

Full Paper

Chromium(III) ion Selective PVC Membrane Electrode Based on a Schiff base Ligand, 3-Aminoacetophenone thiosemicarbazone

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Abstract- An attempt has been made to develop a highly selective Cr³⁺-ion selective PVC membrane electrode based on a 5% newly synthesized 3-aminoacetophenonethiosemicarbazone as an ionophore with 62% DBP, 30% PVC and 3% NaTPB as an anion excluder. The electrode exhibits a near Nernstian potential response of 19.7±0.2 mV per decade over a wide concentration range (1.0×10⁻⁸ M to 1.0×10⁻¹ M) with a detection limit of 7.4×10⁻⁸ between pH 1.5-6.8 with a fast response time (10 s). The selectivity coefficient values were determined by matched potential method (MPM), indicate higher selectivity for chromium(III) ion with improved performance as compared to other carriers reported earlier. The proposed electrode exhibits an adequate shelf life (14 weeks) without any considerable divergence in potentials. Further the electrode was also successfully applied to determine the content of chromium in water samples collected from different sites of river Yamuna in Delhi.

Keywords- Ion-Selective Electrode, PVC Membrane, Potentiometry, 3-Aminoacetophenonethio semicarbazone

1. INTRODUCTION

Transition metals and their complexes are used in various industries such as leather tanning, electroplating, metal finishing, chemicals manufacturing etc. Thus these metals enter in water supply through industrial waste [1]. Chromium is also an essential trace element in

human nutrition, required for normal carbohydrate fat metabolism whose deficiency is associated with cardiovascular diseases and diabetes [2]. Several sophisticated analytical techniques such as AAS, ICP-AES, X-ray fluorescence, HPLC, DDP, have been applied for the determination of trace amounts of chromium. Many of these methods involve several time-consuming manipulations, expensive equipments, expert operators and much space. Therefore, there is critical need for the development of selective, portable, inexpensive diagnostic tools for the determination of chromium. Recently, the development of ion-selective electrodes (ISEs) are well established in most frequent application in the fields of environmental, agricultural, industrial and clinical analysis. This is due to their several advantages, such as high speed, ease of preparation, simple instrumentation, relatively fast response, wide working concentration range, adequate selectivity and low cost [3]. These make ISE potentiometry very attractive for chemical and pharmaceutical analysis. Extensive efforts have been made to develop good sensitive electrodes for chromium ion [4-22]. However, most of the reported electrodes exhibit narrow working concentration range [7,18,19], non-Nernstian response [19], high response time [11,16,19] and showed significant interference from foreign ions [10,14,16]. An important requirement for the preparation of a selective ion electrode is that the electro active material, which is used in the membranes, should exhibit high lipophilicity and strong affinity for a particular metal ion to be determined and poor affinity for others. Electrodes comprising Schiff bases as electro active ingredient have been reported to exhibit excellent selectivity for specific metal ions [23,24]. Schiff base ligands have been extensively studied in coordination chemistry mainly due to their facile syntheses, easily tuneable steric, electronic properties, good solubility in common solvents [25]. The Schiff bases are becoming increasingly important as biochemical, analytical and antimicrobial reagents. In order to achieve wider applicability, the limitations need to be removed. Efforts in this direction are on using different materials for preparing of membranes.

Continuing efforts in this direction, we recently synthesized a highly selective chromium electrode using a Schiff base ligand, 3-aminoacetophenonethiosemicarbazone, as a novel neutral carrier for the potentiometric monitoring of ultra-trace amounts of Cr^{3+} ion. The results of this investigation are presented in the following.

