Chromium(III)-selective Electrode Using *p*-(4-Acetanilidazo)calix[4]arene as an Ionophore in PVC Matrix

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A new poly(vinyl chloride) membrane, containing synthesized *p*-(4-acetanilidazo)calix[4]arene as a membrane carrier, was used to fabricate a chromium(III) selective electrode. The optimum composition of the best performing membrane contained *p*-(4-acetanilidazo)calix[4]arene:DBBP:NaTPB:PVC in the ratio 10:100:1:100 w/w. This electrode exhibited a near Nernstian slope of 19.8 ± 0.2 mV/decade of activity in the working concentration range of 9.8×10^{-7}-1.0×10^{-1} M. It displayed a stable potential response in the pH range 2.8-5.7. The electrode exhibited a fast response time of less than 14 s and could be used for at least 12 weeks without any considerable divergence in potentials. This electrode showed very good selectivity over most of the common cations including Li^+, K^+, Na^+, Ni^{2+}, Co^{2+}, Cu^{2+}, Sr^{2+}, Ba^{2+}, Cs^+, Pb^{2+}, Zn^{2+}, Mg^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+}, and La^{3+}. It could be employed successfully for the determination of Cr(III) ion activity in real samples.

Key Words : Chromium selective sensor, Calixarene, Ion selective electrodes, Chemical sensor

Introduction

Chromium finds its widespread use in steel manufacturing, leather tanning, wood treatment, electroplating, paint and pigment, metal finishing and alloy manufacturing industries. Chromium is essential for carbohydrate and fat metabolism. Its deficiency may lead to diabetes and cardiovascular diseases. The estimated safe and adequate daily dietary intake for chromium in adults is 50-200 μg per day.[1,2] On the other hand it is well known for its carcinogen effects. Its higher concentration can also cause epigastria pain, nausea, vomiting, diarrhea and hemorrhage. Due to the vital importance of Cr(III) in complex biological systems and industrial systems, environmental and industrial samples, the development of new selective and sensitive method for its quick estimation is a challenging goal. Although sophisticated analytical techniques like AAS, XRF, HPLC, and ICP-AES have been generally employed for the trace level determination of metals, yet these techniques are disadvantageous in terms of routine analysis and cost. Potentiometric monitoring offers many advantages such as simple instrumentation, speed and ease of preparation, low cost, online monitoring, wide dynamic range, good selectivity and nondestructive analysis. Due to these advantages a number of ion selective electrodes have been reported in the recent past[3-11] and the list is continuously growing tremendously.

Diverse ionophores have been introduced for the fabrication of cation selective electrodes which include crown ethers, calixarenes, porphyrines, metal chelates and ligands, Schiff's bases, and macrocylcic compounds.[12-14] Out of these, calixarenes have received attention due to their highly selective complexation behavior towards metal ions. These cyclic oligomers of phenol-formaldehyde condensates are a category of supramolecular receptors exhibiting rigid cavi-

ties, generally in a molecular recognition.[15] A large variety of cation substrates can be complexed by such macrocyclic structures due to the various available cavity sizes and this property of calixarenes has been largely exploited for the development of a number of cation selective electrodes.[16-20] This efficiency depends on the lipophilicity, conformational flexibility and high mobility. Calixarenes, which are appropriately designed, exhibit a large variety of functions *e.g.* as inclusion compounds, selective complexing agents for metal ions, and catalysts. The complexation ability of calixarenes largely depends up on the type of the substituents on the upper and lower rims. Lower rim modifications have been explored extensively due to the ease of substituent's attachment on the hydroxyl group. These substituted calixarenes have been found to possess highly significant ionophoric properties for metal ions. On the other hand, only a little work has been carried out on the upper rim modified calixarenes and efforts are needed in this direction.

This work presents a new, highly selective, and a sensitive Cr(III) electrode based on a synthesized, upper rim substituted calixarene *i.e.* *p*-(4-acetanilidazo)calix[4]arene, as an excellent neutral carrier for chromium(III) ions. This calixarene derivative contains azo groups at the upper rim which serve as the binding site for the metal ions.[21] These circularly arranged ligands form cyclic metal ion receptors which facilitate their selective complexation with metal ions. This suitability has been further confirmed as the PVC membrane electrodes containing *p*-(4-acetanilidazo)calix[4]arene as a neutral carrier, shown a highly selective behavior towards Cr(III) ions. In the present study, various experimental conditions such as; the percentage weight composition of the membrane ingredients, concentration of the internal solution of this ion selective electrode have been optimized to obtain the better detection limit as well as

working concentration range. The prepared electrode has been used for the determination of the Cr(III) ion concentration in real samples.

