A Comparative Study of Chromium(III) Ion-Selective Electrodes Based on N,N-Bis(salicylidene)-o-phenylenediaminatechromium(III)

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A comparative study was made between three types of Cr(III) ion-selective electrodes: PVC membrane electrode, silver coated electrode and modified carbon paste electrode based on N,N-bis(salicylidene)-o-phenylenediaminatechromium(III) complex (Crsalophen). As anticipated, electrodes with a solid contact, rather than a traditional liquid inner contact, give lower detection limits because of diminished ion fluxes. Often, however, ill-defined solid contact gives rise to instabilities and interferences by oxygen gas. The carbon paste electrode provides a more sensitive and stable device than that afforded by PVC and coated electrodes. The best performance was obtained by an electrode based on the paste containing 3.5 wt% Cr-complex, 48.5% graphite plasticized with a mixture of 24.0 wt% tris(2-ethylhexyl) phosphate (DOPh) + 24.0 wt% dioctyl sebacate (DOS). The sensor has a linear dynamic range of 7.5×10^{-6} to 1.0×10^{-2} M, with a Nernstian slope of 20.1 ± 0.6 mV decade^{-1}, and a detection limit of 1.8×10^{-6}. It has a short response time of a bout 8 s and is applicable in a pH range of 4.5-7.7. It was successfully used as an indicator electrode in potentiometric titration of Cr(III) with EDTA and in determination of Cr(III) in water samples and chromium in (Crsalophen).

INTRODUCTION

Chromium is an essential element for all vertebrates. In humans, it plays a role in the metabolism of glucose and some lipids (mainly cholesterol) whose deficiency is associated with cardiovascular diseases and diabetes [1]. Chromium is used in various industries such as leather tanning, electroplating, metal finishing and chemicals manufacturing, and thus enters water supply through industrial wastes [2]. Therefore, it is of interest to develop fast and efficient methods for its determination in various types of samples.

Several sophisticated analytical techniques, such as AAS, ICP-AES, X-ray fluorescence, HPLC, DDP have been applied for determination of trace amounts of chromium. Many of these methods involve several time-consuming manipulations, extraction steps, derivatization reactions that are liable to various interferences, and are not applicable to colored and turbid solutions either. Ion-selective electrode is faster, less elaborate, low-cost and environmental-friendly. With these properties in mind, it is suggested that ISEs be used as more desirable alternatives.

A number of ISEs based on PVC membrane [3-16], and coated wire electrodes [17-19] employing different neutral ionophores, have been made for determination of chromium ion. To our best knowledge, no carbon paste electrode for the detection of Cr ions has been reported to date.

In conventional polymeric membrane ion-selective electrodes (ISEs), the sensing membrane is interposed between two aqueous phases, the sample and the inner solution. These electrodes, however, still have certain inherent limitations.

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They are mechanically complicated, and thus difficult to fabricate in small size. In addition, the flux of ions from the membrane, in contact with the inner electrolyte solution that contains a salt of the primary ion, toward the sample causes the concentration in the contacting aqueous layer to be *ca.* 10^{-6} M. Consequently, the lower detection limit was found to be around 10^{-6} M [20-22]. One strategy to overcome this drawback is elimination of the inner solution by using a solid inner contact. In a solid-contact or "coated wire" ISE, the polymer membrane is directly cast on the solid surface, with no internal reference solution being interposed. It has been known for a long time that such systems suffer from potential drifts and erratic emf changes [23]. These instabilities have mainly been attributed to uncontrolled redox processes at the metal surface. It was hypothesized that, during conditioning of the ISE, a thin aqueous layer emerges between the membrane and the metal electrode, and that the dominating redox process is the reduction of O_2 dissolved in this layer. Changes in pH and/or the partial pressure of O_2 were proposed as sources of instabilities [23].

In recent years, research is intensified to develop solid contact electrodes with low LODs; however, most of these electrodes lacked long-term stability so that they were only useful for special applications, *e.g.*, as detectors in flow injection analysis [24].

Cleary, there is an urgent need for a recipe that would make the fabrication and optimization of potentiometric sensors with low detection limit, high stability and reproducibility a straightforward process. The advantages of carbon paste electrodes, such as chemical inertness, robustness, low cost, renewability, very low background current, stable response, low ohmic resistance and no need for internal solution over conventional polymeric membrane and coated wire electrodes has attracted the attention of researchers in recent years [24-28].