2. EXPERIMENTAL SECTION

2.1. Reagents and equipments

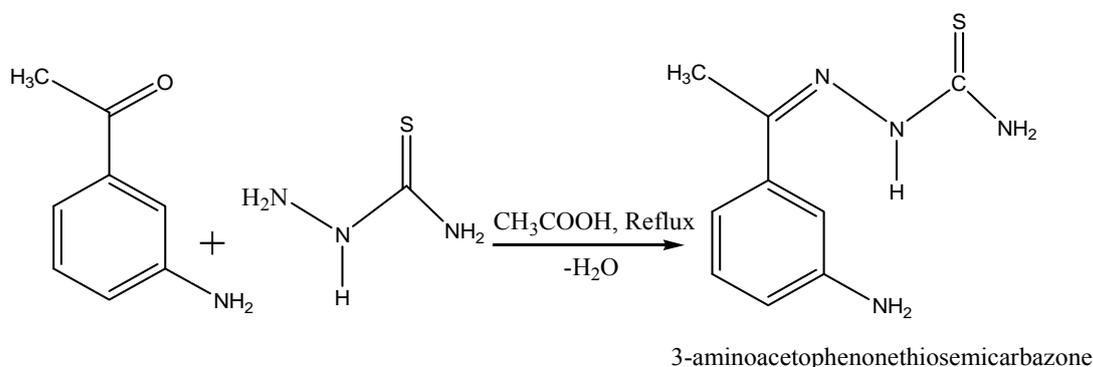
All the reagents used in this study were of analytical grade. 3-aminoacetophenone, thiosemicarbazide and glacial acetic acid were of procured from (Aldrich, USA), high molecular weight poly(vinyl chloride) (PVC) (Fluka, Switzerland), nitrobenzene (NB), tri-n-butylphosphate (TBP), dibutylphosphate (DBP), dioctylphthalate (DOP), n-butylacetate

(NBA) and sodiumtetra-phenylborate (NaTPB) were obtained from (Merck, Germany) and used as received. The nitrate salt of all the cations were of analytical grade and used without any further purification expect for vacuum drying over P_4O_{10} . Cationic salt 0.1 M solution was prepared in doubly distilled water and standardized whenever necessary.

The analysis for carbon, hydrogen and nitrogen was on Vario EL III elemental analyzer, IR spectrum was obtained on a Thermo Nicolet Nexus FT-IR spectrometer in KBr, 1H NMR spectra was recorded on Hitachi FT-NMR, Model R-600 spectrometer using DMSO as a solvent, Mass spectra were recorded on JEOL, JMS, DX-303 Mass spectrophotometer. The electronic spectra were recorded on Shimadzu UV mini-1240 spectrophotometer. HA 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.

2.2. Synthesis of Schiff base ligand

Hot ethanolic solution (20 mL) of 3-aminoacetophenone (1.35 g, 0.01 mol) was mixed with hot ethanolic solution of thiosemicarbazide (0.91 g, 0.01 mol) in the presence of 2-3 drops of glacial acetic acid. The content was refluxed for about 2-3 hours on a waterbath. On cooling the contents the brown coloured compound separated out. The same was filtered, washed with 50% ethanol, recrystallised in ethanol and dried in vacuum over P_4O_{10} . Scheme 1.



Scheme 1. Synthesis of Schiff base ligand 2.2.1. 3-aminoacetophenonethiosemicarbazone

Yield 85%, m.p.125 °C. Elemental analysis % found for $C_9H_{12}N_4S$, C, 51.90; H, 5.72; N, 26.89 and calculated %C, 51.92; H, 5.76; N, 26.92. Mass (m/z): 208 (M^+) amu, FT-IR (KBr) (ν_{max} , cm^{-1}) Fig. 1: 1618 and 1506 for azomethine group may be assigned to symmetric or asymmetric $-C=N-$ vibrations [26], 830(s) due to $-C=S-$ group, 3305, 3229, 1447 and 1323 appears due to $-NH_2$, $-NH$ and $-C=N$, NH_2 groups. 1H -NMR (DMSO, 300 MHz): δ - 2.02 ppm(t) (3H, H_3C-C-), 8.08 ppm(s) (1H, $HN-CO$), 3.14(d) (2H, H_2N-CO), 7.47-6.39 ppm(m) (4H, -ph-), 4.83 ppm(d) (2H, -ph- NH_2).

