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Abstract

A poly(vinyl chloride) membrane based on glyoxal bis(2-hydroxyanil) as membrane carrier was prepared and investigated as a Cr(III)-selective electrode. The electrode has a linear dynamic range of $3.0 \times 10^{-6} - 1.0 \times 10^{-2}$ mol l^{-1}, with a Nernstian slope of 19.8 ± 0.5 mV per decade and a detection limit of 6.3×10^{-7} mol l^{-1}. It has a fast response time of < 20 s and can be used for at least 3 months without any considerable divergence in potential. The proposed electrode revealed good sensitivities for Cr(III) over a wide variety of metal ions and could be used in a pH range of 2.7–6.5. Above all, the membrane sensor has been used very successfully for the analysis of some food materials and alloys for the determination of Cr(III) ion.
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Keywords: Ion-selective electrode; Glyoxal bis(2-hydroxyanil); Chromium (III) ion selective electrode

1. Introduction

The increasing use of ion sensors in the fields of environmental, agricultural and medicinal analysis is stimulating analytical chemists to develop new sensors for the fast, accurate, reproducible and selective determination of various species. In the past few decades, considerable efforts have led to the development of selective sensors for alkali, alkaline earth and heavy metals. Among heavy metals, trivalent metals 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 a large number of ISEs based on PVC membrane were reported for many inorganic ions [2], but very little was published on PVC-based trivalent ions. The first report on Cr(III) was in 1980 [3] in which study a PVC based chromium-wire electrode was made by incorporating (Aliquat $336S^+ - Cr(SCN)_4^-$) ion-pair, and the electrode gave a fully response in the $Cr(SCN)_4^-$ concentration range of $10^{-5} - 10^{-2}$ mol l^{-1} and has the Nernstian slop of 58 mV per pCr. In 1987 [4] a Cr(III) selective electrode with

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PVC membrane based on 8-quinoline-dithiocarboxilate was described. In 1989 another ion selective electrode based on chromium dithizonate was built that was a precipitate based selective electrode [5]. Singh et al. used a Cr(III)-selective electrode based on the macrocyclic compound for determination of chromium ion in some food materials [6]. A PVC-based Cr(III)-selective electrode, which was recently been prepared, is based on 4-methylaminoazobenzene [7] with a concentration range of 1.66×10^{-6}–1.0×10^{-2} mol l^{-1} and limit of detection of 8.0×10^{-7} mol l^{-1}. The Nernstian slopes of 19.5 mV per decade and pH range of 3.0–5.5 were reported for this electrode. The selectivity coefficient of some metal ions such as Ag(I) and Mn(II) are small (about 10^{-1}) for foregoing electrode. Hence, it is expected to interfere during potential measurements. However, these sensors [3–7] suffer from the disadvantages of significant interferences from some cations, deviation from Nernstian behavior, small linear range and narrow pH range.

With the availability of improved highly selective materials, the possibility of developing specific sensors has opened up new channels. Efforts were initiated in our laboratory to develop selective electrodes for Cr(III) using glyoxal bis(2-hydroxyanil) (Fig. 1) as a sensor material. The results presented in this paper show that the sensor developed for Cr(III) ion using the above material as the electroactive phase in PVC matrix has a wide working concentration range, low detection limit, good Nernstian slope, high selectivity over a wide variety of other cations and wider pH range than previous paper [7]. The sensor has a fast response time and gives reproducible results.

2. Experimental

2.1. Reagents

Reagent grade dibutyl phthalate (DBP), dioctyl phthalate (DOP), nitrobenzene (NB), acetophenone (AP), tetrahydrofuran (THF), high relative molecular weight PVC and nitrate or chloride salts of all cations (from Merck or Fluka) were used as received. The 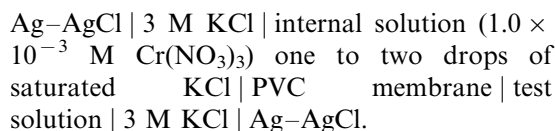ionophore glyoxal bis(2-hydroxianil) (GBH) was obtained from Fluka and used without any further purification. Doubly distilled deionized water was used throughout.