In this work, the complex Cr(salophen) was prepared (Fig. 1), characterized and used as an ionophore in fabrication of ISEs for determination of Cr(III). The mechanism of action of this electrode is attributed to dissociation of the Cr(III)(salophen) complex to a certain degree in the paste to its components Cr^{3+} and salophen. The analyte-ion-selective charge separation at the aqueous/organic interface occurs as a result of the concentration gradient of Cr^{3+} ions in the organic
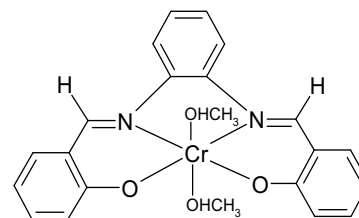

Fig. 1. Structural representation of the compound of N,N-bis(salicylidene)-o-phenylenediaminatechromium (III) complex (Crsalophen) used as ionophore in the Cr-CMCPE

and aqueous phases.

The performance of Cr(III)-selective electrodes using PVC membrane, silver coated electrode and carbon paste electrode based on the N,N-bis(salicylidene)-o-phenylenediamine Cr(III) complex (Fig. 1) were compared. The results, presented in this paper, revealed that characteristics of the carbon paste electrode surpass those of the PVC electrode and the coated wire electrode. Indeed, these results are similar to those found in recent reports [26,29].

The carbon paste electrode was used for potentiometric determination of Cr(III) in different media and was tested as an end-point indicator in the potentiometric titration of chromium with EDTA .

EXPERIMENTAL

Reagents

Reagent grade bis(2-ethylhexyl)adipate (DOA), dioctyl phthalate (DOP), dibutyl phthalate (DBP), tris(2-ethylhexyl) phosphate (DOPh), dioctyl sebacate (DOS), tetrahydrofuran (THF), high molecular weight poly(vinyl chloride), Graphite powder, as well as chlorides, nitrates, sulphates, of all cations were purchased from Aldrich and used as received. All solutions were prepared with doubly distilled water.

Synthesis of N,N'-disalicylidenephenylene-diaminate-chromium(III) chloride complex, Cr(salophen) (CH₃OH)₂Cl. To a hot solution of 0.324 (1 mmol) of salophenH₂ in 20 ml of methanol was added 0.266 g (1 mmol) of CrCl₃.6H₂O and the hot mixture was stirred for 1 h and left to cool. The green precipitate that formed was filtered, washed with methanol and left to dry. Analyses were performed for $C_{20}H_{22}N_2O_4ClCr$: C, 56.71; H, 4.73; N, 6.02; Cl, 7.63. Found: C, 56.82; H, 4.85; N, 6.11; Cl, 7.55. The chromium was

determined by AAS and found 11.24 (calculated 11.17). These results are consistent with the formula $Cr(Salophen)(CH_3OH)_2Cl$. IR (υ, cm^{-1}, KBr): 3430 (OH) and 1610 (C=N).

Potentiometric Determination

The potential measurements were carried out at 25 ± 0.1 with a digital millivoltmeter (SR-MUL-3800). pH measurements were made on a digital pH meter (HANNA pH 211). Saturated calomel electrode (SCE) was used as a reference electrode. The electrochemical system is presented as follows:

Hg, $Hg_2Cl_2(s)$, KCl(sat.) ‖ sample solution │ carbon paste electrode
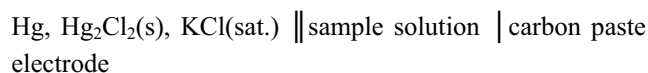
The activities of metal ions were based on activity coefficients γ, data calculated from the modified form of the Debye-Huckel equation which is applicable to any ion.

$$\log\gamma = -0.511 \, Z^2 \, [\mu^{1/2} \, (1 + 1.5 \, \mu^{1/2}) - 0.2 \, \mu]$$

where μ is the ionic strength and Z the valency.

Preparation of PVC Membrane Electrode

PVC-membranes were prepared as previously described elsewhere [30]. The membranes were prepared by dissolving optimized amounts of PVC, plasticizer and ionophore in 5 ml of THF. The mixture was shaken vigorously and the clear solution was poured into a glass dish 5 cm in diameter. The solvent was allowed to evaporate overnight, leaving a homogeneous, flexible and transparent membrane. Small disks (10 mm) were punched from the cast films and mounted in a home made electrode bodies. The electrodes were filled with internal filling solution that was 0.1 M NaCl and 0.001 M $CrCl_3$ and pre-conditioned by soaking in 0.01 M $CrCl_3$.

Preparation of the Coated-Wire Electrodes

The coated-wire electrodes were prepared according to a previously reported method [31]. Varying amounts of the ionophore and PVC were dissolved in about 5 ml of THF along with DOPh & DOS as solvent mediator. Silver wire, about 1 mm diameter and 50 mm length was first polished on a cloth pad, then washed with acetone. One end of the wire was then coated by repeated dipping into membrane solution in THF. A membrane was formed on the wire surface, which was allowed to dry overnight. The prepared electrodes were finally conditioned by soaking in 0.01 M of $CrCl_3$.

