Anal Bioanal Chem (2002) 372 : 506–510
DOI 10.1007//s00216-001-1134-5

ORIGINAL PAPER

Ashok Kumar Singh · Amit Panwar · Rupam Singh
Seema Baniwal

A new macrocyclic polystyrene-based sensor for chromium (III) ions

Received: 16 June 2001 / Revised: 28 August 2001 / Accepted: 8 September 2001 / Published online: 11 January 2002

Abstract A new tetradentate dihydrogen perchlorate macrocyclic ligand (2,4,9,11-tetraphenyl-1,5,8,12-tetraazacyclotetradeca-1,4,8,11-tetraene dihydrogen perchlorate) was prepared and characterised. The macrocycle behaves as a selective chelating ion-exchanger for some metal ions. The polystyrene-based membrane electrode is found to exhibit quite promising selectivity for Cr^{3+} ions. It can be used to estimate chromium concentrations in the range 3.16×10^{-6}–1.00×10^{-1} M with a near-Nernstian slope of 17.5 mV per decade of concentration between pH 3.0 to 6.5. The electrode is found to possess a fast response time of 15 s and was used over a period of three months with good reproducibility ($s = \pm 0.3$ mV). The selectivity coefficient values for mono-, di- and trivalent cations indicate excellent selectivity for Cr^{3+} ions over a large number of other cations. Anions such as Cl^- and SO_4^{2-} do not interfere and the electrode also works satisfactorily in a mixed organic-water solution. The sensor has been used as an indicator electrode for the potentiometric titration of Cr^{3+} with EDTA. The practical utility of the membrane sensor has also been demonstrated in solutions contaminated with detergents (CTAB and SDS). Above all, the membrane sensor has been very successfully used to determine Cr^{3+} in some foods.

Keywords Chromium (III)-selective electrode · Sensor · Macrocycle

Introduction

Ion-selective electrodes (ISEs) provide a convenient and fast method for the determination of metal ions. In the past few decades, considerable efforts have led to the development of selective sensors for alkali and alkaline earth metals as well as for heavy metals. Among the heavy metals, trivalent ones have received less attention in spite of their widespread occurrence in food products, sea- and fresh water, plants and animals [1].

A literature survey revealed that very little work has been done on the development of ISEs for trivalent ions, e.g., Cr^{3+}, Al^{3+} , Bi^{3+}, Au^{3+}, etc. Few electrodes have been reported. These include the Au^{3+} selective electrode, based on the membrane of tetraphenylarsonium tetrachloroaurate immobilized in PVC, which was employed for the determination of gold in minerals [2]. Ortuno and coworkers [3] used an $[AuCl_4]^-$selective electrode based on a mixture of 1,2,4,6-tetraphenyl pyridinium tetrachloroaurate, dibutyl phthalate and PVC for the estimation of gold in Ag-Pd-Au alloys. Another coated graphite epoxy ion-selective electrode for Bi^{3+} based on the ion pair between the [Bi(EDTA)] anion and tricapryl methyl ammonium cation (Aliquat 3365) incorporated onto a poly(vinyl chloride) matrix has been developed by Teixiera and coworkers [4].

Among trivalent ions, chromium is regarded as vital trace element in humans. In view of the wide spread occurrence of chromium, efforts were initiated to develop a Cr^{3+}-selective electrode [5]. Recently, we reported a PVC-based membrane electrode exhibiting excellent selectivity for Cr^{3+} ions [6]. In this paper we report the use of $[Ph_4(14)\text{-tetraene}]\cdot 2HClO_4$ as a sensor material for a polystyrene-based membrane electrode. These macrocyclic compounds have attracted a great deal of attention as artificial ionophores [17]. These ‘armed’ macrocycles, as result of their structural characteristics, bind metal cations with varying degrees of strength and, therefore, are suitable electroactive materials for the use in membrane electrodes [8].

The results presented herein show that the polystyrene-based macrocyclic membrane electrode has a wide working concentration range, a fast response time and shows reproducible results.