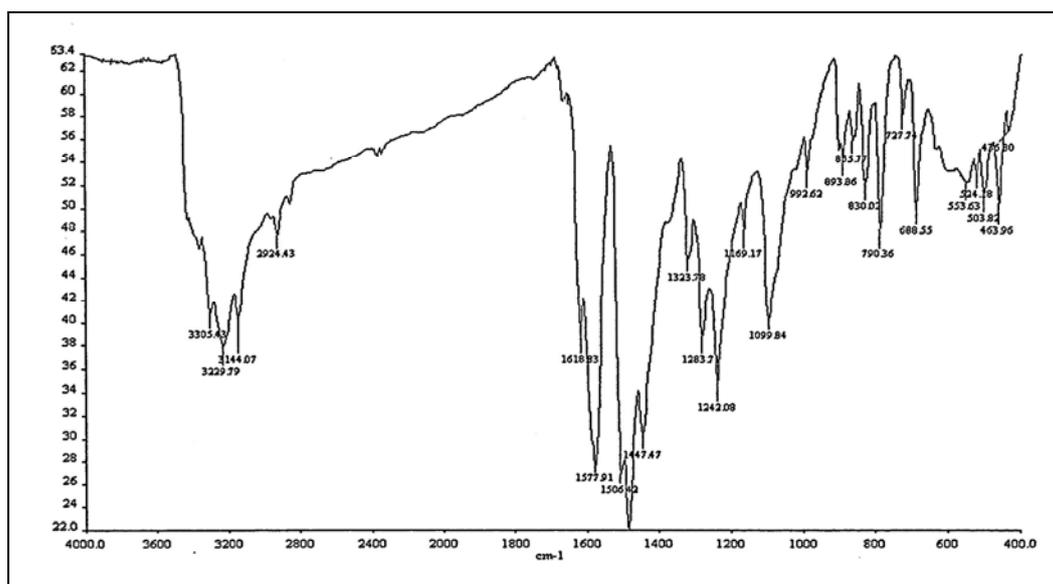


Fig. 1. IR spectra of Schiff base ligand 3-aminoacetophenonethiosemicarbazone

2.3. Electrode preparation

The PVC based membranes were prepared according to a method reported by Craggs et al. [27]. Varying amounts of the ionophore 3-aminoacetophenonethiosemicarbazone, plasticizers as nitrobenzene (NB), tri-n-butylphosphate (TBP), dibutylphosphate (DBP), dioctylphthalate (DOP), n-butylacetate (NBA), anion excluder sodiumtetraphenylborate (NaTPB) and PVC(as shown in Table 1 were dissolved in the minimum amount of tetrahydrofuran (THF). The solution was then allowed to evaporate for 24 hrs at room temperature to get transparent membrane of about 0.2 mm thickness. The viscosity of the solution solvent evaporation was carefully controlled to obtain membranes with reproducible characteristics and uniform morphology and thickness to avoid variations in electrode response. This was then cut to size and glued to one end of a Pyrex glass tube with araldite. The ratio of membrane ingredients, time of contact and concentration of equilibrating solution were optimized so that the membrane develops reproducible and stable potential.

2.4. Potential measurements

The potential measurements were carried out with a digital potentiometer (Model 5652 A, ECIL, India) in conjugation with SCE as reference electrodes. The membranes were equilibrated with a 1.0×10^{-1} M Cr (III) nitrate solution for 2-3 days and the potential measurements were carried at $25 \pm 0.1^\circ\text{C}$ using the following cell assembly: External saturated calomel electrode (SCE) / internal solution 0.1 M Cr (NO₃)₃ / membrane / test solution / internal saturated calomel electrode (SCE).

The concentration of Cr (NO₃)₃ in the test solution was varied over the range of 1.0×10⁻⁸ M to 1.0×10⁻¹ M.

2.5. Sampling

The sampling of the river water Yamuna was carried out in June 2009, in high grade plastic bottles (2L capacity) in triplicate and mixed to get a composite sample for each site. All the sample bottles were stored in ice boxes till brought to the laboratory for analysis. Five samples were taken from each site, which were homogenized and the composite samples were stored in high grade Teflon bottles.

3. RESULTS AND DISCUSSION

The Schiff base ionophore 3-aminoacetophenonethiosemicarbazone (**I**) has two coordination sites due to the presence of nitrogen and sulphur as donor atoms to form the metal chelate complexes. Ionophore used as electrode should have adequate complex formation constant and rapid exchange kinetics due to conformational changes between Schiff base ionophore and its metal complexes in the membrane. In addition, they should be very soluble in the membrane matrix, and have a sufficient lipophilicity to prevent leaching from the membrane in to the sample [28].

The ionophore was used as an ion selective electrode for a number of metal ions like alkaline earth metal ions, transition metals. Their potential responses and slopes were measured and shown in Fig. 2 and Table1. It can be seen that the membrane based on 3-aminoacetophenonethio-semicarbazone gives the best Nernstian response to the concentration of Cr(III) in a wide concentration range.

