
Treatment plant samples			
1.	5.2±0.03	–	4±0.04
2.	7.5±0.03	–	7±0.03
3.	0.60±0.05	–	0.52±0.05
4.	0.33±0.05	–	0.30±0.05

**Fig. 3** Plot of emf versus volume of EDTA

terfering ion (1×10^{-3} M) and varying concentrations of Cr(III) ion (1×10^{-1} to 1×10^{-7} M). The selectivity coefficients of different cations determined are given in Table 1. From the selectivity coefficient values, we found that the presence of Fe(III) affects the electrode response strongly ($K_{Cr,Fe(III)}=7.6 \times 10^{-1}$), whereas interference due to Fe(II) is

Table 4 Comparison of chromium-ion-selective electrodes

Electrode	Linear range (M)	Detection limit (M)	Response time (s)	pH range	Life time (months)
Chattopadhyaya et al. [7]	1.0×10^{-6} – 1.0×10^{-1}	1.0×10^{-6}	15	2.8–7.6	8
Singh et al. [8]	1.8×10^{-6} – 1.0×10^{-1}	–	15–25	3.0–6.5	4
Abbaspour et al. [24]	1.7×10^{-6} – 1×10^{-2}	8×10^{-7}	10–15	3.0–5.5	3
Present work	1.0×10^{-7} – 1.0×10^{-1}	6×10^{-8}	15–20	1.8–5.5	5

weak ($K_{Cr,Fe(II)}=1.8 \times 10^{-2}$). Therefore, hydroxylamine hydrochloride was used to reduce Fe(III) to Fe(II) for the satisfactory analysis of samples containing Fe(III) ions (Table 2).

Lifetime

The electrode was used over a period of 5 months without any significant effect on the membrane potential. Whenever a drift in potential was observed the electrode was regenerated by conditioning it in 0.001 M Cr(III) solution for 20 min. The lifetime of ion-selective electrodes mainly depends on ionophores and plasticizers used, and also on the number of times it is used [26]. After 5 months the response deteriorated, possibly be due to the aging of the PVC matrices, ionophore, and plasticizer [26].

Analytical application

Table 2 shows the results obtained by direct potentiometry of synthetic samples containing various ions. As the analysis results show that these metal ions do not interfere seriously, which is also reflected from the selectivity coefficient study (Table 1), the electrode was used to determine the concentration of chromium in the artificial trivalent chrome plating solutions (Table 2). Chromating solutions used for conversion coatings of Zn and Al effluent samples from plating shops and water samples from treatment plants were collected and effluent samples were collected from plating shops and analyzed by the CWISE fabricated in the present work. The results obtained by the proposed sensor are in good agreement with titrimetric method [20] (Table 3) and by AAS. The sensor was used as an indicator electrode in the potentiometric titration of Cr(III) with EDTA. A 10.0 mL volume of a 1×10^{-3} M solution of Cr(III) was titrated against 1×10^{-2} M EDTA solution. The sharp break point with the addition of EDTA is obtained because of the decrease in Cr(III) concentration due to its complexation with EDTA (Fig. 3).

Conclusion

The CWISE developed in the present work exhibited good reproducibility over a period of about 5 months and is comparable to or better than the previously reported

ones (Table 4). Analytical applications of the sensor prove that it holds promise for regular and routine analyses for the determination of Cr(III).

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