Experimental

Reagents and apparatus

All reagents were of analytical grade. Doubly distilled water was used for the preparation of metal salts solutions of different con-

A.K. Singh (✉) · A. Panwar · R. Singh · S. Baniwal
Department of Chemistry,
Indian Institute of Technology-Roorkee, Roorkee 247 667, India,
e-mail: akscyfcy@isc.rurkiu.ernet.in

centrations by dilution of standard stock solutions. Organic solvents were purified by distillation and purity was checked by measuring the boiling points. Food items were purchased from the local market.

Potentiometric and pH measurements were made at 25±0.1 °C with an ECIL (Hyderabad, India) pH digital pH/potentiometer, in conjunction with saturated calomel electrodes (SCE) as reference electrodes. IR spectra of the ligand were recorded on a Perkin-Elmer 1600 series FTIR in the range 4000–650 cm^{-1} and ^1H NMR were recorded on Bruker DRX 300 NMR spectrometer.

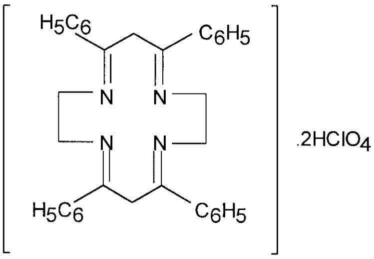
Synthesis and characterisation of the ligand

The ligand was prepared as follows: 6.68 mL (0.1 M) of ethylene diamine was dissolved in a minimum quantity of methanol and cooled in an ice bath to about 5 °C. 22.42 g (0.1 M) of 1,3-diphenyl-1,3-propanedione (diluted with 10 mL of methanol) was then added. The solution was slowly heated to reflux for 4 h, then cooled and 6.0 mL (0.1 M) of 68% perchloric acid was added slowly under constant stirring. This gave fine crystals of the ligand which were then washed with a small quantity of ether, recrystallised from methanol and dried under vacuum over P_4O_{10} to afford the compound with a melting point of 135 °C.

In IR spectra, the characteristic bands for the ligand appeared in the region 1630–1660 cm^{-1} and were assigned as C=N vibrations [9,10]. The observed adsorption bands in the visible and ultraviolet regions were also recorded (not given in this manuscript) and the spectral behaviour was consistent with the square planer co-ordination [11] of the compound.

^1H NMR of the ligand in DMSO gave singlets at 2.74 ppm and a multiplet at 6.80–7.36 ppm attributable to the CH_2 (4H) protons and the C_6H_5 (20H) protons of 1,3-diphenyl-1,3-propanedione, respectively. A singlet observed at 3.37 ppm was assigned to the CH_2 (8H) protons of ethylene diamine.

The observed elemental analysis of the compound was consistent with the theoretical data obtained on the basis of the following structure:



Found: C, 75.28; H, 6.20; N, 10.38; Cl, 6.60%. Calcd. for $C_{34}H_{34}N_4O_8Cl_2$: C, 75.34; H, 6.32; N, 10.33; Cl, 6.54%.

Electrode preparation

A number of membranes [16, 17, 18, 19, 20, 21] were prepared which were of adequate strength using the minimum amount of binder (polystyrene),which gave reproducible and stable potentials with fast response times and which did not develop cracks on prolonged use. To meet these requirements, compositions varying in the ratio of macrocycle to polystyrene were tested (Table 1). The mixture was heated to 80 °C (the softening point of polystyrene) under a pressure of 6000 to 6500 psi (1 psi=6894.76 Pa) in a dye kept in a metallurgical specimen mount press. Membranes were fabricated under optimum conditions of temperature and pressure which were established after lengthy preliminary investigations. Following preparation, the membranes were investigated under a microscope to observe the surface cracks and homogeneity. Suitable membranes were then exposed to electrochemical examination and only those membranes which gave reproducible and stable potentials with a fast response time were selected for further studies. Membrane to membrane (and batch to batch) reproducibility was assured by carefully controlling the production conditions. The membrane (2.5 cm diameter and 0.5 mm thick) was affixed to one end of a small pyrex glass tube with Araldite, while the other end remained open.

