Cr(III) Selective PVC Membrane Electrodes Based on Schiff Base
1- (2- Pyridyl Azo)2-Naphtol Complex as an Ionophore

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Abstract: A novel and selective method for determination of trace amounts of Cr(III) ions using with Schiff base 1- (2- Pyridyl Azo)2-Naphtol has been explored as ionophore for preparing PVC-based membrane sensors selective to the Cr^{3+} ion. Potentiometric investigations indicate high affinity of these receptors for Cr(III) ion. The best performance was shown by the membrane of composition (w/w) of ionophore: 1 mg, PVC: 30 mg, DOP: 69 mg and KTpClPB as additive were added 50 mol % relative to the ionophore in 2 ml THF. The proposed sensor's detection limit is $6.0 \times 10^{?7}$ M over pH 4 at room temperature (Nernstian slope 33.06 mV/dec.) with a response time of 15 seconds and showed good selectivity to Cr(III) ion over a number of interfering cations.

Key words: Schiff base · Cr(III)-ion selective electrode · Potentiometry · Ionophore · 1- (2- Pyridyl Azo)2- Naphtol

INTRODUCTION

Toxicological studies have proved that the degree of toxicity of an element directly depends on the species in which it is present. Cr(III) is considered as an essential micronutrient for humans and mammals in order to maintain glucose metabolism, where as Cr(VI) is a potentially carcinogenic agent.[1] The significant drawbacks of Cr(VI) are breathing disturbances, liver and digestion malfunctions, dermal corrosion and skin allergies.[2] Therefore, It is necessary to control the level of chromium in industrial effluent, natural and drinking waters. Speciation of chromium in environmental samples is of prime importance.

Therefore there are numerous methods and techniques concerning chromium speciation and determination including liquid-liquid extraction after complex formation 3-4, solid-liquid extraction 5-8, LC-AAS 9-11, FIA-AAS 38,39, spectrophotometric 12,39, ICP-AES 13 and NAA14. However, some of these techniques are currently, time consuming and have elaborate sample preparation steps and low enrichment factors.

Solid phase extraction (SPE) methods are the best alternatives for traditional classic methods due to selective removal of trace amounts of metal ions from their matrices. SPE determinations can be carried out on different efficient ways. One of the most appropriative performation features of SPE is achieved by using octadecyl silica membrane disks. SPE reduce the use of toxic solvent, disposal costs and extraction time 15-16. The octadecyl silica membrane disks involves shorter sample processing time and decreased plugging due to the large cross-sectional area of the disk and small pressure drop which allows higher flow-rates; reduced channeling resulting from the use of sorbent with smaller particle size and a greater mechanical stability of the sorbent bed 17.

In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of chromium 18-19,35 and lead 20. Meanwhile, other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of lead 21-23, copper 24-26, silver 27-28, mercury 29-30, cadmium31, palladium 32, Ce 33 and UO_2 34.

years, the octadecyl-bonded silica SPE disks have been utilized for the extraction and separation of different organic compounds from environmental matrices 35-40. Moreover, the SPE disks modified by suitable ligands are successfully used for selective extraction and concentration of metal ions 41-42,46.

In a recent series of papers, 43-45 we have described the application of metal-DNA conjugates to nucleic acid

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sequence determination with catalytic signal amplification; the assay relies on the esterase activity of a DNA-linked Cr(III) complex. For optimization of the system and exploration of structure- activity relationships, a sensitive probe would be useful, which allows straightforward detection of esterase activity of ligated Cr^{3+} in low concentration.

In this study, we prepare PVC membrane electrodes based on Schiff base 1- (2- Pyridyl Azo)2-Naphtol as an ionophore and were used for the determination of Cr(III) ion. The proposed sensor revealed good selectivity and response for Cr^{3+} over a wide variety of other interfering metal ions.

Experimental

Reagents: High molecular weight PVC and 1- (2- Pyridyl Azo)2-Naphtol(PAN) was purchased from Fluka, dioctyl sebacate (DOS), dioctyl adipate (DOA), dioctyl phthalate (DOP), 2- nitrophenyl octyl ether (*o*-NPOE), potassium tetrakis (4-chlorophenyl) borate (KT*p*ClPB) and tetrahydrofuran (THF) were purchased from Aldrich, were used to prepare the PVC membranes. The nitrate salts of cations used (all from Merck) were used without any further purification. Doubly distilled water in a quartz apparatus was used to preparation of all aqueous electrolyte solutions.