3.1. Working concentration range and slope

Before starting any experimentation, the membranes were equilibrated with 1.0×10⁻¹ M Cr(III) solution. The experiments have shown that 2-3 days equilibration time is required for generating reproducible and stable potential. Different plasticizers and NaTPB were added to the membranes with aim to improve the performance of electrode. It is well known that the addition of plasticizers not only improves the work ability of the membranes, but also contributes significantly towards the improvement in the working concentration range, stability, linearity, sensitivity and life time of electrode [29,30]. However, the selectivity remains usually unaffected and mainly depends on the metal-ionophore interaction. The plasticizer to be used in membranes should exhibit high lipophilicity, high molecular weight, low tendency for exudation from the polymer matrix, low vapor pressure and high capacity to dissolve the substrate and other additives present in the membrane. Additionally, its viscosity and dielectric constant should be adequate [31]. It should be noted that the presence of lipophilic anion in cation selective membrane electrodes not only

diminishes the ohmic resistance [32], but also enhances the response. Thus five plasticizers namely NB, TBP, DBP, DOP, NBA and anion excluder NaTPB were added in an attempt to improve the performance of electrode. For this purpose, the performance characteristics of several membranes having ingredients in the different preparations are listed in Table 1. Among these plasticizers, the use of 62% DBP in the presence of 30% PVC, 5.0% ionophore and 3% NaTPB (membrane no.3) gives the best sensitivity with a Nernstian slope of 19.7 ± 0.2 mV per decade in the concentration range of 1.0×10^{-8} M to 1.0×10^{-1} M. The practical limit of detection was 7.4×10^{-8} M as determined from the intersection of the two extrapolated segments of the calibration graph based on recommended procedure by IUPAC [33,34]. The overall optimized membrane potentiometric response characteristics have been summarized in Table 2, Fig. 2.

Table 1. Composition and characteristics of Cr(III) ISE's based on Schiff base ligand

S. No.	PVC	Plasticizer	Ionophore	Excluder NaTPB	Slope (mV/decade)	Response time (s)	Working concentration range (M)
1	33	59 (NB)	0	8	8.5 ± 0.7	25	1×10^{-6} to 1×10^{-4}
2	30	61 (TBP)	4	5	20.5 ± 0.4	13	1×10^{-7} to 1×10^{-3}
3	30	62 (DBP)	5	3	19.7 ± 0.2	10	1×10^{-8} to 1×10^{-1}
4	33	59 (DOP)	3	5	22.8 ± 0.5	14	1×10^{-7} to 1×10^{-4}
5	33	60 (NBA)	4	3	21.5 ± 0.8	18	1×10^{-5} to 1×10^{-2}

Table 2. Characteristics of optimized chromium ion-selective membrane electrode

Properties of the electrode	Values
Type of electrode	Plasticized PVC membrane electrode
Optimum composition w%	5:3:62:30 [I:NaTPB:DBP:PVC]
Conditioning time and concentration	2-3 days, 1.0×10^{-1} M
Linear working range	1.0×10^{-8} M to 1.0×10^{-1} M
Slope	19.7 ± 0.2 mV per decade
pH	1.5-6.8
Detection limit	7.4×10^{-8} M
Lifetime	14 weeks

