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Anion recognition through novel C-thiophenecalix[4]resorcinarene: PVC based sensor for chromate ions

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Abstract

Novel ionophore, C-thiophenecalix[4]resorcinarene (**I**) has been synthesized and characterized by IR, NMR and C, H, N analysis. Poly(vinyl chloride) (PVC) based membranes of ionophore (**I**) using dibutylphthalate (DBP), dioctylphthalate (DOP), 1-chloronapthalene (CN), tris(2-ethylhexyl) phosphate (TEHP) and bis(2-ethylhexyl)sebacate (DOS) as plasticizing solvent mediators were prepared and used as CrO_4^{2-} selective sensors. Of the various sensors prepared, the one with membrane composition 2:66:120 mg (I: PVC: DBP) exhibited the best performance. This sensor works well over a wide concentration range 5.6×10^{-6}–1.0×10^{-1} M (detection limit ∼ 0.30 ppm) with Nernstian compliance (29.0 mV per decade) between pH 6.5–10.0 with a fast response time of ∼13 s. The selectivity coefficient values as determined by fixed interference method (FIM) indicate excellent selectivity for CrO_4^{2-} ions over a large number of anions. The sensor exhibits adequate shelf-life (∼5 months) with good reproducibility (S.D. ± 0.2 mV). The sensor has been used in the potentiometric titration of chromate with Pb(II). Determination of chromium in electroplating waste using the sensor was successfully achieved.

Keywords: Chromium; Sensors; Calixarenes; Chromium-selective electrodes; Chromate ions

1. Introduction

Chromium compounds are extensively used in corrosion control, oxidation processes, leather industry, electroplating, etc. In India, leather manufacturing industries are extensively using chromium compounds for tanning process and a large quantity of aqueous waste containing high chromium concentration is being discharged as such. It is reported that chromium concentration in discharged waste is up to several thousands parts per million causing serious threat to microorganisms of aquatic systems and human life in nearby areas. Cr(III) and Cr(VI) are the predominantly present oxidation states in aqueous systems, of these Cr(VI) is a well known carcinogen with exposure occurring in both occupational and environmental samples [1]. Environmental Protection Agency (EPA) has adopted up to 0.01 ppm of total chromium as maximum contaminant level in community water systems. Presently, sophisticated techniques viz., AAS, ICP, etc. are employed for the determination of trace amount of chromium. However, these methods are disadvantageous in terms of cost and unsuitability for routine analyses of large number of samples [2–5]. Recently, ion-sensors are being used for such quantification, as these provide a convenient, fast and 'on-line' method of analysis.

Extensive efforts have been made to develop a good sensitive sensor for chromium [6–14]. However, most of the developed sensors do not permit chromium estimation at lower concentrations (<1 ppm) [9–12,14], exhibit poor selectivity in the presence of common anions [6,8–11,14], show non-Nernstian response [6,7] and high response time [13,14]. Crown ethers, cryptands, porphyrins, calixarenes, hydrogen-

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bonding ionophores etc. are being employed for ion-sensing because of their selective complexation properties. Among these, calixarenes and resorcinarene receptors have attracted recent attention because of the flexibility in synthesizing the ionophores of desired binding properties. The lower or upper rim and methylene bridge of these compounds can be easily modified to achieve desirable structures to bind specific guest species [15]. Recently, we have prepared a new C-thiophenecalix[4]resorcinarene derivative expected to act as a ionophore showing affinity for anions [16,17]. Therefore, PVC based membranes incorporated with C-thiophenecali [4]resorcinarene as neutral ionophore were prepared and investigated for their response towards anions. The results, reported in present communication, show that these membranes show high selectivity towards chromate ions over large number of anions and could, therefore, be used as a selective sensor for its quantification.