Potential measurements

The membranes were equilibrated with l.0 M chromium (III) chloride solution for 3 days – the optimum time necessary for generating reproducible and stable potentials with low noise when interposed between the test and internal reference solution of 1.00×10^{-1} M concentration. Potentials were measured by direct potentiometry [1] at 25±0.1 °C using ceramic junction calomel electrodes as the internal and external reference electrodes and a nitrate salt bridge. The cell set up was the same as that reported earlier [12,13]. pH adjustments were made with nitric acid or ammonia solutions.

Internal reference electrode (SCE)	Cr^{3+} 0.1M internal solution	Membrane	Test solutions	External reference electrode (SCE)

Evaluation of selectivity coefficient

The potentiometric selectivity of the membrane was evaluated in terms of selectivity coefficients using the fixed interference method [14].

Sample preparation and estimation of Cr^{3+}

The dry ashing method [15] with ash aid solution was used for hydrogenated vegetable oil and chyawanprash was used for preparing the samples for chromium estimation.

Hydrogenated vegetable oil (HVO) and chyawanprash

5 g of the sample was taken in a silica crucible and to this 2 mL of ash aid solution were added. This mixture was then heated overnight at 400–450 °C in a muffle furnace. The ash obtained was dissolved in 2 mL HNO_3 and 1 mL HCl. It was then stirred on a hot

Table 1 Composition of polystyrene-based membranes of [Ph_4(14)tetraene]·$2HClO_4$ and their performance characteristics as Cr^{3+} – selective electrodes

Membrane number or Electrode number	Composition of membrane (w/w)		Working concentration range (M)	Slope (mV) per decade of concentration	Response time (s)
	[Ph_4(14) tetraene]	Polystyrene			
1	2	1	9.44×10^{-6}–1.00×10^{-1}	22.2	20
2	4	1	3.16×10^{-6}–1.00×10^{-1}	17.5	15
3	6	1	7.06×10^{-6}–1.00×10^{-1}	19.0	20
4	8	1	1.58×10^{-5}–1.00×10^{-1}	19.5	20
5	10	1	1.12×10^{-5}–1.00×10^{-1}	17.3	30

plate until the organic residue was completely oxidised. The solution was then filtered and made up to a final volume of 25 mL with distilled water. The solutions were placed in sealed brown bottles and were used directly for atomic absorption spectrometry analysis (using a Perkin Elmer AAS ICP 6500) and also by the sensor developed for this purpose after adjusting the pH of the sample.

Results and discussion

Response and life time

The response time indicated in Table 1 was calculated as the time necessary to reach 90% of the final steady value. The values presented correspond to the mean of several experiments taken over 2 months, and did not show any alteration during this period. The static response time of the proposed membrane (i.e., the time in which stable and constant potentials are reported) was almost 15 s in the entire working concentration range and the potentials stayed constant for more than three minutes after which a very slow divergence was observed. The standard deviation for twenty identical potential measurements at 1.00×10^{-3} M concentration of Cr^{3+} ions (reference solution=1.00×10^{-1} M) was ± 0.3 mV.

Under laboratory conditions, the membrane, if properly stored in distilled water and if cross-contamination is avoided, can be used for a period of three months without observing any drift in potentials, response time, slope or detection limit. Thereafter, a slight change in slope and response time was observed, however, this could be corrected by re-equilibrating the membrane with 1.00 M Cr^{3+} solution for 7 h (less time was needed relative to the initial equilibration time). With this treatment the assembly could be re-used for 3 months and then replaced by a fresh membrane.

Working concentration range and slope

The potential response of the membrane obtained with pure solutions is illustrated in Fig. 1. It is noteworthy that the membrane electrode no.2 with a composition of 4:1 polystyrene:ligand showed the best results and could measure Cr^{3+} ions in the range 3.16×10^{-6}–100×10^{-1} M as per IUPAC recommendations and it also exhibited near–Nernstian behaviour (slope of 17.5 mV/decade of concentration).

pH and non-aqueous solvent effect

The pH dependence of the membrane sensor was tested over the range 1.0–9.0 at two concentrations of Cr^{3+} ions (1.00×10^{-2} and 1.00×10^{-3} M) and is shown in Fig. 2. Potentials stayed constant from pH 3.0 to 6.5 and this was taken as the working pH range of the proposed assembly. The pH was adjusted with nitric acid or ammonia solution. It has been observed that in the pH range 3.0–6.5, trivalent chromium will exist as $CrOH^{2+}$ since the basic salt has some solubility and Cr(III) remains in the solution; in this pH range the response of the electrode is, therefore, due to $CrOH^{2+}$.