Preparation of Polymeric Ion-selective Electrodes: The compositions of PVC-based Cr(III)-selective electrodes were summarized in Table 1 and the typical one (m-8) was 30 mg PVC, 69 mg plasticizer, 1 mg ionophore and KT*p*ClPB (50 mol % of ionophore). The ionophore, plasticizer and PVC were dissolved in the appropriate volume of THF and mechanically stirred. All membrane cocktails were cast in glass rings placed on glass plates

for conventional ionselective electrodes. Solvent from PVC membrane was allowed to evaporate for at least 24 hours at room temperature. The thickness of the resulting membrane measured by micrometer was about 0.3 mm.

Potentiometric Measurements: The electrochemical properties of Cr(III)-selective electrodes were investigated in the conventional configuration. Small disks were punched from the cast membranes and mounted in Philips electrode bodies (IS-561). For all electrodes, 0.1 M KCl solution was used as an internal filling solution. All electrodes were finally conditioned for [24] h by soaking in $1.0 \times 10^{?2}$ M $Cu(NO_3)_2$ solution. A Ag/AgCl coated wire was used as an internal reference electrode. The external reference electrode was an Orion sleeve-type double junction

Ag/AgCl reference electrode (Model 90 - 20) with two chambers. This reference electrode has two different filling solution: inner chamber filling solution is green colored solution saturated with AgCl, outer chamber filling solution consists of 10% KNO_3. The potential measurements were carried out at 25±1°C with Kosentech 16-channel potentiometer (KST101-1) coupled to a computer by setting up the following cell assembly: Ag/AgCl | 0.1 M KNO3 || 0.05 M Tris-HCl (sample solution) || PVC membrane|Internal filling solution (0.1 M KCl)|AgCl/Ag.

The electrochemical measurements were conducted after within 1 mV variance of open circuit potential with 5 minutes. The dynamic response curves were produced by adding standard solutions of cations to magnetically stirred pH 4 buffer solution (0.05 M Tris (hydroxymethyl) aminomethane-HCl). The selectivity coefficients (log K_{Cr3+}^{j}) were determined by the separate solution method (SSM) using nitrate salts of the cations involved.

Table 1: The compositions of membranes and their potentiometric characteristics of the Cr(III)-selective electrode over

pH 4. Membrane	*o*-NPOE[a]	DOA[a]	DOP[a]	DOS[a]	KT*p*ClPB[b]	LOD	Slope (mV)
m-1	77				0	-5.35	17.48
m-2	88				100	-5.89	27.09
m-3	77				60	-4.60	25.09
m-4		66			70	-3.86	9.74
m-5		66			100	-5.15	25.60
m-6			66		0	-6.15	24.89
m-7			66		20	-5.99	37.85
m-8			69		50	-6.60	33.06
m-9			66		100	-5.03	26.03
m-10				66	20	-5.71	25.96s
m-11				66	25	-6.22	44.08
m-12				66	100	-4.73	15.04

All membranes are comprised of ionophore 1mg and PVC 33mg.   [a]in mg. [b]in mol % relative to the ionophore

Detection limits were estimated at the intersection of two linear lines, the one extrapolated from a high concentration range and the other parallel to the X-axis drawn through the mean potential value of the lowest metal ion concentration used in the plot of the potential change and the concentration of Cr^{3+}.

RESULTS AND DISCUSSION

Schiff bases as ligands seem to be a potential ionophore for soft heavy metal ions in the PVC membrane electrodes, because of its excellent metal-binding properties, rapid exchange kinetics and water insolublilty. 24-25 1- (2- Pyridyl Azo)2-Naphtol was used as an ionophore for preparing PVC membrane ion-selective electrodes for a wide variety of metal ions. We said in our previous study16 that the Cr^{3+} ISE membrane compositions were optimized to produce the best sensitivity and selectivity towards Cr(III) ion, because the sensitivity of the ion-selective electrodes depend on the nature of ionophore used as well as significantly on the membrane compositions and selectivity of the electrodes depends on the nature of ionophore. The optimization was carried out with varying of the ratio in PVC membrane components such as plasticizer and additive (KTpClPB).