2. Experimental

2.1. Reagents

All reagents were of analytical reagent grade and used without further purification. Dibutylphthalate (DBP) and dioctylphthalate (DOP), Reidel, India; 1-chloronapthalene (CN) and tris(2-ethylhexyl) phosphate (TEHP), E. Merck, Germany; bis(2-ethylhexyl)sebacate (DOS) and high molecular weight poly(vinyl chloride) (PVC), Aldrich, USA were used as obtained. Analytical reagent-grade tetrahydrofuran (THF), sulfuric acid and sodium hydroxide were obtained from Ranbaxy, India. Solutions of different concentrations were prepared by successive dilution of 0.1 M stock solutions.

2.2. Synthesis of C-thiophenecalix[4]resorcinarene(***I***)

To a solution of resorcinol (18.06 g, 0.164 mol) dissolved in 70 ml of ethanol, was added 20 ml concentrated HCl, maintaining the reaction mixture below 50 °C. Thiophene-2-aldehyde (19.04 g, 0.17 mol) was added drop wise over a period of 30 min to obtain a heterogeneous reaction mixture. The mixture was slowly heated to give a homogenous solution. It was refluxed for 8 h to obtain dark brown coloured precipitates, filtered and washed with water to remove excess HCl [18]. The precipitates of C-thiophenecalix[4]resorcinarene thus obtained were crystallized from hot acetone (Fig. 1).

The yield was 70%, m.p. >320 °C (dec.). IR (KBr): n (–OH str. and C–H str.) 3400–3050 cm^{-1} (b); ^{1}H NMR (CDCl$_3$): δ4.4 (s, 4H, meso –CH), 6.21 (s, 8H, Ar–H), 6.59 (t, 4H, thiophene–H), 6.84 (d, 8H, thiophene–H) and 7.69 (s, 8H, –OH); analytically calculated for $C_{44}H_{32}O_8S_4$: C, 64.68%; H, 3.95% and S, 15.69%; found: C, 64.48%; H, 3.80% and S, 15.50%.

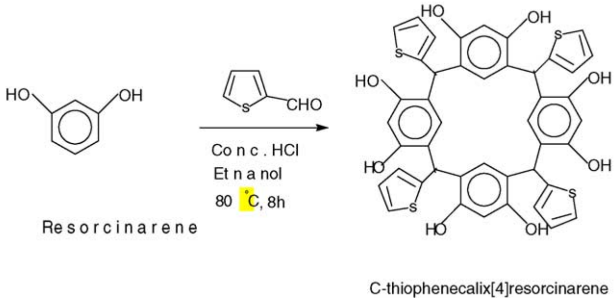

Fig. 1. Synthesis and structure of C-thiophenecalix[4]resorcinarene.

2.3. Potential measurements

The potential measurements were carried out at 25 ± 0.1 °C with a digital potentiometer (Model 5652 A, ECIL, India) and Century Microvoltmeter (Model CVM 301, India) by setting up the following cell assembly, employing saturated calomel electrodes (SCE) as a reference electrodes.

SCE/internal solution (0.1 M, CrO$_4^{2-}$)/membrane/test solutions/SCE.

2.4. Preparation of membranes

CrO$_4^{2-}$ selective membranes were prepared by dissolving a mixture of ionophore (2 mg), plasticizers (DBP, DOP, TEHP, DOS, or CN) (120 mg) and PVC (66 mg) in THF. The solution was poured into acrylic rings placed on a glass plate and the solvent was then allowed to evaporate at room temperature. The resulting membrane of 0.5 mm thickness was obtained. It was then cut to size and attached to “Pyrex” tube and equilibrated in 0.5 M CrO$_4^{2-}$ solution for 2–3 days. A number of such membranes were prepared and those, which generated stable potentials and exhibited quick response were selected for further studies. The composition of such membranes is given in Table 1.