Experimental Section

Reagents and equipments. Dibutyl(butyl)phosphonate (DBBP) from (Mobil, USA), 1-chloronaphthalene (CN), tris(2-ethylhexyl)phosphate (TEHP), dibutyl phthalate (DBP), tri-*n*-butylphosphate (TBP) and dioctyl phthalate (DOP) from (Merck, Germany), high molecular weight poly(vinyl chloride) (PVC) (Fluka, Switzerland) and sodium tetraphenyl borate (NaTPB) from (BDH, UK) were used as obtained. All the reagents used for this study were of analytical grade. Metal salt solutions were prepared in doubly distilled water. The potential measurements were performed with a multichannel potentiometer (Kosentech, Korea, Model AS MP8). A Perkin-Elmer model 3100 atomic absorption spectrophotometer (AAS) with a graphite furnace was used to determine the concentration of metal ion in the standard solutions.

Synthesis of *p*-(4-acetanilidazo)calix[4]arene. *p*-(4-acetanilidazo)calix[4]arene (I) (Figure 1) was synthesized as described elsewhere.[21] A solution of 4-aminoacetanilide (10 mM) was added slowly into a cold solution of calix[4]arene (2.36 mM) and sodium acetate trihydrate (30 mM) in MeOH-DMF (26 mM; 5:8 v/v) to give a pale brown solid. *p*-(4-acetanilidazo)calix[4]arene, obtained by this procedure was filtered and washed with water and methyl alcohol. It was used after drying completely. The chemical characterization of the synthesized compound was carried out by the spectroscopic methods. The obtained results were similar to those already reported.[21]

Electrode preparation and cell setup. Electrode membranes were prepared as suggested by Craggs *et al.*[22] Varying amounts of the ionophore along with appropriate amount of PVC were dissolved in tetrahydrofuran (THF) solvent. The obtained solution was poured into polyacrylate rings, placed on a smooth glass plate and allowed to evaporate at room temperature in a dust free closet. Transparent mem-
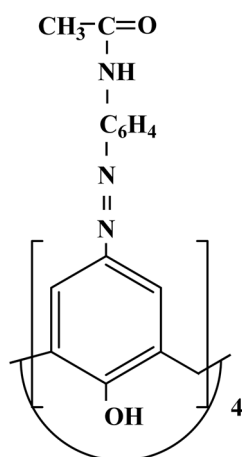
$CH_3-C=O$
|
NH
|
C_6H_4
|
N
‖
N

Figure 1. Chemical structure of *p*-(4-acetanilidazo)calix[4]arene.

brane was obtained after 48 hours. Its circular part having the 5 mm diameter was cut out and attached to one end of a hollow Pyrex glass tube. The effect of different plasticizers e.g. DBBP, CN, TBP, TEP, DBP and DOP as well as the anion excluder *i.e.* sodium tetraphenylborate was also studied. These additives affected the performance of membrane almost in each case. Varying amounts of these compounds were added to the ionophore, PVC, and THF solution prior to pouring it into the acrylic rings. The ratio of membrane ingredients was optimized after a good deal of experimentation. Best efforts were made to prepare a membrane that generates reproducible and stable potentials. Further, the dummy membranes having only PVC as membrane ingredient were also tested to observe whether any background potential is produced due to binding material. Conditioning of all the membranes was done with 0.1 M Cr^{3+} solution. The minimum time required for conditioning was 48 hours otherwise the membranes produced unstable potentials. The potential measurements were carried out using the following cell setup at 25 ± 0.1 °C. Internal reference electrode (SCE)/ Internal solution 0.01 M $CrCl_3$/PVC Membrane/Test solution/External reference electrode (SCE). The saturated calomel electrodes (SCE) were used as internal and external reference electrodes. The concentration of the metal ion in the test solutions varied from 1.0×10^{-7} to 1.0×10^{-1} M. All the standard metal ion solutions were prepared by serial dilution with 1.0×10^{-1} M as stock solution. pH values of diluted solutions were checked and maintained between 3-4. Each solution was stirred and potential readings were recorded. These potential values were plotted against negative logarithmic values of chromium ion activity to obtain the standard calibration curve.