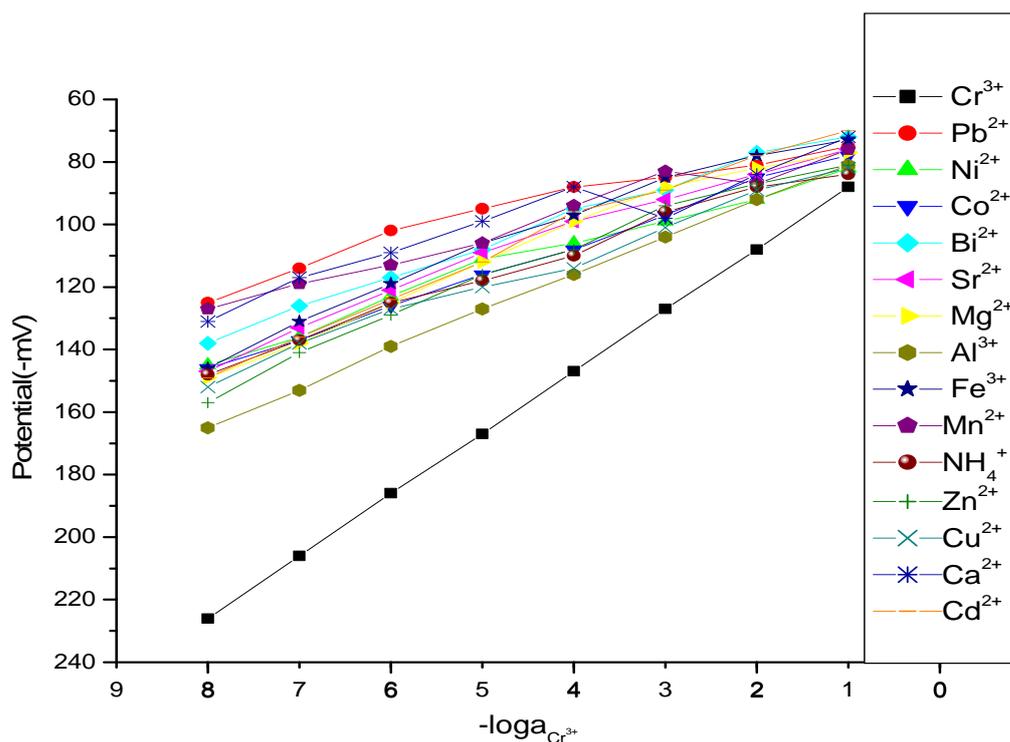


Fig. 2. Potentiometric response curves for different cations

3.2. Spectroscopic studies of Schiff base ligand with Cr (III) ions

The interaction mechanism of chromium ion with Schiff base ionophore was discussed on the basis of UV-Visible spectrophotometry. Thus, in order to investigate such mechanism UV-Visible spectra of carriers without and with Cr^{3+} were recorded. A UV-Visible spectrum of Schiff base ionophore 1.0×10^{-2} M concentration dissolved in DMSO was recorded first. It was then used for quantitative complexation with chromium by adding increasing amount of the chromium ion 1.0×10^{-2} M concentration. The UV-Vis spectra of Schiff base ligand as carrier [C] show the absorption band at 339 nm in Fig. 3(a). In Fig. 3(b) shift in the peak was observed at 363 nm with increased absorptivity when chromium ion interacted with the carrier, which shows that the size of the ionophore increases on interaction of chromium with the carrier. The absorption intensity changes as a function of $[\text{Cr}^{3+}]/[\text{C}]$ molar ratio.

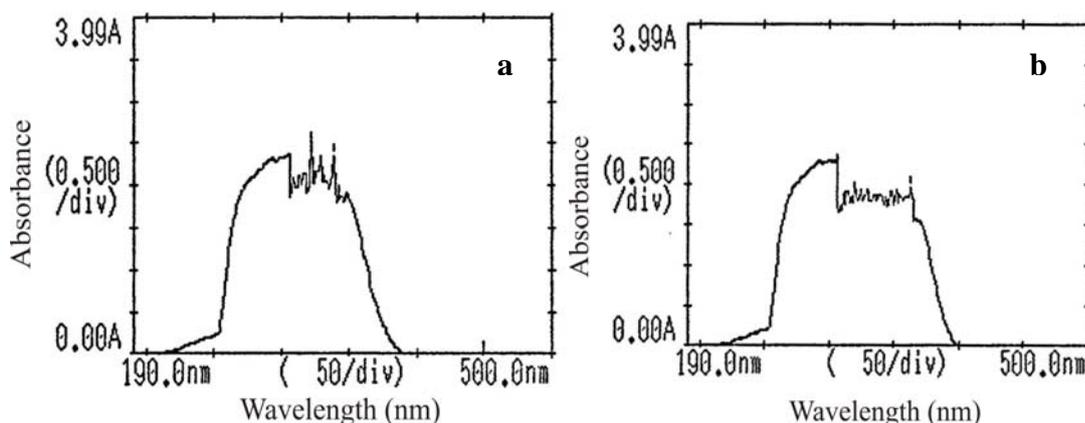


Fig. 3. UV-Vis spectra of 1.0×10^{-2} M ionophore as a carrier in DMSO in absence (a) and in presence (b) of 1.0×10^{-2} M Cr^{3+}

3.3. Effect of internal solution

The influence of the concentration of internal solution on the potential response of the polymeric electrode for Cr(III) was studied. The concentration was varied from 1.0×10^{-1} M to 1.0×10^{-5} M, and the potential response of the electrode was observed. It was found that the best results in terms of slope and working concentration range has been obtained with internal solution of activity 1.0×10^{-1} M concentration of $\text{Cr}(\text{NO}_3)_3$ solutions was quite appropriate for the smooth functioning of the proposed electrode.