3. Results and discussion

3.1. Performance characteristics of sensor

The potentiometric response characteristics of a CrO$_4^{2-}$ sensor based on C-thiophenecalix[4]resorcinarene as electroactive material, with various plasticizers (TEHP, DOP, DOS, CN and DBP) in PVC matrix were measured in the concentration range of 1.0 × 10^{-7}–1.0 × 10^{-1} M. A perusal of data presented in Table 1 shows that the sensor No.1 without plasticizer exhibited a narrow working concentration range of 7.9 × 10^{-5}–1.0 × 10^{-1} M with a slope 30 mV per decade of activity (Fig. 2). Solvent mediators are frequently used to enhance the performance characteristics of plasticized membranes. It is well documented that the addition of the plasticizers not only improves the workability of the membranes but also contributes significantly towards the improvement

Table 1
Composition of PVC membranes of C-thiophenecalix[4]resorcinarene and performance characteristics of CrO_4^{2-} selective electrode based on them

Sensor no.	Composition of membranes (mg)							Working concentration range (M)	Slope (mV per decade)	Response (time s^{-1})
	I	PVC	TEHP	DOP	DOS	CN	DBP			
1	2	66						7.9×10^{-5}–1.0×10^{-1}	30	30
2	2	66	120					3.1×10^{-5}–1.0×10^{-1}	31	17
3	2	66		120				3.5×10^{-5}–1.0×10^{-1}	32	13
4	2	66			120			4.4×10^{-5}–1.0×10^{-1}	32	22
5	2	66				120		1.7×10^{-5}–1.0×10^{-1}	29	13
6	2	66					120	5.6×10^{-6}–1.0×10^{-1}	29	08

in the working concentration, stability and shelf-life of the sensor [19,20]. However, the selectivity is usually unaffected and mainly depends on the metal–ionophore interaction. Adequate plasticizer to be used in membranes should exhibit high lipophilicity, high molecular weight, low vapour pressure and high capacity to dissolve the substrate and other additives present in the membrane [21]. The addition of plasticizers to the membrane enhanced sensitivity of the sensors, as the membranes fabricated using DBP showed a linear and stable response for CrO_4^{2-} over the concentration range 5.6×10^{-6}–1.0×10^{-1} M with a Nernstian slope of 29.0 mV per decade (Fig. 2). Since, sensor (no. 6) having a composition of 2:66:120 mg (I: PVC: DBP) exhibited the lowest detection limit (~0.3 ppm CrO_4^{2-}) and stable potential response, the same was chosen for further studies.

The time required for the sensor to reach 95% steady potential, after successive immersion in a series of CrO_4^{2-} solutions, each having a 10-fold difference in concentration, ranges from 8–13 s. The membranes were stored in 0.5 M CrO_4^{2-} solutions when not in use. In general, prolong usage of many PVC based membranes causes leaching of ionophore to the solution, resulting in degradation of their performance. C-thiophenecalix[4]resorcinarene being a neutral ionophore exhibits high lipophilicity and therefore, the membrane based on this ionophore produces less leaching in aqueous systems. Further, it has been reported that physical properties of the plasticizer also influences the shelf-life of the sensor [22]. The proposed sensor with DBP as plasticizer had longer shelf-life due to low viscosity and high dielectric constant of the plasticizer as compared to other plasticizers used in these studies. The sensor was fairly stable and was used over a period of 5 months without showing any drift in potential.