Preparation of the Carbon Paste Electrode

Modified carbon paste electrode was prepared by thoroughly mixing weighed amounts of (ionophore), high purity graphite and plasticizers in plastic Petri dishes until a uniformly wet paste was obtained and used for sensor construction as previously described [25].

Electrode bodies were made from 1 ml polypropylene syringes, the tip of which had been cut off with a cutter. The mixture was packed to the end of a (3 mm i.d., 1 ml). Electrical contact to the carbon paste was made by a copper wire. A fresh electrode surface was formed by squeezing out a small amount of paste and scraping off the excess against a conventional paper and then polishing the electrode on a smooth paper to obtain a shiny appearance. The electrode was used directly for potentiometric measurements without pre-conditioning.

Evaluation of Potentiometric Selectivity

Potentiometric selectivity of the sensor towards different inorganic cations in the chloride form and several anions were evaluated by applying the matched potential method (MPM) [32]. According to this method, the activity of Cr(III) was increased from $a_A = 1.0 \times 10^{-5}$ M (reference solution) to $à_A = 5.0 \times 10^{-5}$ M, at pH 5.8, that is slightly acidic and the changes in potential (ΔE) corresponding to this increase were measured. Next, a solution of an interfering ion of concentration a_B in the range 1.0×10^{-1}-1.0×10^{-2} M was added to a new 1.0×10^{-5} M (reference solution) until the same potential change (ΔE) was recorded. The selectivity factor, $K_{A,B}$, for each interferent was calculated using the following equation: $K_{A,B} = (à_A - a_A)/a_B$

Determination of Chromium(III) in a Cr(III) Complex and Water Samples

An amount of 1 g of Cr(III) complex was accurately weighed and a mixture of HNO_3 and H_2SO_4 (1:1) was added, followed by digestion on a hot plate with stirring until all the fumes ceased. The solution was made up to 100 ml in a volumetric flask. The analysis of water samples does not require pretreatment before potentiometric determination using the present sensor. Analyses were performed on 80 ml of water samples followed by spiking with either 1.0×10^{-3} M or 1.0×10^{-2} M $CrCl_3$ by the standard addition method.

RESULTS AND DISCUSSION

A comparison of the performance characteristics of Cr(III)-selective electrodes using PVC membrane, coated-silver wire electrode and carbon paste electrode based on the N,N-bis(salicylidene)-o-phenylenediaminatechromium(III) complex was made. The results clearly revealed that the carbon paste electrode gives a Nernstain slope of 20.1 ± 0.6 mV decade^{-1}, the widest concentration range 7.5×10^{-6}-1.0×10^{-2}, the fastest response time (≤ 8 s) and the lowest detection limit 1.8×10^{-6} over PVC membrane and coated-silver electrode as given in Table 1.

Evaluation of Performance Characteristics of Cr(III) Electrode

The performance characteristics reported for a given ionophore depend significantly on the paste composition; therefore, several pastes of varying ratios of ionophore/plasticizer/graphite were prepared for the systematic investigation of the optimum paste composition for Cr-CMCPE. The results are summarized in Table 2.

Table 1. Response Characteristics of Cr(III) Sensors

Parameter	PVC electrode	Silver coated electrode	Carbon paste electrode
Slope (mV decade^{-1})	21.8 ± 0.2	18.2 ± 1.2	20.1 ± 0.6
Concentration range (M)	2.8×10^{-5}-1.0×10^{-2}	2.1×10^{-5}-5.0×10^{-2}	7.5×10^{-6}-1.0×10^{-2}
Low of detection (M)	4.7×10^{-6}	3.1×10^{-6}	1.8×10^{-6}
Response time (s)	12-15	10-15	5-10