2.2. Electrode preparation

The general procedure to prepare the PVC membrane was similar to our previous work [8]. First, we mixed thoroughly 2.4 mg ionophore GBH, 69.6 mg of powdered PVC, 128 mg of plastisizer DBP in a glass dish of 2 cm diameter. The mixture was then completely dissolved in 5 ml of THF. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (0.3 mm i.d.) was dipped into the mixture for ∼10 s so that a membrane was formed. The tube was then pulled out from the mixture and kept at room temperature for 24 h. The tube was filled with internal filling solution (1.0×10^{-3} mol l^{-1} $Cr(NO_3)_3 \cdot 9H_2O$). The electrode was finally conditioned for 24 h in a 1.0×10^{-3} mol l^{-1} solution of $Cr(NO_3)_3 \cdot 9H_2O$. A silver/silver chloride was used as an internal reference electrode.

2.3. EMF measurements

All EMF measurements were carried out with the following assembly:

Ag–AgCl | 3 M KCl | internal solution (1.0×10^{-3} M $Cr(NO_3)_3$) one to two drops of saturated KCl | PVC membrane | test solution | 3 M KCl | Ag–AgCl.

A Metrohm digital research pH meter (Model 624) was used for measuring the potential at 25.0 ± 1.0 °C. Activities were calculated according to the Debye–Hückel procedure [9].

2.4. Food materials and alloys

The wet ashing method [6] was used for preparing of the samples for chromium determination.
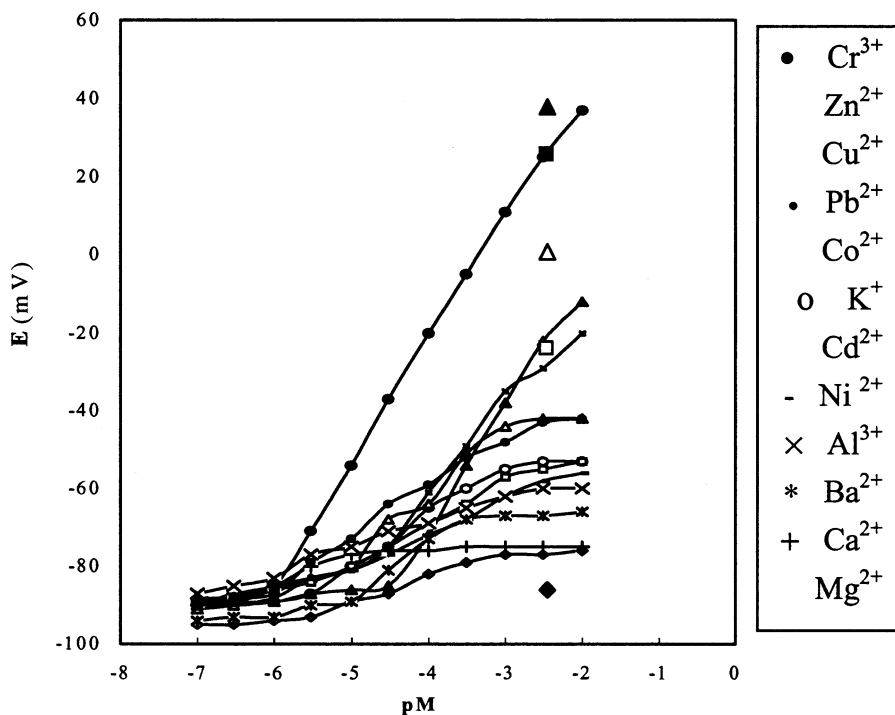
Fig. 1. Structure of Glyoxal bis(2-hydroxyanil).

2.4.1. Cacao powder, coffee and tea leaves

About 1 g of the sample was placed in a beaker and 10 ml of HNO_3 and 4 ml of $HClO_4$ were added, followed by digestion on a hot plate until the organic residue was completely oxidized. The solution was finally diluted to 100 ml after filtering it through a filter paper (Whatman No. 1).

2.4.2. Alloys

A 0.05–1.0 g sample of the alloy was completely dissolved in 20–40 ml of hydrochloric acid (1 + 1) on a water-bath, and then 2–3 ml of 30% hydrogen peroxide were added. The excess of peroxide was decomposed by heating the solution on a water-bath and the mixture was cooled and filtered through a filter paper. The filtered mixture was diluted to 500 ml with distilled water in calibrated flask.

The solution were analyzed using an atomic absorption spectrometer (Shimadzu) model 670 and also using sensor developed here, after adjusting the pH of the sample.