3.4. Best pH range and non-aqueous effect

To study the influence of pH on the performance of electrode, the potential was studied by the use of 1.0×10^{-2} M of Cr^{3+} ions in the pH range of 1.0-7.0. To adjust the pH, very small volumes of concentrated NaOH or HCl were used. It was found that the potential remains constant within a pH range 1.5-6.8, this can be taken as the working pH range of the electrode. The results as shown in Fig. 4 at lower pH than 1.5 a sharp change in potential below pH 1.5 may be due to the response of the membrane to hydronium ion (protonation of nitrogen atoms in acidic media) while above 6.8, due to the formation of insoluble of chromium hydroxide, was observed. The effect of non-aqueous medium has also investigated by using electrode no. 3 in methanol-water, ethanol-water and acetone-water mixtures. The electrode worked satisfactorily up to 20% (v/v) of non-aqueous content. Hence, the electrode assembly can only be used in a non-aqueous medium when its concentration is not more than 20%.

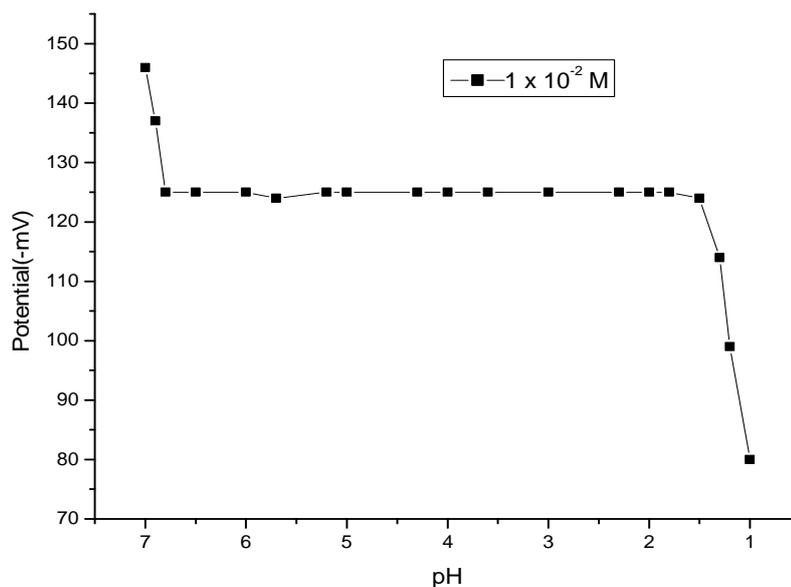


Fig. 4. Effect of pH on the potential response of Cr(III) selective electrode

3.5. Dynamic response time and life time of electrode

It is an important factor for any ion-selective electrode. According to IUPAC recommendation, the response time of the electrode is defined as the time between the additions of analyze to the sample solution and the time when a limiting potential has been reached [35]. In this study the practical response time of the proposed electrode was recorded by changing the concentration of chromium ion in a series of solution, in the range of 1.0×10^{-7} to 1.0×10^{-1} M. The resulting data depicted in Fig. 5 shows that the time needed to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of Cr^{3+} ions, each having a tenfold difference in concentration is 10s (electrode no. 3). The main factor responsible for the limited life time of an electrode is believed to be the loss of one or more of its components while contacting with aqueous solutions. Sufficient lipophilicity of ionophores and plasticizers ensures stable potentials and long lifetimes [29-31,34]. Among all the membranes prepared in this study, the lifetime of the electrode having DBP plasticizer was maximum and found to be 14 weeks. During this period, the electrodes were used over extended period of time (one hour per day). The performances with respect to slope and detection limit were measured and results are summarized in Table 3. After 14 weeks a slight gradual decreases in the slopes (from 19.7 ± 0.2 to 17.6 ± 0.5 mV per decade) was observed. However, it is important to emphasize that the membranes were stored in a 1.0×10^{-1} M Cr^{3+} solution when not in use.