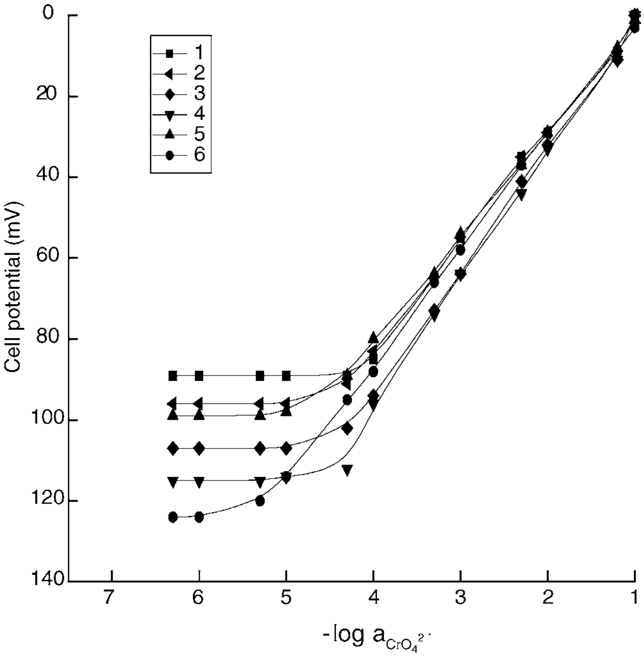

Fig. 2. Variation of membrane potential with activity of CrO_4^{2-} ions, without solvent mediator (1), with solvent mediators, TEHP (2), DOP (3), DOS (4), CN (5) and DBP (6).

3.2. *Effect of pH and non-aqueous solvents*

In the aqueous phase, chromate exists in different ionic forms ($HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-}, $HCr_2O_7^-$). The distribution of Cr(VI) species is dependent on both the total concentration of Cr(VI) and pH of the equilibrium solution. The following equations describe the distribution of chromium species in aqueous solution [23].

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+$$

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

$$HCr_2O_7^- \rightleftharpoons Cr_2O_7^{2-} + H^+$$

The CrO_4^{2-} anion prevails in basic or slightly acidic solution while the $Cr_2O_7^{2-}$ anion is dominant in acidic Cr(VI) aqueous solution [24].

$$\underset{\text{pH} > 6.5}{CrO_4^{2-}} \rightleftharpoons \underset{\text{pH } 4\text{–}6}{HCrO_4^-} \rightleftharpoons \underset{\text{pH} < 4}{Cr_2O_7^{2-}}$$

The pH of aqueous 10^{-3}–10^{-4} M CrO_4^{2-} solution was altered by dilute NaOH or HNO_3 solutions and the potential of the solutions was monitored. The effect of pH on the sensor's potential response shows that the useful working pH range wherein the potentials remain constant is 6.5–10.0 (Fig. 3). As pH value decreases below 6.5, the potential values are drastically changed. This corresponds to the decrease

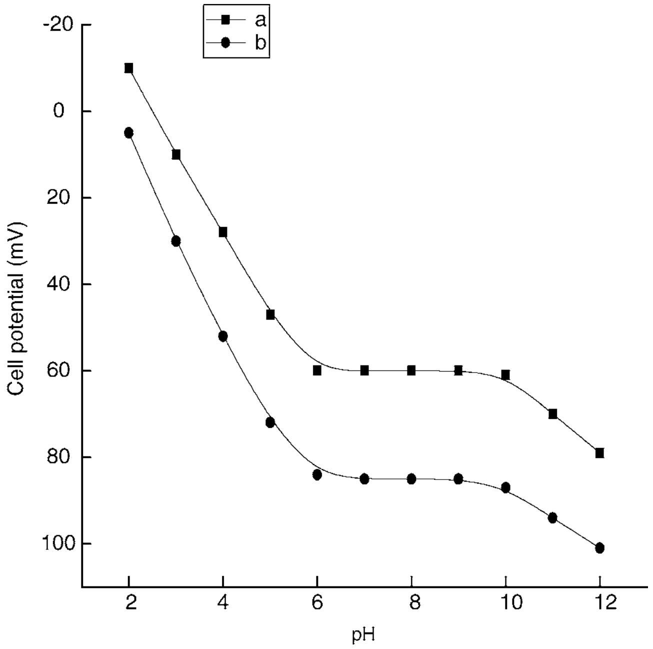

Fig. 3. Effect of pH on cell potential; $[CrO_4^{2-}]$ = 1.0 × 10^{-3} M (a) and 1.0 × 10^{-4} M (b).

in the measurable concentration of chromate and formation of dichromate and polychromate [25], to which the sensor does not appear to respond in Nernstian manner.