The Schiff base 1- (2- Pyridyl Azo)2-Naphtol was employed as Cr(III) selective ionophore in the preparation of Cr (III) ion selective electrode. The responses of the four electrodes (with different plasticizer) are shown in Figure 1. The electrodes of m-2, m-8 and m-11 exhibit wider linear response range and m-8 has closer Nernstian slope among them. The polymeric membranes are investigated to measure the ability of the ionophore to act as an ion carrier in the absence and presence of the ion exchanger. The response of the membranes without additive ion-exchanger (KTpClPB) gave the worse sensitivity and selectivity than those with KTpClPB. Most of membrane electrodes were prepared with KTpClPB in this work. The potentiometric response of the membranes was evaluated as to the slope and detection limit towards Cr(III) ion. The slope and detection limit for membranes were determined in accordance with IUPAC recommendations.[26] Figure 2 illustrates typical response curves for Cr(III) ion, measured in pH 4.0 buffer solution by membranes (m-6, m-7, m-8, m-9) containing different amount of additive (KTpClPB), respectively. They show that the ionophore gives best sensitivity towards Cr(III) ion containing in 50 mol % additives. The effects of the membrane composition, the nature of plasticizers, ionophores and lipophilic additive on the potentiometric response of the Cr^{3+} ISE were summarized and investigated in Table 1.
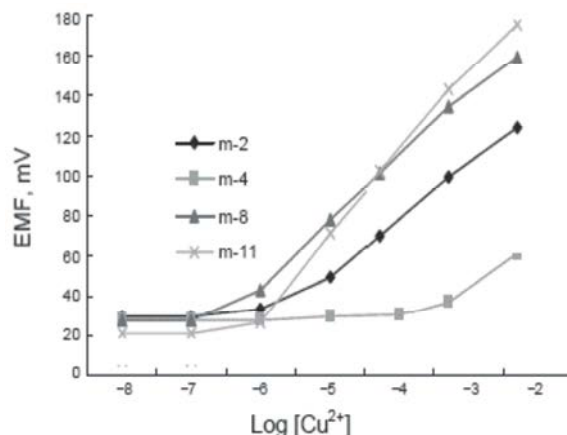

Fig. 1: Potentiometric responses of the membrane prepared from different plasticizers with ionophore towards Cr^{3+}.
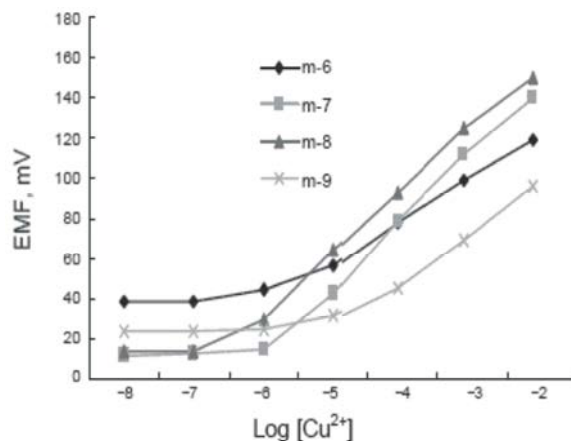

Fig. 2: Response curves of membranes containing different % of additive measured over pH 4.

The membrane (m-8) prepared by DOP as a plasticizers, 50 mol % of additive displays a good Nernstian response to Cr^{3+} over the wide range. The slope of the calibration curve was 33.06 mV/decade for Cr^{3+} at room temperature and the limit of detection (LOD) is $6.0 \times 10^{?7}$ M. The different slope can be attributed to the complication factor and sensing rate according to the membrane formulation. It should be noted that the presence of lipophilic anions in cation-selective membrane electrodes provides the decrease of the ohmic resistance as well as the improvement of their sensitivity and selectivity.

The selectivity coefficients of the new membranes are very important for determining their quality as ISEs. The selectivity coefficients represent their response to the species to be easured over other ions present in solution. The selectivity coefficients of the electrodes were determined by the separate solution method (SSM).

Table 2: Selectivity coefficients over various interfering ions for membrane (m-8) electrode.

Membrane					log $K_{Cr3\text{-}j}^{pot}$						
m-8	$Cr^{3+}0$	Co^{2+}-3.85	Mn^{2+} -3.15	Ni^{2+}-3.61	Sr^{2+}-4.22	Ba^{2+}-3.63	Cd^{2+}-3.55	Zn^{2+}-3.68	Ca^{2+}-3.80	Mg^{2+}-3.30	Pb^{2+}-3.25
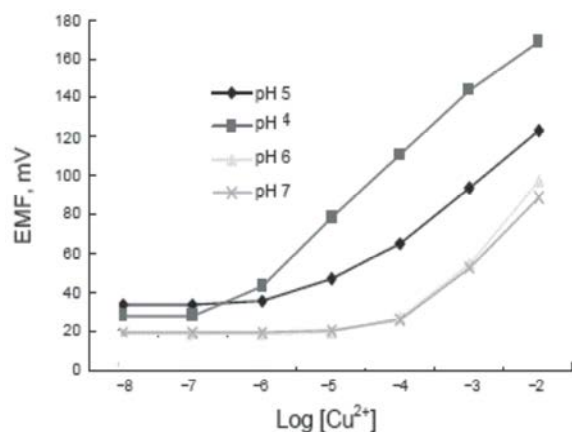
Fig. 3: Potentiometric responses of the Cr^{3+} ISE membrane (m-8) over different pH.
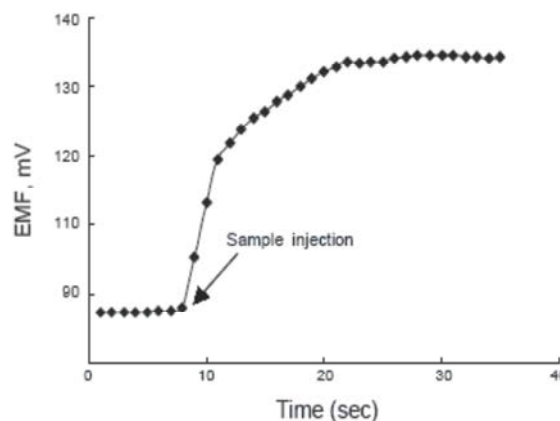
Fig. 4: Response-time profile of the Cr^{3+} ISE membrane (m-8).