3. Results and discussion

Due to its sufficient insolubility in water [10] and the presence of four donating atoms (nitrogen and oxygen atoms) in its structure, GBH was expected to act as a suitable ion carrier in the PVC membrane with respect to special transition and heavy metal ions. The potential response of various ion-selective electrodes based on GBH are shown in Fig. 2. Among these ions, Cr^{3+} with more sensitive response seems to be suitably determined with electrode based on GBH. Except for the Cr^{3+} ion-selective electrode, in all other cases the slope of the corresponding potential–pM plots is much different from the expected Nernstian slope, and the plots also suffer from limited linear range. However, the chromium ion results in a near-Nernstian potential response at a wide concentration range. This is most probably due to both the selective behavior of the ionophore against Cr^{3+} in comparison with other cations used and the rapid exchange kinetics of the cation between the aqueous and membrane phases.
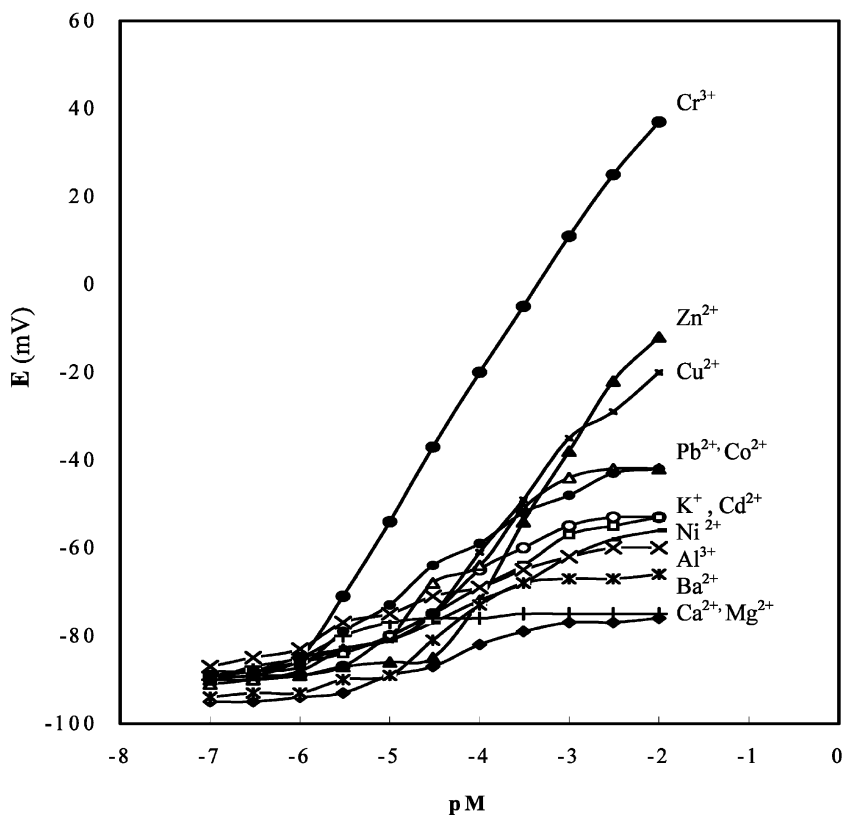
Fig. 2. Potential response of various ion-selective membrane based on GBH. Conditions: membrane ingredients, 33% PVC, 66% DBP, 1% GBH; internal solution, 1.0×10^{-3} mol l^{-1} Cr(NO$_3$)$_3 \cdot$9H$_2$O.

It is well known that the sensitivity and selectivity of the ion-selective sensors not only depend on the nature of ionophore used, but also significantly on the membrane composition and the properties of plasticizers and additives used [9,11–13]. Thus, the influences of the membrane composition, the nature and amount of plasticizers and amount of oleic acid as a suitable lipophilic additive on the potential response of the Cr^{3+} sensor were investigated. The results are summarized in Table 1. It is seen that, among four different solvent mediators used, the use of 64% DBP in the presence of 1.2% ionophore (No. 12 Table 1) results in the best sensitivity, with Nernstian slope of 19.8 mV per decade over a wide concentration range.

It is well documented in literature that uncharged ionophores can only be used in cation selective membrane if a cation exchanger is present

[7]. In the absence of ion exchangers the membrane may function due to impurities. For this reason we choose one of the membrane compositions with 0.0% of ionophore. As Table 1 reveals there is no potentiometric response for 0.0% of the ionophore.