The utility of the sensor was investigated in partially non-aqueous media using methanol–water, ethanol–water and acetone–water mixtures. The sensor worked satisfactorily up to 30%(v/v) in partially non-aqueous medium without any appreciable change in working concentration range or slope. Higher concentrations of non-aqueous solvents were not explored keeping in view the leachability of the ionophore from the membrane matrix.

3.3. Potentiometric selectivity

Selectivity coefficient values describing the performance of the sensor in presence of interfering ions was determined by fixed interference method (Table 2). Selectivity coefficient values indicate that the sensor response to various anions decreases in the order of $HSO_3^- > C_2O_4^{2-} > Cl^- > I^- > HCO_3^- > F^- > SO_4^{2-} > HPO_4^{2-}=SO_3^{2-} > SCN^- > NO_3^- > NO_2^- > CO_3^{2-} > S_2O_3^{2-} > N_3^- > Br^- > ClO_4^- > VO_3^- > MnO_4^-$.

This selectivity pattern clearly shows a deviation from conventional Hofmeister anion response pattern for highly lipophilic anions such as ClO_4^-, SCN^-, I^- and NO_3^-. The deviation from the Hofmeister series resulted from the unique interactions between the ionophore and anions, rather than hydration free energy of the anions. As the values of selectivity coefficients are less than 1.0, the sensor is selective over the anions listed in Table 2. Thus, these ions would not cause any interference in the estimation of Cr(VI).

Table 2
Selectivity coefficient values obtained by fixed interference method at 1.0 × 10^{-2} M interfering ion concentration level

Interfering ion	Selectivity coefficient
HSO_3^-	1.7 × 10^{-1}
SO_4^{2-}	2.9 × 10^{-2}
HPO_4^{2-}	2.8 × 10^{-2}
$C_2O_4^{2-}$	4.4 × 10^{-2}
$S_2O_3^{2-}$	2.2 × 10^{-2}
CO_3^{2-}	2.5 × 10^{-2}
SO_3^{2-}	2.8 × 10^{-2}
MnO_4^-	5.6 × 10^{-3}
NO_2^-	2.5 × 10^{-2}
F^-	3.1 × 10^{-2}
Cl^-	3.8 × 10^{-2}
NO_3^-	2.8 × 10^{-2}
HCO_3^-	3.4 × 10^{-2}
SCN^-	2.5 × 10^{-2}
Br^-	1.4 × 10^{-2}
ClO_4^-	1.2 × 10^{-2}
N_3^-	1.7 × 10^{-2}
VO_3^-	1.1 × 10^{-2}

3.4. Interference of common anions

SO_4^{2-} and Cl^- are commonly present anions in aqueous systems. Therefore, in order to determine the optimum tolerance level of these anions, working concentration range for CrO_4^{2-} ions was determined in the presence of different concentration levels of these anions [26–30]. The CrO_4^{2-} concentration was varied from 1.0 × 10^{-7} to 1.0 × 10^{-1} M while fixed concentration of Cl^- and SO_4^{2-} ions, i.e. 1.0 × 10^{-3}, 1.0 × 10^{-4} and 1.0 × 10^{-5} M was maintained in synthetic mix-