Results and Discussion

Selection of the membrane. In preliminary experiments, the synthesized ionophore was used as a neutral carrier to prepare PVC based membranes and was tried to detect various metal ions. A number of membrane electrodes were prepared and conditioned in 0.1 M solution of different metal ion solutions namely Li^+, Na^+, K^+, Co^{2+}, Zn^{2+}, Cu^{2+}, Hg^{2+}, Cd^{2+}, Pb^{2+}, Ag^+, Ni^{2+}, La^{3+}, Ca^{2+}, Cr^{3+}, and Mg^{2+} solutions for 2-3 days. The best potential response of the electrode was recorded for Cr^{3+} ions while all other ions exhibited lower potential response or no response at all. It suggested that Cr(III) ions could interact with the ionophore to form a better complex with the electron rich cavity in the comparison of the bivalent cations. This may be due to its higher charge and suitability which facilitated its attachment to the ionophore in a better way. Further, the rapid exchange kinetics of the resulting ligand-metal ion complex is responsible for the selective behavior of the ionophore towards Cr^{3+} in comparison to the other trivalent metal ions. Therefore, this membrane was used to develop a chromium(III) ions selective electrode. It is well known that some additives like anion excluders are useful as these compounds enhance the sensitivity and selectivity of cation selective membrane

by reducing its resistance.[23] Also, in case of PVC based neutral carrier membranes, plasticizers if compatible with the ionophore, can provide a smooth surface to the membrane and thus enhance the response characteristics. Although the role of plasticizers is not very firmly established till date but it is assumed that these additives enhance the homogeneity of the PVC based membranes and provide liquid channels within the membrane which facilitates the movement of charge carriers, which ultimately improves the response time and the sensitivity of the membranes. It can also improve the dielectric constant of the polymeric membrane and also the movement of ionophore and its metal complex.[24,25] Therefore, the effect on the performance of the membrane after the addition of anion excluder, sodium tetraphenyl borate (NaTPB) and plasticizers like DBP, DOP, TEP, TBP, CN, and DBBP was also studied. The ratio of membrane ingredients, time of contact and concentration of equilibrating solution were optimized so that the membrane could develop reproducible, noiseless, and stable potentials. Membrane to membrane reproducibility was assured by carefully following the optimum conditions of fabrication.

Effect of the concentration of internal solution on the response of sensor. The performance of the electrode was analyzed by using different concentrations of Cr(III) ions as the internal solution *i.e.* 1.0, 1.0×10^{-1}, 1.0×10^{-2}, and 1.0×10^{-3} M. The best results regarding working concentration range and slope were obtained with an internal solution of activity 1.0×10^{-1} M. For 1.0×10^{-2} and 1.0×10^{-3} M concentrations, a reduced working concentration range *i.e.* 9.8×10^{-7} - 3.2×10^{-2} M (approximately same in both the cases) with a Nernstian slope was obtained while the results obtained for 1.0, and 1.0×10^{-1} M Cr(III) solution were similar. Therefore, 1.0×10^{-1} M Cr^{3+} ion solution was selected as an internal solution for further studies.

Effect of membrane composition on the working concentration range and the slope. The compositions of each best performing membrane and the results obtained for these are presented in Table 1. As expected dummy membranes, containing PVC only produced no potential. It revealed that there was no contribution or interference due to the binding material. It is clear from the data that the membrane containing PVC and ionophore only, in the ratio 10:100 shows a linear response in a narrow concentration range *i.e.* 4.0×10^{-5} - 1.0×10^{-1} M and its slope was record-
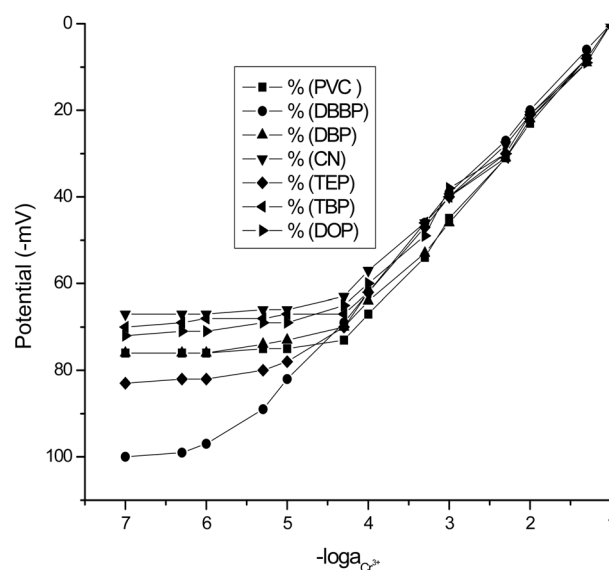