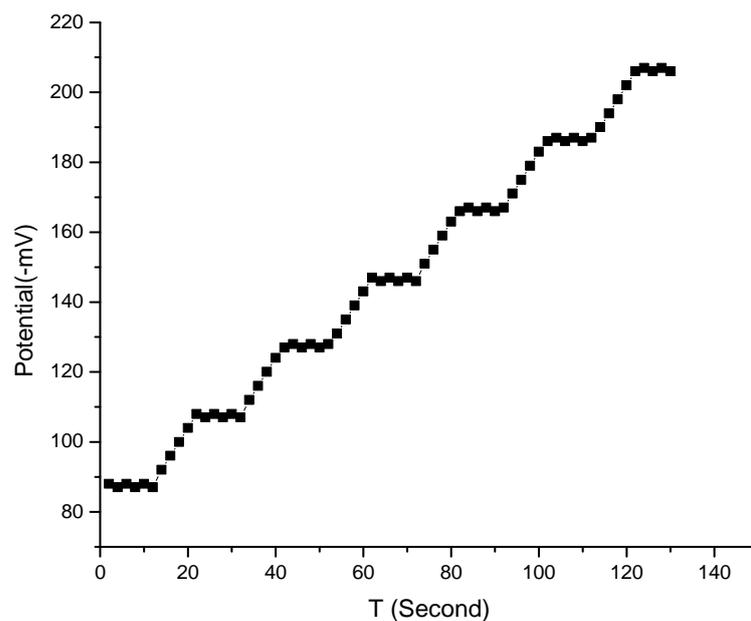


Fig. 5. Dynamic response time of the membrane electrode

Table 3. The life time study of the Cr(III)-selective electrode

No. of weeks	Slope(mV/decade)	Detection limit(M)
1	19.7	7.4×10^{-8}
2	19.7	7.4×10^{-8}
3	19.7	7.4×10^{-8}
4	19.7	7.4×10^{-8}
5	19.7	7.4×10^{-8}
6	19.7	7.4×10^{-8}
7	19.6	7.7×10^{-8}
8	19.5	8.1×10^{-8}
9	19.4	8.7×10^{-8}
10	19.3	9.1×10^{-8}
11	19.2	9.5×10^{-8}
12	19.1	4.1×10^{-7}
13	19.0	4.5×10^{-7}
14	18.9	4.8×10^{-7}
15	17.6	6.7×10^{-6}

3.6. Selectivity coefficient of proposed electrode

The influence of interfering ions on the potential response behavior of the ion-selective membrane electrode is usually described in terms of selectivity co-efficient [37]. Different methods of selectivity determination have found in the literature. In this work, we determined selectivity coefficients with most widely used procedure match potential method (MPM) [38,39]. This method has an advantage of removing limitations imposed by Nicolsky-Eisenman equation while calculating selectivity coefficient by other methods. These limitations include non-Ernestina behaviour interfering ion and problem of inequality of charges of primary and interfering ions. According to the MPM, the selectivity coefficients are defined as the activity ratio of the primary ion (A) and the interfering ion (B) that gives the same potential change in a reference solution. Thus, one should measure the change in potential upon changing the primary ion activity. Then the interfering ion would be added to an identical reference solution until the same potential change is obtained.

The selectivity coefficient $K_{A,B}^{pot}$ is determined as:

$$K_{A,B}^{pot} = \Delta A_{Cr^{3+}} / a_B$$

Where $\Delta A_{Cr^{3+}} = (a'_{Cr^{3+}} - a_{Cr^{3+}})$ that $a_{Cr^{3+}}$ is the initial activity of primary ion which is then increased to $a'_{Cr^{3+}}$ resulting in some change in potential, a_B is the activity of the interfering ion which added to $a_{Cr^{3+}}$ causes the some change in potential as observed when $a_{Cr^{3+}}$ was increased to $a'_{Cr^{3+}}$. The resulting values are summarized in Table 4.

Table 4. Selectivity coefficient $K_{A,B}^{pot}$ values of Cr^{3+} selective electrode by MPM

S. No.	Interfering ion (B)	Selectivity coefficients	S. No.	Interfering ion (B)	Selectivity coefficients
1	K^+	1.0×10^{-2}	8	Co^{2+}	4.8×10^{-2}
2	NH_4^+	2.0×10^{-2}	9	Ca^{2+}	3.1×10^{-2}
3	Cd^{2+}	4.4×10^{-2}	10	Ba^{2+}	3.4×10^{-2}
4	Pb^{2+}	3.0×10^{-2}	11	Fe^{3+}	4.0×10^{-2}
5	Cu^{2+}	3.8×10^{-2}	12	Sr^{2+}	3.2×10^{-2}
6	Ni^{2+}	4.1×10^{-2}	13	Mg^{2+}	3.7×10^{-2}
7	Zn^{2+}	2.1×10^{-2}	14	Al^{3+}	3.3×10^{-2}

It is evident from the selectivity coefficient data, that electrode exhibits high performance for Cr^{3+} over a number of other cations used. The surprising high selectivity of the membrane electrode for Cr^{3+} ion, most probably arise from strong tendency of the ionophore for the Cr^{3+} ions. A value of selectivity coefficient equal to 1.0 indicates that the electrode responds equally to primary as well as interfering ion. However, values smaller than 1.0 indicate that membrane electrode is responding more to primary ion than to interfering ions and in such a

case the electrode is said to be selective to primary ion over interfering ion. Hence, the electrode is sufficiently selective over a number mono-, di- and trivalent cations studied and can therefore be used to estimate chromium in presence of these ions by direct potentiometry.