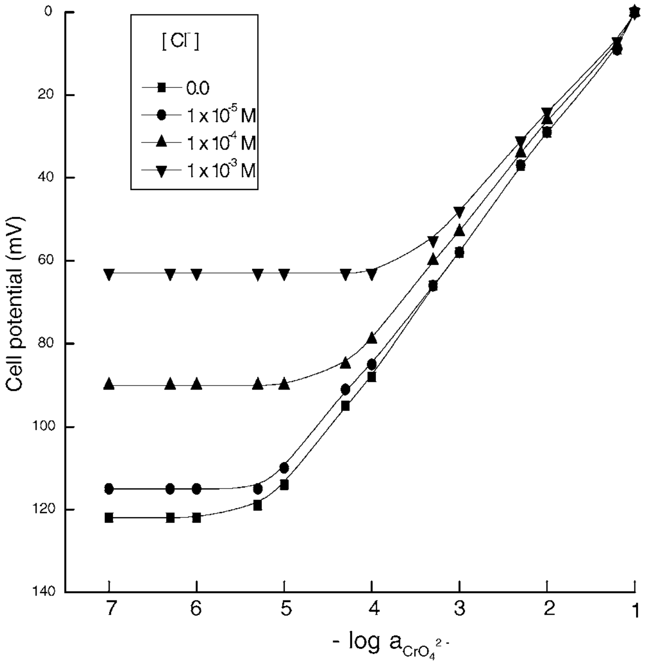

Fig. 4. Variation of cell potential with activity of CrO_4^{2-} at different concentration levels of Cl^- ions.

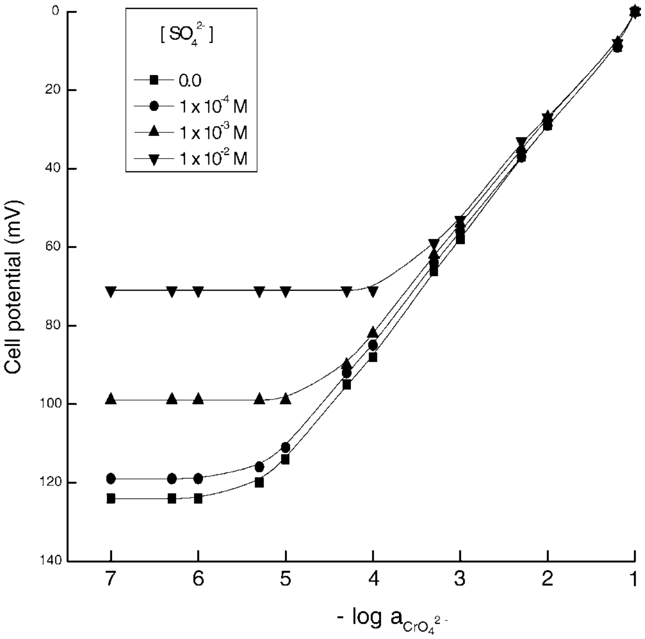

Fig. 5. Variation of cell potential with activity of CrO_4^{2-} at different concentration levels of SO_4^{2-} ions.

tures. Fig. 4 indicated that Cl^- ions present in concentrations $\leq 1.0 \times 10^{-5}$ M can be tolerated over the whole working concentration range of the sensor. However, at higher concentrations, a divergence from the potential versus CrO_4^{2-} activity plot was observed. Thus, the sensor can be used for the estimation of CrO_4^{2-} over reduced concentration ranges 2.2×10^{-5}–1.0×10^{-1} and 2.8×10^{-4}–1.0×10^{-1} M in the presence of 1.0×10^{-4} and 1.0×10^{-3} M Cl^- ions, respectively. Similarly, SO_4^{2-} can be tolerated at a concentration level of $\leq 1.0 \times 10^{-4}$ M over the entire concentration range (Fig. 5) and the working concentration range of the sensor reduces to 2.5×10^{-5}–1.0×10^{-1} and 1.8×10^{-4}–1.0×10^{-1} M in the presence of 1.0×10^{-3} and 1.0×10^{-2} M SO_4^{2-} ions, respectively. Therefore, these studies reveal that the developed sensor is selective over the commonly present interfering ions.