In order to demonstrate the utility of the electrode assembly in mixed organic-water solution, the potentials were recorded in solutions of chromium ions containing 15, 25 and 45% v/v ethanol and methanol as the organic content. Results are depicted in Fig. 3. The membrane sensor seemed to work well in solutions with 25% and 30% organic content while solutions with 45% organic content disturbed the functioning of the membrane. In

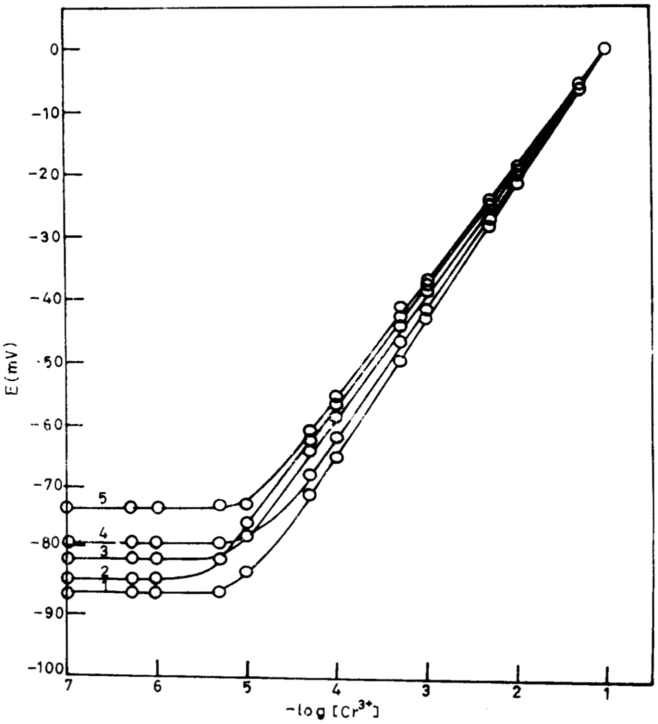


Fig. 1 Variation of membrane potentials of macrocyclic ligand with concentration of Cr^{3+} ions (taken as chromium chloride)

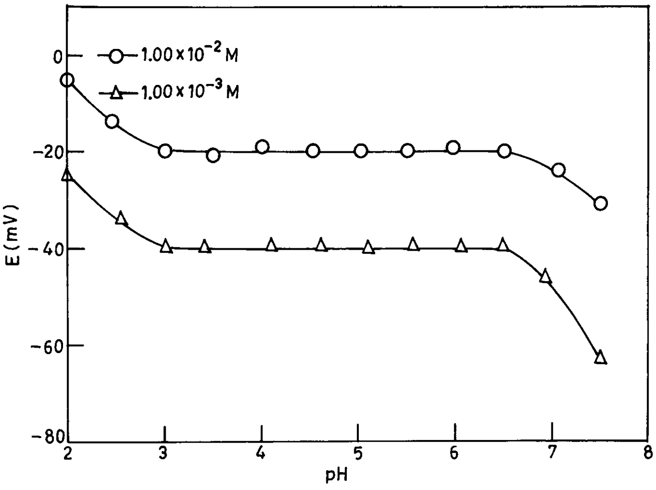


Fig. 2 Variation of membrane potentials with pH at 1.00×10^{-2} and $1.00\times10^{-3}[Cr^{3+}]$