Table 2. Composition and Response Characteristics of Cr-CMCPE

No.	Composition (wt%)			Electrode characteristics			
	C	G	P	S (mV decade^{-1})	C.R (M)	LOD (M)	R (s)
1	-	53.5	46.5 (DOPh)	13.5 ± 0.7	3.0×10^{-5}-1.0×10^{-3}	9.5×10^{-6}	30
2	3.5	48.5	48.0 (DOPh)	15.5 ± 0.2	9.0×10^{-6}-1.0×10^{-2}	2.5×10^{-6}	12
3	3.5	48.5	48.0 (DBP)	13.2 ± 0.4	6.0×10^{-5}-1.0×10^{-2}	3.0×10^{-5}	25
4	3.5	48.5	48.0 (DOS)	30.2 ± 0.3	2.9×10^{-5}-1.0×10^{-2}	7.5×10^{-6}	15
5	3.5	48.5	48.0 (DOA)	14.2 ± 0.1	5.1×10^{-5}-5.0×10^{-2}	2.1×10^{-5}	35
6	3.5	48.5	48.0 (DOP)	25.2 ± 0.3	1.0×10^{-5}-1.0×10^{-2}	9.1×10^{-6}	30
7	3.5	48.5	24.0 (DOPh) + 24.0 (DOS)	20.1 ± 0.6	7.5×10^{-6}-1.0×10^{-2}	1.8×10^{-6}	8
8	3.5	48.5	24.0 (DOPh) + 24.0 (DPB)	12.6 ± 1.0	4.0×10^{-5}-1.0×10^{-3}	1.5×10^{-5}	23
9	3.5	48.5	24.0 (DOPh) + 24.0 (DOA)	15.6 ± 1.5	4.5×10^{-5}-1.0×10^{-2}	1.0×10^{-5}	30
10	3.5	48.5	24.0 (DOPh) + 24.0 (DOP)	21.1 ± 0.1	9.7×10^{-6}-1.0×10^{-2}	4.1×10^{-6}	20
11	0.3	51.7	24.0 (DOPh) + 24.0 (DOS)	28.1 ± 0.4	9.7×10^{-5}-1.0×10^{-3}	3.8×10^{-5}	30
12	1.5	50.5	24.0 (DOPh) + 24.0 (DOS)	24.6 ± 1.0	3.5×10^{-5}-1.0×10^{-2}	4.0×10^{-6}	15
13	4.5	47.5	24.0 (DOPh) + 24.0 (DOS)	19.6 ± 1.0	2.5×10^{-5}-1.0×10^{-2}	3.5×10^{-6}	18
14	6.0	46.0	24.0 (DOPh) + 24.0 (DOA)	11.2 ± 1.5	6.0×10^{-5}-1.0×10^{-2}	8.5×10^{-6}	25
15	3.5	48.5	65.0 (DOPh) + 35.0 (DOS)	23.1 ± 0.3	8.7×10^{-5}-1.0×10^{-2}	2.5×10^{-6}	10
16	3.5	48.5	35.0 (DOPh) + 65.0 (DOS)	25.1 ± 0.8	7.3×10^{-5}-1.0×10^{-2}	9.8×10^{-6}	13
17	3.5	48.5	80.0 (DOPh) + 20.0 (DOS)	19.1 ± 0.6	1.7×10^{-5}-1.0×10^{-2}	5.0×10^{-6}	10
18	3.5	48.5	20.0 (DOPh) + 80.0 (DOS)	25.1 ± 0.5	4.7×10^{-5}-1.0×10^{-2}	1.0×10^{-5}	13

C: Cr-salophen, G: Graphite, P: Plasticizer, S: Slope, C.R: Concentration range, LOD: Limit of detection, R: Response time.

The addition of plasticizer improves the sensitivity and stability of the sensor. The plasticizer, in particular, has a dual function: it acts both as a liquefying agent, enabling the homogenous solubilization of the paste ionophore, and serves to modify the value of the distribution constant of the ionophore used. The proportion of plasticizer used must be optimized in order to minimize the electrical asymmetry of the paste, to keep the sensor as clean as possible, and to stop leaching to the aqueous phase [33]. It is well established that the polarity and chemical structure of the plasticizer can have a significant influence on the sensitivity, stability, the selectivity and dynamic response range of ISEs [34]. Therefore, five plasticizers namely, DOA, DOP, DBP, DOS and DOPh were added in an attempt to improve the performance of the electrode. The potentiometric response of the electrodes modified by single plasticizer was found to be non-satisfactory (electrodes No. 2, 3, 4, 5 and 6). Comparatively, an electrode modified by a mixture of plasticizers (1:1 DOPh+DOS) gives better, stable and reproducible results (electrode No. 7) and the results obtained are shown in Table 2. It is quite obvious from EMf *vs*. pCr^{3+} plots in Fig. 2, that using a mixture of the plasticizers (DOPh+DOS) results in a Nernstian linear plot over a wide concentration range, whereas using other mixtures of solvent mediators gives slopes of the potentiometric response that are much different from the expected Nernstian value of 19.8 mV per decade as shown in Fig. 2.

Ionophores used in ISEs should have rapid exchange kinetics and adequate formation constants in the paste. In addition, they should have good solublility in the paste matrix and sufficient lipophilicity to prevent leaching from the paste into the sample solution [35].

The influence of the amount of the ionophore on the potential response of the electrode was studied the results of which are summarized in Table 2. As can be seen, the electrode without the ionophore (electrode No. 1) showed insignificant selectivity towards chromium ion, whereas in the presence of the ionophore the sensor displayed remarkable selectivity for Cr^{3+}, as found for electrode No. 7 which displays Nernstain slope towards chromium.