Figure 2. Potentiometric response of the PVC membrane sensor based on *p*-(4-acetanilidazo)calix[4]arene in the presence of different plasticizers.

ed as 23 mV/decade of activity (Figure 2). The addition of anion excluder *i.e.* sodium tetraphenyl borate and plasticizers DBP, DOP, TEP, TBP, CN, and DBBP changed the response characteristics of all the membranes. The best working concentration range obtained for DBBP *i.e.* 9.8×10^{-7} - 1.0×10^{-1} M with a slope of 19.8 mV/decade of activity. This is due to the best homogeneity provided by DBBP and its compatibility to the membrane ingredients which resulted in the best obtained working concentration range and the Nernstian slope. Also, the response time for DBBP was the lowest, among all other studied membrane compositions, containing different plasticizers. Further, as the response characteristics of any membrane depend on the amount of ionophore, the effect of changing quantity of ionophore was also studied. The optimum ratio of best performing membrane is 10:1:100:100 for I:NaTPB:DBBP: PVC. If the amount of ionophore is less than this ratio, it affects the working concentration range adversely, although the effect on slope is not considerable. If the amount is increased further, it shows no improvement in any of the characteristics of the electrode. Therefore, membrane no. 7 was the best performing membrane and this composition

Table 1. Compositions and response characteristics of PVC based membranes having *p*-(4-acetanilidazo)calix[4]arene as electroactive material

S. No	(I)	DBP	DOP	CN	TEP	TBP	DBBP	NaTPB	PVC	Slope ± 0.2 mV/ decade of activity	Response time (s)	Working concentration range (M)
1	10							1.0	100	23.0	~90	7.5×10^{-5} - 1.0×10^{-1}
2	10	80						1.0	100	22.0	45	8.0×10^{-5} - 1.0×10^{-1}
3	10		110					1.0	100	20.0	20	5.6×10^{-5} - 1.0×10^{-1}
4	10			150				1.0	100	20.6	25 - 35	3.8×10^{-5} - 1.0×10^{-1}
5	10				150			1.0	100	20.5	22	8.1×10^{-6} - 1.0×10^{-1}
6	10					170		1.0	100	21.0	24	9.0×10^{-5} - 1.0×10^{-1}
7	10						100	1.0	100	19.8	14	9.8×10^{-7} - 1.0×10^{-1}

was selected for further studies.

   Response time and life time. Membrane no. 1, prepared without any plasticizer exhibited a response time of about 90 s which was reduced marginally when the solvent mediators were added. The best response time was observed for the membranes having plasticizers DBBP, CN and DOP. However, in case of CN and DOP, the slope deteriorated and did not remain within Nernstian or near-Nernstian values in these cases (Table 1) while for membrane containing DBBP (membrane no. 7), the response time was recorded as 14s and its slope also remained near-Nernstian. The potentials generated by this membrane remained stable for more than 3 min and then deviate very slowly. It is important to mention that at higher concentration, the response time was quite low for each membrane while the reported response times are for the lowest working concentrations. To investigate the life time, the electrode was used daily over a period of 12 weeks and its working concentration range and slope were recorded. The results, presented in Table 2, suggest that the proposed electrode works well up to a period of 12 weeks without any significant change in the working concentration range or the slope. After this period their properties start changing considerably and the electrode can not be used further. Therefore, the life time of this electrode has been estimated as 12 weeks. However, the electrode was re-equilibrated with a 0.5 M Cr^{3+} solution whenever any drift in the potential was observed. During routine usage also, the electrode was kept dipped in a 0.1 M Cr^{3+} solution whenever it was not in use to avoid cracking or poisoning of the membrane. Repeated monitoring of potentials (20 measurements) on the same portion of the sample (1.0×10^{-3} M) gave a standard deviation of 0.4 mV, while the deviation for the slope was found to be 0.2 mV.