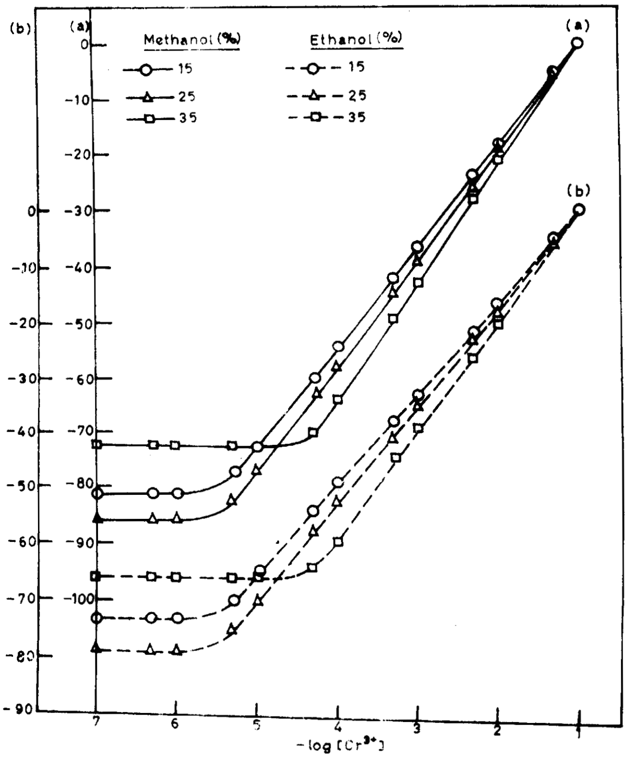


Fig. 3 Potential vs. log[Cr^{3+}] in solvents having non-aqueous content of (*a*) methanol and (*b*) ethanol

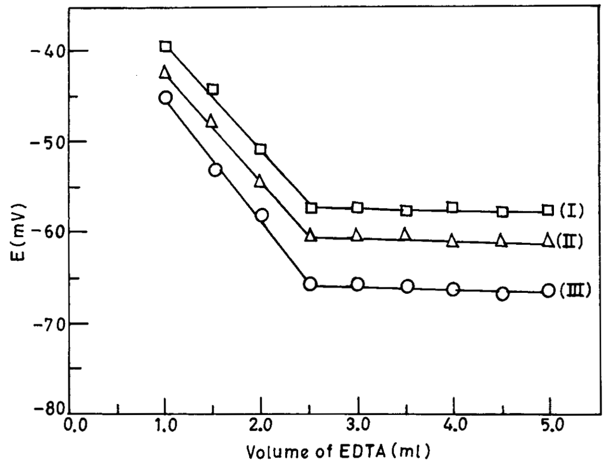


Fig. 4 Potentiometric titrations of 25 mL of (I) 1.00×10^{-3} M Cr^{3+} solution, (II) 10^{-3} M Cr^{3+} + 10^{-4} M Al^{3+}, (III) 10^{-3} M Cr^{3+} + 10^{-4} M Bi^{3+}

these mixtures the working concentration range and slope remained almost constant. However, the slope was found to change above a 25% non-aqueous content.

Potentiometric titration and effect of surfactant

The sensor assembly was used as an indicator electrode in the potentiometric titration of Cr^{3+} with EDTA (Fig. 4). A 25 mL volume of a 1.00×10^{-3} M solution of Cr^{3+} was titrated against 1.00×10^{-2} M solution of EDTA. The addition of EDTA caused a decrease in potential as a result of the decrease in Cr^{3+} concentration due to its complexation with EDTA. The potentiometric titrations of Cr^{3+} could also be successfully carried out in presence of Al^{3+} and Bi^{3+} (Fig. 4). Thus, these plots demonstrate the usefulness of the developed sensor for the potentiometric determination of Cr^{3+} in the presence of other metal ions.