4. ANALYTICAL APPLICATION

4.1. Analysis of Cr^{3+} ions by the water samples of river Yamuna

The proposed Cr^{3+} ion-selective electrode was found to work well under the laboratory conditions. It was successfully applied to the determination of chromium of the water samples collected from the various sites of river Yamuna in Delhi (India) region. The analysis of river water samples does not require pretreatment except pH adjustment. The pH for all samples was adjusted at 4.5. The results observed for analysis were also compared with atomic absorption spectrometry (AAS) analyzer. It is clear from the values in Table 5 that these were

In a good agreement with the results obtained by AAS. Hence, the proposed electrode can be successfully employed for the estimation of Cr (III) in waste water samples.

Table 5. Analysis of Cr^{3+} ions of river water of Yamuna by proposed electrode and AAS

Samp le no.	Name of place	pH found	pH after adjustment	Cr^{3+} concentration as determined by electrode (ppm)	Cr^{3+} concentration as determined by AAS (ppm)
1	Ramghat	6.82	4.5	0.08±0.02	0.08±0.01
2	Soor Ghat	6.59	4.5	0.55±0.03	0.54±0.02
3	Laxmi nagar	6.84	4.5	0.53±0.05	0.55±0.02
4	Okhla Bridge	7.19	4.5	0.59±0.02	0.57±0.03

5. COMPARISON OF THE PROPOSED ELECTRODE WITH PREVIOUSLY REPORTED ELECTRODES

Proposed electrode compare with previously best reported Cr^{3+} electrodes [4,6,8,10,20, 22] in terms of working concentration range, response time and pH range. Our proposed electrode shows better selectivity as compared to most reported electrodes, as found in Table 6 that the interference values of diverse ions are very less.

Table 6. Comparison of proposed Cr³⁺- selective electrodes with the reported electrodes

Ionophore	Working concentration range(M)	Detection limit(M)	Response time(s)	Working pH range	Reference no.
Aurin TCA	1.0×10 ⁻¹ to 1.0×10 ⁻⁶	N.M.*	10	3.5-6.5	8
4-Dimethyl amino benzene	1.0×10 ⁻² to 1.66×10 ⁻⁶	8.0×10 ⁻⁷	<20	3.0-5.5	10
TTCT	1.0×10 ⁻¹ to 1.0×10 ⁻⁶	7.0×10 ⁻⁷	15	3.0-5.5	6
Oxalic acid bis(cyclohexylidene hydrazide Schiff bases	1.0×10 ⁻² to 1.0×10 ⁻⁷	6.3×10 ⁻⁶	<20	1.7-6.5	4
	8.0×10 ⁻⁷ to 1.5×10 ⁻⁶	1.0×10 ⁻⁶	<10	3.0-6.0	20
N-(Acetoacetanilide)-1,2-diaminoethane	1.0×10 ⁻⁸ to 1.0×10 ⁻²	1.58×10 ⁻⁹	22	2.0-5.5	22
3-aminoacetophenone-thiosemicarbazone	1.0×10 ⁻⁸ to 1.0×10 ⁻¹	7.4×10 ⁻⁸	10	1.5-6.8	Proposed work

*Not Mentioned

6. CONCLUSION

The results obtained from the above mentioned study revealed that a potentiometric PVC membrane based on a newly synthesized Schiff base ligand 3-aminoacetophenonethiosemicarbazone as an ionophore with a DBP as plasticizer and NaTPB as anion excluder in a ratio 5:3:62:30 [I:NaTPB:DBP:PVC] can be used for the determination of Cr(III) ions. The response time of the electrode is quite low and it could successfully be used for 14 weeks without showing any significant drift in any of the response characteristics. The proposed electrode can be successfully employed to determine Cr(III) quantitatively in the water samples of river Yamuna collected from four different sites of Delhi.

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