Among the electrodes evaluated in Table 2, electrode 7 which is composed of 3.5% (ionophore), 48.5% (graphite), 48.0% (DOPh+DOS), exhibits the best response characteristics. Therefore, this composition was used to study the various operation parameters of the electrode. The electrochemical
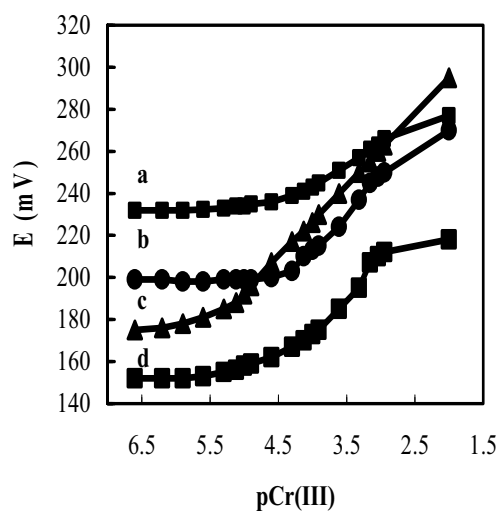

Fig. 2. Potentiometric response of Cr-CMCPE using different mixed plasticizers: (a) DOPh-DOA, (b) DOPh-DOP, (c) DOPh-DOS and (d) DOPh-DBP.

performance characteristics of this electrode were systematically evaluated according to the IUPAC recommendations [36].

Dynamic Response Time of Cr-CMCPE

It is well known that the dynamic response time of the modified electrode is one of the most important factors in its evaluation. The response time of the electrode is defined as the time between the addition of analyte to the sample solution and the time when a limiting potential has been reached. [36]. In practice, response time was recorded by increasing the Cr(III) ion concentration in solution from 1.0×10^{-5} to 1.0×10^{-2} M and the result, depicted in Fig. 3, clearly indicates that the measured response time is 5-10 s.

Electrode Renewal and Reproducibility

The slope of the calibration graph obtained by this electrode was found to decrease slightly after 2-4 times of use starting at 20.1 ± 0.6 mV and reaching 17.6 ± 1.2 mV at the last measurement. The drift is known as the slow non-random change with time in the emf of an ion-selective electrode cell. For the present electrode the decrease may be attributed to surface contamination and memory effect. Therefore, the electrode surface should be polished to expose a new fresh
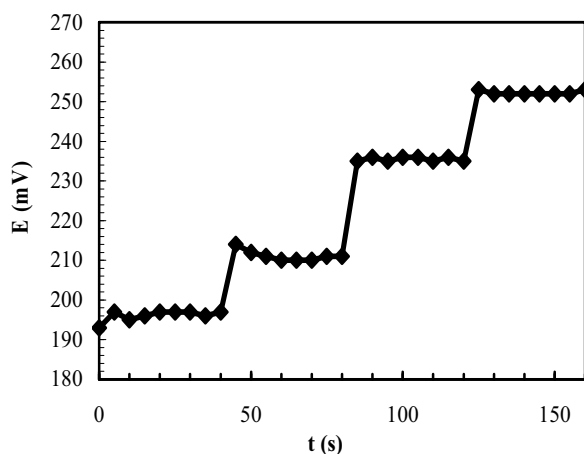
Fig. 3. Typical potential-time plot for response of Cr-CMCPE.

Fig. 4. pH dependence of Cr-CMCPE determined in the presence of 1.0×10^{-3} M CrCl$_3$.

layer ready for use.

In this electrode, a new surface was obtained by squeezing out a small amount of the paste, scrapping off the excess against a printing paper and polishing the electrode on a smooth paper to obtain a shiny appearance again. Accordingly, a paste of optimum composition and suitable weight (~1.2 g) can be used for several months without any deterioration or change in the response of the electrode.

The repeatability of the potential reading of the electrode was examined by subsequent measurements of 1×10^{-3} M chromium(III) solution immediately after measuring the first set of solutions at 1.0×10^{-2} M chromium. The standard deviation of measuring emf for five replicate measurements was found to be 1.214 for 1.0×10^{-3} M solution and 0.514 for 1.0×10^{-2} M solution. Considering the low value of the standard deviation for these replicate measurements it is clear that the repeatability of the present electrode is satisfactory.