   pH dependence of the potential response. pH dependence of the proposed ion-selective electrode was studied over the pH range 2.0-7.0 at the 1.0×10^{-3} M Cr^{3+} concentration after adjusting the pH of the solutions with HNO_3 and NaOH (Figure 3). It is clear that the potential remained constant in the pH range 2.8-5.7, which can be considered as the working pH range of the proposed sensor. Above this pH range, a
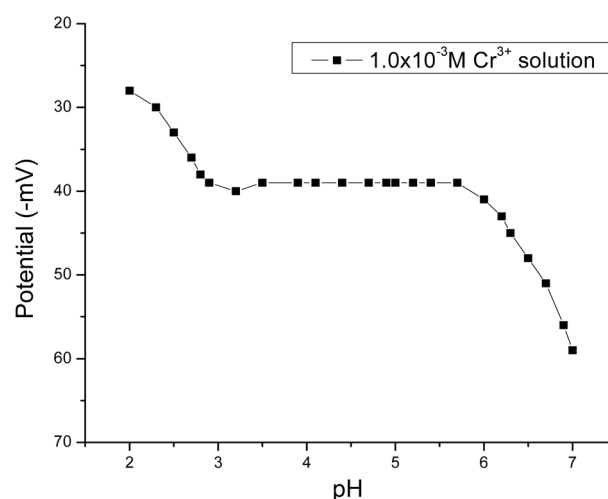

Figure 3. Effect of pH on the cell potential of electrode no. 7.

sharp decrease in potentials may be attributed to the hydrolysis of chromium ions and formation of some soluble or insoluble hydroxyl complexes while for pH values below this range, the increase in potentials may be due to the increased competition of hydrogen ions flux, and the sensor may be exhibiting response to hydrogen ions also.

   Potentiometric selectivity. The influence of interfering ions on the response behavior of ion-selective membrane electrodes is usually described in terms of selectivity coefficients. The fixed interference method and the mixed solution method are among the most commonly used to determine the selectivity coefficient of the sensors. However, these methods suffer some limitations if ions of unequal charges

Table 2. The observed working concentration range of slope of the chromium(III)-selective electrode observed per week

Number of weeks	Working concentration range (M)	Slope ± 0.2 mV/ decade of activity
1	9.8×10^{-7} - 1.0×10^{-1}	19.8
2	9.8×10^{-7} - 1.0×10^{-1}	19.8
3	9.8×10^{-7} - 1.0×10^{-1}	19.8
4	9.9×10^{-7} - 1.0×10^{-1}	19.8
5	1.1×10^{-6} - 1.0×10^{-1}	19.9
6	1.1×10^{-6} - 1.0×10^{-1}	19.8
7	1.5×10^{-6} - 1.0×10^{-1}	19.6
8	1.6×10^{-6} - 1.0×10^{-1}	19.6
9	1.9×10^{-6} - 1.0×10^{-1}	19.3
10	2.2×10^{-6} - 1.0×10^{-1}	19.1
11	2.2×10^{-6} - 1.0×10^{-1}	19.0
12	2.7×10^{-6} - 1.0×10^{-1}	18.9

Table 3. Potentiometric selectivity coefficient values ($K^{Pot}_{Cr^{3+},B}$) (interfering ions B), observed for the fabricated Cr^{3+} selective electrode, using matched potential method

Interfering ion B	Matched potential method
Li^+	1.1×10^{-3}
NH_4^+	1.6×10^{-3}
Na^+	2.9×10^{-3}
K^+	2.7×10^{-3}
Ag^+	5.1×10^{-3}
Hg^{2+}	3.2×10^{-4}
Cu^{2+}	2.4×10^{-4}
Ni^{2+}	7.3×10^{-4}
Co^{2+}	3.6×10^{-4}
Ca^{2+}	4.1×10^{-4}
Cd^{2+}	1.9×10^{-4}
Mg^{2+}	2.7×10^{-4}
Ba^{2+}	4.8×10^{-4}
Pb^{2+}	6.9×10^{-4}
Zn^{2+}	3.7×10^{-4}
Sr^{2+}	1.1×10^{-3}
Cs^+	4.5×10^{-3}
Al^{3+}	1.2×10^{-3}
Fe^{3+}	5.7×10^{-2}
La^{3+}	7.0×10^{-3}

Table 4. Data for the Cr^{3+} concentration determined in waste water samples by AAS and the electrode no. 7

Sample no.	pH found	pH after adjustment	Cr^{3+} concentration as determined by the sensor (ppm)	Cr^{3+} concentration as determined by AAS (ppm)
1	2.1	3.5	5.30 ± 0.05	5.40 ± 0.01
2	2.0	3.5	6.20 ± 0.08	6.30 ± 0.01
3	5.6	3.5	12.80 ± 0.07	12.60 ± 0.01
4	5.2	3.5	13.20 ± 0.04	13.30 ± 0.01

Sample no. 1 and 2 are from electroplating industry while sample no. 3 and 4 are from lather tanning industry

Table 5. Comparison of proposed Chromium(III)-selective electrode with some of the existing electrodes