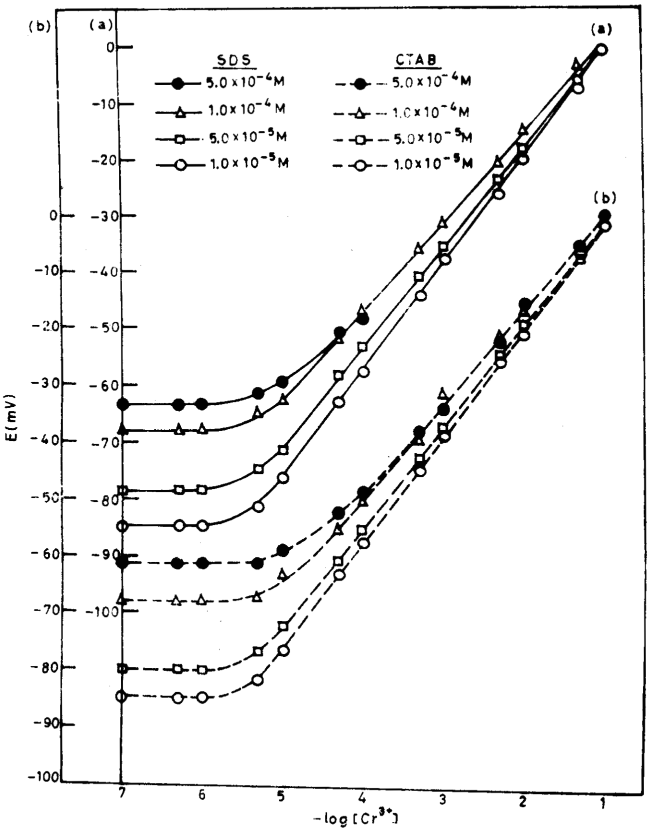


Fig. 5 Potential vs. log[Cr^{3+}] plots in presence of (*a*) cetyl trimethyl ammonium bromide (CTAB) and (*b*) sodium dodecyl sulfate (SDS)

The proposed electrode assembly may also been applied to estimate the metal ions in presence of detergents and other similar substances. The applicability of membrane sensors containing varying concentrations of cetyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) and the potential response are illustrated in Fig. 5. It is evident that smaller concentrations of these surfactants (<5.00) do not disturb the functioning of the membrane sensor. Higher concentrations ($\geq1.00\times10^{-4}$ M) may cause interference as the working concentration range and slope decreased with increasing concentration of surfactant ions. Since surfactants were likely to be present in trace amounts only, no interference was to be expected when using the sensor under these conditions.

Table 2 Selectivity coefficient values (K^{pot}) of interfering ions for the membrane electrode for chromium ion

Interfering ions (B)	Selectivity coefficient by fixed interference method (at 1.00×10^{-2} M concentration of interfering ions)
Li^+	$1.80 \times 10^{-1} \pm 0.11$
K^+	$1.50 \times 10^{-1} \pm 0.08$
NH_4^+	$1.58 \times 10^{-1} \pm 0.04$
Zn^{2+}	$1.33 \times 10^{-1} \pm 0.12$
Na^+	$1.30 \times 10^{-1} \pm 0.19$
Mg^{2+}	$3.55 \times 10^{-2} \pm 0.24$
Fe^{3+}	$2.82 \times 10^{-2} \pm 0.06$
Ba^{2+}	$1.41 \times 10^{-2} \pm 0.21$
Ca^{2+}	$1.12 \times 10^{-2} \pm 0.15$
Sr^{2+}	$1.00 \times 10^{-2} \pm 0.13$
Pb^{2+}	$8.91 \times 10^{-3} \pm 0.10$
Cd^{2+}	$7.94 \times 10^{-1} \pm 0.07$
Ni^{2+}	$2.66 \times 10^{-3} \pm 0.07$
Cu^{2+}	$2.37 \times 10^{-3} \pm 0.19$
Hg^{2+}	$1.41 \times 10^{-4} \pm 0.28$
Al^{3+}	$7.50 \times 10^{-4} \pm 0.12$
Bi^{3+}	$7.08 \times 10^{-4} \pm 0.18$
Co^{2+}	$3.76 \times 10^{-1} \pm 0.18$