pH Dependence

The influence of pH on the response of the Cr-CMCPE was examined for the 1×10^{-3} M CrCl$_3$ solution. The pH was adjusted by adding small volumes of (0.1-1 M) HCl or NaOH to the test solutions and the variation in potential was followed. It can be seen from Fig. 4 that the variation in potential due to pH change is considered acceptable in the pH range 4.5-7.7. However, there is an observed drift at pH values lower than 4.5 which may be due to H$^+$ interference. On the other hand,
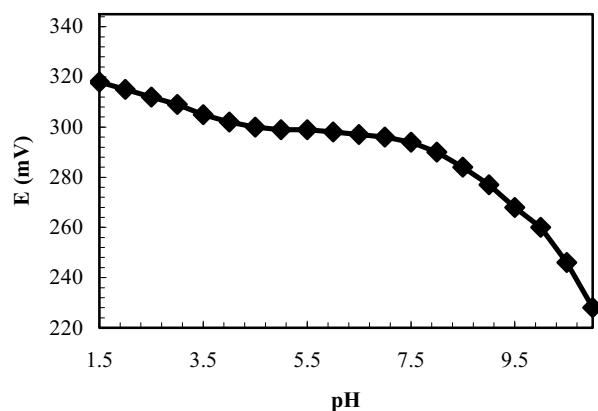
the potential decreases gradually at pH values higher than 7.7. The decrease may be attributed to the formation of the free chromium hydroxide base in the test solution.

Potentiometric Selectivity

The potentiometric selectivity coefficient of an electrode, as one of its most important characteristics, is defined by its relative response for the primary ion over the other ions present in the solution [32]. Different methods of selectivity determination are known in the literature. In this work the selectivity coefficients were evaluated by the matched potential method (MPM).

This method measures selectivity coefficients of ionic and nonionic speices; it has an advantage of removing limitations imposed by Nikolskii-Eisenman equation while calculating selectivity coefficients by other methods. These limitations include non-Nernstian behavior of interfering ions and problems of inequality of charges of primary and interfering ions [37]. The values of the selectivity coefficients, listed in Table 3, reflect a very high selectivity of this electrode for chromium cation over most of the tested species. Al^{3+} and Pb^{2+} caused only slight interference but Hg^{2+} caused strong interference. However, they do not cause any interference at low concentration ($\leq 5.0 \times 10^{-4}$). Measurements of interference by Hg(II) in dilute solutions were made and continued by increasing concentrations of Hg(II) until cloudiness appeared in the solution at pH about 5.0 when measurements were

Table 3. Selectivity Coefficients of Various Interfering Ions for Cr-CMCPE

Interfering ions, B	$-\log K_{A,B}$	Interfering ions, B	$-\log K_{A,B}$
Na^+	4.53	Pb^{2+}	0.89
K^+	4.18	Hg^{2+}	0.45
NH_4^+	4.36	Ni^{2+}	3.95
Li^+	3.96	Ba^{2+}	4.15
Ca^{2+}	4.13	Mg^{2+}	3.82
Cd^{2+}	4.08	Cu^{2+}	2.51
Zn^{2+}	2.19	Al^{3+}	0.92
Co^{2+}	3.92	Ce^{3+}	2.85

stopped and the potential reading was recorded. The selectivity coefficient was calculated.

Moreover, the effect of some anions such as nitrate, chloride and sulfate, perchlorate and thiocyanate on the response of the Cr-CMCPE was studied. No significant change in the slope of the emf *vs*. pCr^{3+} was observed for chloride and sulfate indicating no interference by these anions. However, nitrate ions caused moderate interference at 1.0×10^{-2} but much lower interference at smaller concentrations.

Effect of Aquo-Organic Medium on Cu-CMCPE

Real samples may contain non-aqueous ingredients, so the performance of the Cr-CMCPE was tested in partially non-aqueous media in the ratios: 5%, 20% and 40%. The solvent combinations used were: ethanol-water, methanol-water and acetonitrile-water mixtures as shown in Table 4. It was found that the electrode does not show any appreciable change in the working concentration range and the slope in 5% and 20% non-aqueous media. However, more than 40% non-aqueous media show drifts in potentials with time. These drifts are probably due to leaching of the ionophore at higher organic content.

Analytical Applications

The proposed Cr-CMCPE was successfully applied as an indicator in titration of 3.5 ml Cr^{3+} (1.0×10^{-3} M) with a standard EDTA solution (1.0×10^{-2} M). The resulting titration curve is shown in Fig. 5. It has a sharp inflection point, and the amount of Cr^{3+} ions in solution can be accurately determined with the present electrode in accordance with the stoichiometry of the reaction. In addition, the electrode was used successfully for determination of Cr(III) in mineral water, tap water and chromium in Crsalophen using the standard addition method the results of which are summarized in Table 5. It is noted that recovery in tap water was high, probably due to interference from nitrate ions.

The results of applying the above methods were compared with the values obtained from the AAS. F test was used for comparing the precisions of the two methods and t-test for comparing the accuracy. The calculated F- and t- test values listed in Table 5 were less than the critical (tabulated) ones. Thus, there is no significant difference between the precisions or the accuracies of the two methods at 95% confidence levels. Thus the sensor can be employed for quantification of Cr(III) in real samples.