4. Analytical application

4.1. Potentiometric titration

The sensor has been used in the titrimetric determination of chromate ions. Potentiometric titration was carried out by taking 1.0×10^{-3} M CrO_4^{2-} solution (25 ml) and the same was titrated against a 1.0×10^{-1} M Pb^{2+} solution at a pH of ~8.0. Addition of Pb^{2+} to the solution caused the formation of Pb–CrO_4 complex, thereby an increase in potentials as a result of decrease in the concentration of CrO_4^{2-} in the solution. The end point obtained from the potentiometric curve is sharp and corresponds to the 1:1 stoichiometry of Pb^{2+}:CrO_4^{2-} complex (Fig. 6). Therefore, the sensor assembly can be successfully used as an indicator electrode.

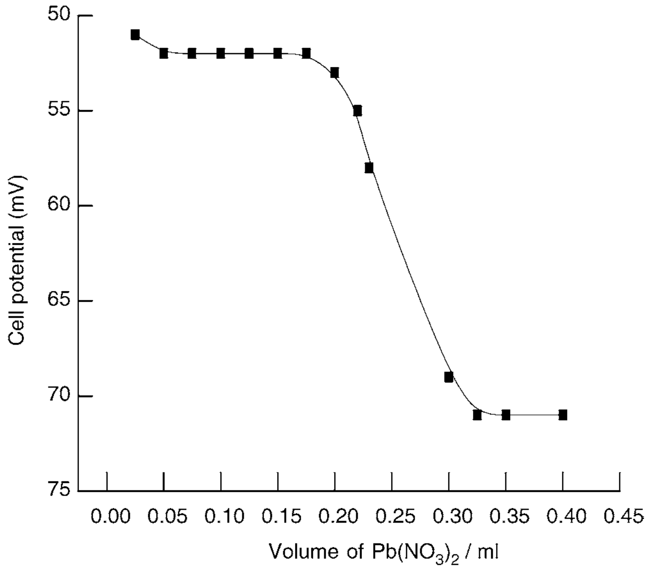

Fig. 6. Potentiometric titration plot of 1.0×10^{-3} M CrO_4^{2-} solution (25 ml) with $Pb(NO_3)_2$ (1.0×10^{-1} M).

Table 3
Determination of chromium in electroplating waste water using AAS and chromate sensor

Samples	pH		Cr(VI) in ppm determined[a]	
	Found	After adjustment	Sensor	AAS
1	2.1	7.2	42.2 ± 0.2	44.1 ± 0.1
2	2.0	7.2	40.1 ± 0.3	41.0 ± 0.2
3	1.9	7.2	41.6 ± 0.2	42.8 ± 0.2

[a] Average of three measurements.

4.2. Analysis of electroplating waste

The proposed chromate sensor has also been used for determining chromium (as chromate) in wastes discharged from electroplating industry. Three samples from a local electroplating unit were collected, filtered and stored without any further pretreatment. Suitable aliquots of sample solution were analyzed, after neutralizing with ammonia within pH

Table 4
Comparison of the proposed CrO_4^{2-} sensor with reported electrodes

S. no.	Reference no.	Detection limit (ppm)	Response time (s)	Life time (month)	Selectivity
1	Granzhan et al. [11]	2.0	NM	NM	Good
2	Hasan et al. [13]	0.4	30	6 weeks	Very good
3	Jain et al. [14]	2.9	20	12	Good
4	Proposed sensor	0.3	13	5	Excellent

NM: not mentioned.

range 7.0–8.0. The analyses were performed by direct potentiometry using calibration plot and the results showed the chromate content in the wastewater obtained from triplicate measurements with the sensor was found to be in agreement with that determined by atomic absorption spectrometry(AAS) (Table 3).

5. Conclusions

The results demonstrate the usefulness of the novel C-thiophenecalix[4]resorcinarene as selective ionophore for the quantification of chromate ions through ion-sensors. The developed sensor exhibits fast, stable, reproducible and selective response over a prolong period. A comparison of proposed sensor with reported electrodes presented in Table 4 indicates that the sensor is superior not only with regard to working concentration range and response time but also with regard to selectivity.

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