The pH dependence of the potentials of the proposed electrode for different concentrations of chromium(III) ion were tested over the pH range 2–7 and the results are depicted in Fig. 3. The pH was adjusted with nitric acid or sodium hydroxide solution. As it can be seen, the potential response remains almost constant over the pH range 2.7–6.5, which can be taken as the working pH range of the electrode. It is reported that in this working pH rang of the electrode, trivalent chromium will exist as $Cr(OH)^{2+}$ [4,6,7]. Since the basic salt has some solubility, Cr(III) remains in the solution and in this pH range the response of the electrode is

Table 1
Optimization of membrane ingredients

Number	Composition (%)				Slope (± 0.5 mV per decade)	Response range (mol l^{-1})
	PVC	Plasticizer	GBH	Oleic acid		
1	33.0	66(DBP)	1.0	–	31.24	1.1×10^{-6}–1.0×10^{-2}
2	33.0	66(DOP)	1.0	–	13.96	3.0×10^{-7}–3.0×10^{-4}
3	33.0	66(AP)	1.0	–	8.18	1.0×10^{-6}–1.0×10^{-3}
4	33.0	66(NB)	1.0	–	9.43	1.0×10^{-6}–3.0×10^{-4}
5	32.0	64(DBP)	1.0	3.0	28.28	1.0×10^{-6}–3.0×10^{-4}
6	32.0	66(DBP)	1.0	1.0	27.43	1.0×10^{-6}–3.0×10^{-4}
7	28.0	66(DBP)	6.0	–	30.28	3.0×10^{-6}–4.1×10^{-3}
8	30.0	66(DBP)	4.0	–	27.51	4.0×10^{-6}–9.3×10^{-3}
9	37.0	62(DBP)	1.0	–	22.82	4.4×10^{-6}–1.1×10^{-4}
10	35.0	64(DBP)	1.0	–	22.11	2.4×10^{-6}–2.1×10^{-4}
11	35.2	64(DBP)	0.8	–	15.17	2.1×10^{-6}–3.1×10^{-3}
12	34.8	64(DBP)	1.2	–	19.77	3.0×10^{-6}–1.0×10^{-2}
13	34.0	66(DBP)	0.0	–	1.64	

due to $Cr(OH)^{2+}$. At pH higher than 6.5, the potential of membrane electrode decreased due to the formation of chromium hydroxides in solution. On the other hand, the increasing potential at lower pH means that the electrode responses to hydrogen ions.

The effect of ionic strength of the test solution on the response of the electrode was investigated. The ionic strength was adjusted by sodium chloride. The results show that the variation of the concentration of sodium chloride from 0.1 to 0.5 mol l^{-1} does not cause any significant difference
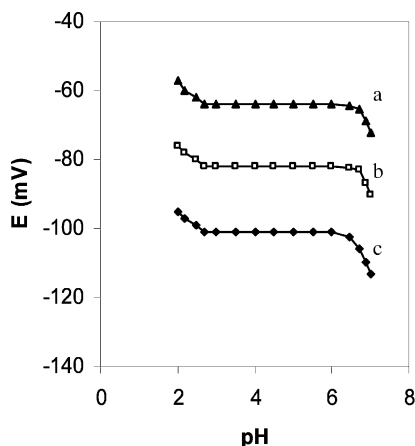

Fig. 3. Effect of pH of test solution on the potential response of the Cr^{3+} ion-selective electrode.

in the response of the electrode. At NaCl concentration greater than 0.5 mol l^{-1} decreases the slope of the plots without any significant change in the linear range.

The proposed electrode was examined at various concentrations of inner reference $Cr(NO_3)_3$ solution, in the range of 1.0×10^{-4}–1.0×10^{-2} mol l^{-1}. It was found that the variation of the internal Cr^{3+} solution does not cause any signification difference in potential response except for an expected change in the intercept of the resulting Nernstian plots. A 1.0×10^{-3} mol l^{-1} concentration of reference solution is quite appropriate for smooth functioning of the system.

For analytical application the response time of membrane sensor is critically important. The average time required the membrane electrode to reach a steady potential response within ± 1 mV of the final equilibrium value after successive immersion of a series of Cr^{3+} solutions, each having a 10 fold-difference in concentration, was investigated. The static response time of the PVC membrane thus obtained was less than 20 s over all linear concentration range. The equilibrium potential essentially remained constant for 5 min. The standard deviation (S.D.) of ten replicate measurements is ± 0.5 mV. Also the lifetime of electrodes based on ionophore GBH in solvent polymeric membranes depends on the distribution coefficient

Table 2
Selectivity coefficients ($K_{A,B}^{MPM}$) of various interfering cations