They were evaluated by the separate solution method. The selectivity coefficients towards Cr^{3+} were determined against the interfering cations, Pb^{2+}, Co^{2+}, Cd^{2+}, Mn^{2+}, Zn^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ni^{2+}, Ba^{2+}. The selectivity coefficients (log K_{Cr3+j}) with respect to the corresponding nitrate over interfering ions tested are shown in Table 2.

From these, it can be considered that 1- (2- Pyridyl Azo)2-Naphtol as an ionophore employed is selective towards Cr(III) ion against above interfering ions. Among all membranes tested, the best result was obtained from m-8. As can be seen, with the exception of Cr^{3+}, for all diverse ions used, the selectivity coefficients are in the order of 10^{-3} or smaller, indicating that they could not significantly disturb to the functioning of the Cr^{3+} selective electrode. It should be noted that Mn^{2+} provides negligible interference (-log = 3.13) for the determination of Cr(III) ion. Thus, it is clear that the membrane electrode has good selectivity over and divalent cations. Meanwhile, the effect of counter anions was investigated using the Cr(III) salts of chloride and nitrate, indicating that no significant changes in the working concentration range and slope were observed. The selectivity data for the electrode (m-8) employed in this study indicates that the extent of complex formation between ionophore and metal ion and the geometrical structure are the major factors determining the selectivity. The result indicates that the geometry and legating cavity of the 1- (2- Pyridyl Azo)2-Naphtol should be significant factor for determining a selectivity toward others. Based on data of m-8 in Table 1 and 2, the good sensitivity and highest

selectivity towards Cr(III) ion are attributed to the strong complexation of Cr(III) ion to 1- (2- Pyridyl Azo)2-Naphtol which has geometrically the proper cavity to coordinate to the ligand and its complexation with other cations should be weaker than the Cr(III) complexation.

The electrode was applied to the direct measurement of Cr^{3+} in prepared solutions.

The potential was measured by direct potentiometry in pH 4.0 buffer solution. The pH dependence on the potentiometric response of the novel membrane electrode (m-8) is studied in a variety of pH solutions and shown in Figure 3.

The results indicate that the potentiometric response for m-8 electrode depends on the solution pH employed, but the potential obtained from m-8 electrode gives a similar value between pH 6 and pH 7. Therefore, the potentiometric response of PVC polymeric Cr^{3+} ISEs based on 1- (2- Pyridyl Azo)2-Naphtol was examined for many metal ions in pH 4.0 buffer solution in order to avoid the formation of metal-hydroxide hydroxide complex at higher pH. A potential-time plot for the electrode is shown in Figure 4. The static response time of the membrane electrode thus obtained was < 20 sec for the increased concentration from 1.0×10^{-3} M to 1.0×10^{-4} M Cr(III) ion solution, indicating that the equilibrium can reach very quickly in pH 4. The membranes responded rapidly to change in Cr(III) concentration within 15 s. The prolonged stability of these membranes was measured as a function of time; it was evidenced in both the slopes of the calibration curve and the detection limits.

The membranes would be stored in pH 4.0 buffer solution when not in use. After two weeks, the electrodes were responding at 90% of the initial response. By the end of one month, the response observed was still responding at 89% of the initial value.

CONCLUSION

As a final point, the membrane electrode incorporating 1- (2- Pyridyl Azo)2-Naphtol as an ion carrier can be used for the development of a Cr(III) ionselective electrode. Among membranes tested, polymeric membrane m-8 based on 1- (2- Pyridyl Azo) 2-Naphtol with DOP and liphophilic additive of 50 mol % displays a good Nernstian response (33.06 mV/decade) over pH 4 at room temperature to Cr^{3+} ion and the limit of detection of $5 \times 10^{?7}$ M within short time 15s. Most of metal ions could not hamper the selectivity to the Cr(III) ion. It can be concluded that the membrane electrode has a rapid potential response and excellent selectivity towards Cr(III) ion over other interfering metal ions. It could be used successfully for the determination of Cr(III) ion content in environmental and waste water samples.

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