Comparison with Other Electrodes

The performance characteristics of the proposed electrode and those of some reported electrodes [3-19] were compared and it was found that some electrodes are superior to this electrode. However, this electrode has some unique features. It is the first carbon paste electrode for Cr(III) determination. Due to their advantages over conventional polymeric membrane and coated wire electrodes, carbon paste electrodes (CPEs) have attracted attention mainlyas ion selective electrodes such as chemical inertness, robustness, low cost, renewability, very low background current, stable response, low ohmic resistance and easy surface renewal.

Table 4. Effect of Partially Non-Aqueous Medium on the Working of Cr-CMCPE

Non-aqueous content (%v/v)	Slope (mV decade^{-1})	LOD (M)	Response time (s)
0	20.1 ± 0.6	1.8×10^{-6}	≤ 8
Ethanol			
5	20.0 ± 0.3	1.9×10^{-6}	≤ 8
20	19.6 ± 0.5	2.2×10^{-6}	≤ 10
40	19.1 ± 0.4	3.5×10^{-6}	≤ 12
Methanol			
5	19.9 ± 0.2	2.1×10^{-6}	≤ 10
20	19.3 ± 0.4	2.6×10^{-6}	≤ 12
40	18.3 ± 0.7	4.8×10^{-6}	≤ 15
Acetonitrile			
5	19.7 ± 0.4	2.5×10^{-6}	≤ 10
20	19.1 ± 0.3	3.5×10^{-6}	≤ 15
40	18.0 ± 0.7	5.8×10^{-6}	≤ 20
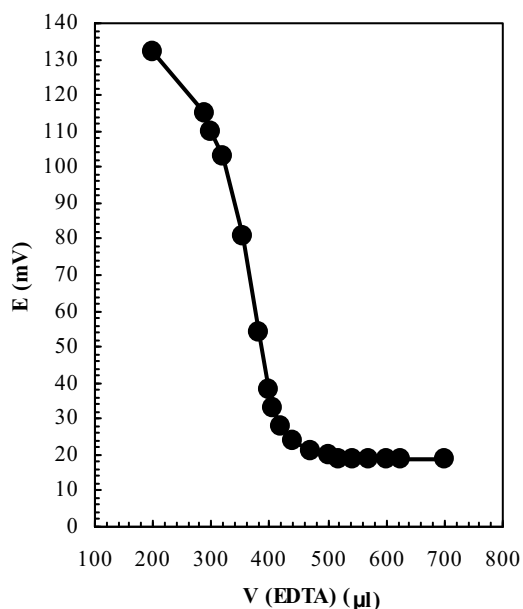
Fig. 5. Potentiometric titration curve of 3.5 ml 1.0×10^{-3} M solution of Cr(III) with 1.0×10^{-2} M EDTA.

CONCLUSIONS

Three types of electrodes for determination of chromium, namely: PVC-membrane, coated-silver wire and carbon paste electrode based on chromium(III) salophen complex were prepared .

The characteristics of these electrodes were compared which showed that those of the carbon paste electrode surpassed those of the other two electrodes.

The proposed chemically modified carbon paste electrode might be useful analytical tool and an interesting alternative in the determination of chromium ion in different real samples. The electrode shows high sensitivity, reasonable selectivity, fast static response, long term stability and a wide concentration range with minimal sample pretreatment.

REFERENCES

[1]   E.S. Manahan, Toxicological Chemistry, Lewis Publishers, an Import of CRC Press, Boca Raton, 1992, p. 449.

[2]   E.D. Kimbrough, Y. Cohen, M.A. Winer, L. Creelman, A.C. Mabuni, Crit. Rev. Environ. Sci. Technol. 29 (1999) 1.

[3]   A.K. Singh, V.K. Gupta, B. Gupta, Anal. Chim. Acta 585 (2007) 171.

[4]   A.H. Zamani, G. Rajabzadeh, R.M. Ganjali, Sens. Actuators B 119 (2006) 41.

[5]   A.M. Akl, K.A. Ghoneim, H.M. Abd El-Aziz, Electroanalysis 18 (2006) 299.

[6]   K.V. Gupta, K.A. Jain, P. Kumar, S. Agarwal, G. Maheshwari, Sens. Actuators B 113 (2006) 182.