Cation	$K_{A,B}^{MPM}$	Cation	$K_{A,B}^{MPM}$
Al^{3+}	1.1×10^{-3}	K^+	2.4×10^{-3}
Ce^{3+}	2.4×10^{-3}	Li^+	2.6×10^{-3}
Cr^{6+}	8.6×10^{-3}	Zn^{2+}	6.8×10^{-3}
Ni^{2+}	1.2×10^{-3}	Mg^{2+}	6.1×10^{-3}
Cu^{2+}	9.6×10^{-3}	Co^{2+}	6.8×10^{-3}
Pb^{2+}	6.0×10^{-3}	Sr^{2+}	4.2×10^{-3}
Na^+	3.3×10^{-3}	Ca^{2+}	3.6×10^{-3}

Conditions: membrane ingredients, 34.8% (PVC), 64% (DBP), 1.2% (GBH) and internal solution (1.0×10^{-3} mol l^{-1} $Cr(NO_3)_3$) and pH 5.5 (test solution).

of the ionophore and the plasticizer between the aqueous and membrane phases [6]. Hence the lifetime of the electrodes must depend on the components of the solution and the measured specimens with electrodes. The experimental results show that the lifetime of the present electrode was more than 120 days. During this time, the detection limit and the slope of the electrode remained almost constant.

The practical utility of proposed sensor was investigated in partially non-aqueous media using 5, 15 and 25% v/v water–methanol and water–ethanol mixture. The results show that when the non-aqueous content is lower than 15%, it does not cause any significant difference in the potential response. A further increase in non-aqueous content causes significant interference. Hence, the proposed sensor can only be used in non-aqueous medium when its content is not more than 15%.

The influence of interfering ions on the response behavior of ion-selective membrane electrodes is usually described in terms of selectivity coefficients, $K_{A,B}^{Pot}$. The methods based on the Nocolsky–Eiseman equation for the determination of potentiometric selectivity coefficients (e.g. the fixed interference method and the mixed solution method) are among the most commonly methods used thus far [14–18]. However, it has been shown that these methods suffer some limitations in terms of values for ions of unequal charges, non-Nernstian behavior of interfering ions, and activity dependence, of values [19–21]. Thus, in this work, the recommended matched potential method

(MPM) [19,20,22], which is totally independent of the Nocolsky–Eisenman equation, was used to overcome the above-stated difficulties. According to the MPM [20], a specified activity (concentration) of primary ions (A) is added to a reference solution and the potential is measured. 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. The MPM selectivity coefficient, $K_{A,B}^{MPM}$, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K_{A,B}^{MPM} = a_A/a_B$. The experimental conditions employed and the resulting values are given in Table 2. As is seen, for all diverse ions used, the selectivity coefficients are in the order of 10^{-2} or smaller, indicating they would not significantly disturb the functioning of the Cr^{3+} ion-selective electrode. Further, the effect of anions such chloride and sulfate on the cell potential were investigated. In the presence of 10^{-3} mol l^{-1} of foregoing anions, no significant change in the working concentration range was observed, but the slope changes from 19.8 to 18.8 mV per decade. These results show that these anions (Cl^- and SO_4^{2-}) do not cause any interference in the determination of Cr^{3+} ion.

The electrode has been used successfully for determination of Cr^{3+} in various food materials

Table 3
Results of determination of chromium in different food materials and alloy samples

Sample	Average chromium concentration (ppm)[a]	
	Proposed sensor	AAS
Coffee	1.2 ± 0.1	1.3 ± 0.1
Cacao powder	1.0 ± 0.2	1.1 ± 0.2
Tea leaves	0.9 ± 0.1	0.9 ± 0.1
17–7 pH (0.07% C, 17% Cr, 7% Ni, 1% Al)	16.8 ± 0.3	17.1 ± 0.1
Inconel 600 (76%Ni,0.08% C, 16% Cr, 0.2% Cu, 8% Fe)	15.8 ± 0.3	16.1 ± 0.2

[a] $\pm$S.D., $n = 5$.

and some alloys. No further treatment of the sample was necessary except for pH adjustments. The results (Table 3) indicate a very good agreement between the two values (obtained by AAS and with the proposed sensor). This also indicates the practical utility of the sensor.

4. Conclusions

The membrane sensor incorporating GBH as the electroactive phase can be used to determine chromium in the wide concentration range. The sensor exhibited good reproducibility over a useful lifetime of 3 months. This electrode is superior to the existing electrodes with regard to the slope, pH range, response time and selectivity over a number of cations. The proposed sensor was successful in determining Cr(III) in real sample analysis, viz. in tea leaves, cocoa powder, coffee and alloy samples.

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