Ionophore used	Working concentration range (M)	Detection limit (M)	Working pH range	Interference	Response time (s)	Ref. no.
Aurin TCA	7.0×10^{-6} - 1.0×10^{-1}	NM*	3.5 - 6.5	Na^+, Zn^{2+}, Pb^{2+}	10	3
Oxalic acid bis(cyclohexylidine)-hydrazide	1.0×10^{-7} - 1.0×10^{-2}	6.3×10^{-7}	1.7 - 6.5	Cd^{2+}, Ni^{2+}	20	4
Tetradentate macrocycle	3.16×10^{-6} - 1.0×10^{-1}	NM	3.0 - 6.5	Zn^{2+}, Mg^{2+}	15	5
Tetraazacyclooctadecane	1.77×10^{-6} - 1.0×10^{-1}	NM	3.0 - 6.5	NM	15	7
4-Dimethyl aminobenzene	1.66×10^{-6} - 1.0×10^{-2}	8.0×10^{-7}	3.0 - 5.5	Cu^{2+}, Ag^+, Fe^{3+}	10	8
Glyoxal bis(2-hydroxyanil)	3.0×10^{-6} - 1.0×10^{-2}	6.3×10^{-7}	2.7 - 6.5	Zn^{2+}	20	9
Tri-*o*-thymotide	4.0×10^{-6} - 1.0×10^{-1}	2.0×10^{-7}	2.8 - 5.1	Na^+, Cd^{2+}	15	10
N,N'-Bis(acetoacetanilide)-triethylenetetraamine	8.3×10^{-7} - 1.0×10^{-1}	6.3×10^{-7}	2.0 - 5.5	NM	22	11
p-(4-Acetanilidazo)calix[4]arene	9.8×10^{-7} - 1.0×10^{-1}	7.3×10^{-7}	2.8 - 5.7	No interference	14	Proposed work

*Not Mentioned

are involved. Thus, in this work we followed the matched potential method (MPM),[26] which is totally independent of the Nicolsky-Eisenman equation and also the varying charge of interfering ions. According to MPM, primary ions (A), in a specified activity, are added to a reference solution containing fixed concentration of primary ions and the potential change is recorded. In a separate experiment, interfering ions (B) are successively added to an identical reference solution, until the measured potential matched the one obtained before by adding primary ions. A value of selectivity coefficient equal to 1.0 indicates that the sensor responds equally to the primary as well as an interfering ion. However, a value smaller that 1.0 indicates that the membrane sensor is responding more to the primary ion than an interfering ion and in such a case the sensor is said to be selective to the primary ion over interfering ions. Further, smaller the selectivity coefficient, higher is the selectivity order. The MPM selectivity coefficient, $K_{A,B}^{MPM}$, is given by the resulting primary ion to interfering ion activity (concentration) ratio, $K_{A,B}^{MPM} = (a'_A - a_A)/a_B = \Delta a_A/a_B$. The values of a_A and a'_A were taken to be 1.0×10^{-3} and 5×10^{-3} M, whereas the value of a_B was experimentally determined. The experimental conditions employed and the resulting values are given in Table 3. It is clear from the obtained data, that selectivity coefficient values are much smaller than 1 for almost all the mono, di or trivalent caions. Hence, the electrode shows good selectivity towards chromium(III) ions over other cations.

Analysis of real samples. Two samples each from an electroplating industry and other from a lather tanning industry were collected and analyzed for the Cr (III) concentration by using the developed electrode. The waste

samples were pretreated to convert Cr(VI) to Cr(III),[27] and pH of the samples were adjusted at 3.5. The obtained results were compared with those obtained by using the Atomic Absorption Spectrophotometer (Table 4). It is clear that the results obtained using both the techniques are comparable and the developed electrode can be successfully used to determine Cr(III) in real samples.

Conclusion

An upper rim modified calixarene compound, has been used as a neutral carrier in PVC matrix, for the fabrication of a highly selective potentiometric electrode for chromium-(III) ions. The response time of this ion selective electrode is low and it can successfully be used for 12 weeks. It works well in the pH range 2.8-5.7 and shows good selectivity for Cr(III) in the presence of other foreign cations which are generally present along with Cr(III) in real samples. A comparative study reveals that proposed electrode is better than some of the existing electrodes in the characteristics namely response time,[4,5,7,9-11] and selectivity,[3-5,7-9,10] while it shows comparable results for the pH range, and working concentration range[8-11] (Table 5).

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