Table 3 Chromium concentrations in various food items

Sample number (N)	Sample	Make	Average chromium concentration (mg mL^{-1}) obtained	
			AAS	Proposed electrode
1	Vegetable oil	Darpan	6.50 ± 0.12	6.20 ± 0.20
		Gagan	5.61 ± 0.11	5.31 ± 0.30
		Ladla	2.83 ± 0.21	2.53 ± 0.14
2	Chayawanprash (Ayurvedic health booster)	–	0.60 ± 0.05	0.42 ± 0.03

Potentiometric selectivity

The potentiometric selectivity coefficients were determined by the modified fixed interference method [20] and also as suggested by Viteri and Diamond [21] at a $l.00 \times l0^{-2}$ M concentration of interfering ions. The selectivity coefficient data (Table 2) indicate good selectivity for mono-, di- and trivalent cations. As such, these were not expected to interfere even at this higher concentration level.

Estimation of Cr^{3+} in various food items

The electrode was successfully used for the estimation of Cr^{3+} in various food items. No other treatment of the sample was necessary except pH adjustments. The results (Table 3) indicate a very good correspondence between the two values (one obtained by AAS and the other using the sensor under investigation). This also demonstrates the practical utility of the sensor.

Conclusions

A membrane sensor incorporating 2,4,9,11-tetraphenyl-l,5,8,12-tetraazacyclotetradeca-l,4,8,l1-tetraene dihydrogen perchlorate as the electroactive phase can estimate Cr^{3+} ions in the concentration range 3.16×10^{-6}–1.00×10^{-1} M. The functional pH range is 3.0–6.5 and the sensor exhibited good reproducibility over a useful lifetime of three months. The ions that interfere with Cr^{3+} electrodes do not cause any significant disturbance with this assembly. Furthermore, the electrode can be used to determine Cr^{3+} ions both by direct potentiometry and titration and can be successfully used in non-aqueous media. The proposed sensor was successfully applied to the estimation of Cr^{3+} in real samples.

Acknowledgements A. Panwar is grateful to CSIR, India for providing financial assistance in the form of a senior research fellowship.

References

1. Parker SP, Hill MG (1984) Concise Encyclopaedia of Science and Technology, McGraw-Hill, New York, 390
2. Hua H, Cau M, Zhon Q, Wei G (1982) Fenxi Huaxue 10:65
3. Ortuno JA, Perez-Ruiz T, Sanchez-Pedrevo C (1986) Anal Chim Acta 185:351
4. Teixeira MFS, Pinto AZ, Fatibello-Filho O (1997) Talanta 45:249
5. Abbaspour A and Izadyar A (2001) Talanta 53:1009
6. Singh AK, Panwar A, Kumar S, Baniwal S (1999) Analyst 124:521
7. Kimura K, Shono T (1990) In: Y. Inoue, G.W. Gokel (eds) Cation binding by macrocycles. Complexation of cationic species by crown ethers. Marcel Dekker, New York, pp 429–463
8. Tsukube H, (1993) Talanta 40:1313
9. Holtzman MS, Cummings SC (1977) Inorg Chem 15:660
10. Welsh WA, Reynold GJ, Henry PM (1977) Inorg Chem 16:2558
11. Lever ABP (1984) Inorganic electronic spectroscopy. Elsevier, Amsterdam
12. Singh AK, Bhattacharjee G, Singh M, Chandra S (1997) Electroanalysis 9:1005
13. Baniwal S, Chandra S, Panwar A, Singh AK (1999) Talanta 50:499
14. Lakshminarayaniah N, Subrahmanyam V (1968) J Phys Chem 72:4314
15. Jacob MB (1951). In: The chemical analysis of foods and food products, 2nd edn. Van Noslt, New York, p 182
16. Morf WE, Kahr G, Simon W (1974) Anal Lett 7:9
17. Morf WE, Ammann D, Simon W (1974) Chimia 28:65
18. Ammann D, Morf WE, Anker P, Meier PC, Pretsch E, Simon W (1983) lon-Sel Electrode Rev 5:3
19. Meier PC, Morf WE, Laubli M, Simon W (1984) Anal Chim Acta 156:1
20. Bakker E, Pretsch E, Buhlmann P (2000) Anal Chem 72:1127
21. Saex de Viteri FJ, Diamond D (1994) Analyst 199:749