A comparative study of Chromium (III) Ion-Selective Electrodes

Table 5. Practical Applications of Cr-CMCPE

Sample	Taken (M)	Found (M)	X ± S.E	R.S.D%	F-Value	t-Values
Mineral water	$(3.84) \times 10^{-6}$	$(3.65 \pm 0.01) \times 10^{-6}$	95.1 ± 0.015	0.53	3.02	1.14
	$(1.00) \times 10^{-5}$	$(0.99 \pm 0.03) \times 10^{-5}$	99.0 ± 0.017	1.45	2.14	1.25
Tap water	$(4.00) \times 10^{-5}$	$(4.47 \pm 0.04) \times 10^{-5}$	111.8 ± 0.040	1.74	4.18	2.15
	$(8.00) \times 10^{-5}$	$(8.82 \pm 0.03) \times 10^{-5}$	110.3 ± 0.025	0.95	1.45	1.89
Cr-salophen	$(5.57) \times 10^{-5}$	$(5.54 \pm 0.02) \times 10^{-5}$	97.0 ± 0.019	0.32	3.18	2.29

X ± S.E: recovery ± standard error; M: molar concentration of Cr(III) samples (taken); R.S.D: relative standard deviation; number of replicate measurements = 4; critical value of F = 9.28 and the critical value of t = 3.707.

[7] R.M. Ganjali, P. Norouzi, F. Faridbod, M. Ghorbani, M. Adib, Anal. Chim. Acta 569 (2006) 35.

[8] K.R. Sharma, A. Goel, Anal. Chim. Acta 534 (2005) 137.

[9] S.S. Hassan, S.M. El-Shahawi, M.A. Othman, A.M. Mosaad, Anal. Sci. 21(2005) 673.

[10] A. Singh, A. Panwar, R. Singh, S. Baniwal, Anal. Bioanal. Chem. 372 (2004) 506.

[11] A.K. Singh, R. Singh, P. Saxena, Sensors 4 (2004) 187.

[12] R.M. Ganjali, M. Emami, M. Salavati-Niasari, M. Yousedfi, Anal. Lett. 36 (2003) 2735.

[13] R.M. Ganjali, F. Mizani, M. Salavati-Niasari, M. Javanbakht, Anal. Sci. 19 (2003) 235.

[14] B.M. Gholivand, F. Sharifpour, Talanta 60 (2003) 707.

[15] A. Abbaspour, A. Izadyar, Talanta 50 (2001) 1009.

[16] K.A. Singh, A. Panwar, S. Kumar, S. Baniwal, Analyst 124 (1999) 521.

[17] A. Abbaspour, A. Izadyar, Talanta 71 (2007) 887.

[18] M. Shamsipur, A. Soleymanpour, M. Akhond, H. Sharghi, H.M. Sarvari, Electroanalysis 17 (2005) 776.

[19] A. Sil, S.V. Ijeri, K.A. Srivastava, Anal. Bioanal. Chem. 378 (2004) 1666.

[20] A. Malon, T. Vigassy, E. Bakker, E. Pretsch, J. Am. Chem. Soc. 128 (2006) 8154.

[21] A. Radu, S. Peper. E. Bakker, D. Diamond, Electroanalysis 19 (2007)144.

[22] E. Bakker, E. Pretsch, TrAC 24 (2005) 199.

[23] M. Fibbioli, W.E. Morf, M. Badertscher, N.F. Rooij, E. Pretsch, Electroanalysis 12 (2000) 1286.

[24] H. Ibrahim, Y.M. Issa, H.M. Abu-Shawish, J. Pharm. Biomed. Anal. 44 (2007) 8.

[25] H.M. Abu-Shawish, S.M. Saadeh, Sens. Lett. 5 (2007) 565.

[26] H. Ibrahim, A. Khorshid, Anal. Sci. 23 (2007) 573.

[27] M.J. Gismera, T.M. Sevilla, P.R. Jesús, Talanta 74 (2007) 190.

[28] M.J. Gismera, T.M. Sevilla, J.R. Procopio, Anal. Sci. 22 (2006) 405.

[29] M.H. Mashhadizadeh, A. Mostafavi, H. Allah-Abadi, H., I. Sheikhshoai, Sens. Actuators B 113 (2006) 930.

[30] B.M. Gholivand, M. Rahimi-Nasrabadi, R.M. Ganjali, M. Salavati-Niasari, Talanta 73 (2007) 553.

[31] A.M. Ardakani, P. Pourhakak, M. Salavati-Niasari, Anal. Sci. 22 (2006) 865.

[32] Y. Umezawa, P. Buhlmann, K. Umezawa, K. Tohda, S. Amemiya, Pure Appl. Chem. 72 (2000)1851.

[33] J. Sánchez, M. Valle, Crit. Rev. Anal. Chem. 35 (2005) 15.

[34] V.K. Gupta, A.K. Singh, B. Gupta, Anal. Chim. Acta 583 (2007) 340.

[35] V.S. Bhat, V.S. Ijeri, K.A. Srivastava, Sens. Actuators B 99 (2004) 98.

[36] R.P. Buck, E. Lindner, Pure Appl. Chem. 66 (1994) 2527.

[37] A.K. Singh, S. Mehtab, A.K. Jain, Anal. Chim. Acta 575 (2006) 25.