All Solid State Chromium(III) Selective Potentiometric Sensor Based on 2-(1-(2-((3-(2-Hydroxyphenyl)-1*H*-pyrozol-1-yl)methyl)benzyl)-1*H*-pyrazol-3-yl)phenol

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Abstract: Highly selective all solid state electrochemical sensor based on a synthesized compound i.e. 2-(1-(2-((3-(2-hydroxyphenyl)-1*H*-pyrozol-1-yl)methyl)benzyl)-1*H*-pyrazol-3-yl)phenol (I) as an ionophore has been prepared and investigated for the selective quantification of chromium(III) ions. The effect of various plasticizers, viz. dibutyl phosphonate (DBP), dibutyl(butyl) phosphonate (DBBP), nitrophenyl octyl ether (NPOE), tris-(2-ethylhexyl)phosphonate (TEP), tri-butyl phosphonate (TBP), dioctyl phthalate (DOP), dioctyl sebacate (DOS), benzyl acetate (BA) and acetophenone (AP) along with anion excluders NaTPB (sodium tetraphenyl borate) and KClTPB (potassium(tetrakis-4-chlorophenyl)borate was also studied. The optimum composition of the best performing membrane contained (I):KClTPB:NPOE:PVC in the ratio 15:3:40:42 w/w. The sensor exhibited near Nernstian slope of 20.1 ± 0.2 mV/decade of activity in the working concentration range of 1.2×10^{-7}–1.0×10^{-1} M, and in a pH range of 3.8–4.5. The sensor exhibited a fast response time of 10 s and could be used for about 5 months without any considerable divergence in potentials. The proposed sensor showed very good selectivity over most of the common cations including Na^+, Li^+, K^+, Cu^{2+}, Sr^{2+}, Ni^{2+}, Co^{2+}, Ba^{2+}, Hg^{2+}, Pb^{2+}, Zn^{2+}, Cs^+, Mg^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+} and La^{3+}. The activity of Cr(III) ions was successfully determined in the industrial waste samples by using this sensor.

Keywords: Chromium selective electrode · Potentiometric sensors · Chemical sensors · Electroactive materials

1 Introduction

Carrier based ion sensors provide a suitable means for selective quantification of one or more analytes within a complex mixture. The utility of these sensors is being increasingly realized by analytical chemists in view of the rapid growth of industries and technologies all over the world as they represent rapid, accurate and low cost procedure for trace metal analysis [1–4]. Generally, sophisticated analytical techniques like AAS (Atomic Absorption Spectroscopy), HPLC (High Performance Liquid Chromatography), XRF (X-Ray Fluorescence), and ICP- AES (Inductively Coupled Plasma–Atomic Emission Spectroscopy) are the choice for the trace level determination of metals, but these techniques are disadvantageous in terms of cost of routine analysis, time consumption and tedious procedure of sample preparation and pretreatment. Therefore, ion sensors are good alternative for the job. Also, ion sensors are of interest because they help to translate the chemistry of new substrate binding systems into tools that can be used to recognize selectively various target species in presence of the potentially interfering analytes. Electrically neutral lipophilic ligands containing an appropriate number of binding sites of high solvating ability can behave as ionophore to prepare ion-selective membrane to detect different metal ions. The selectivity of the given sensor is dictated mainly by the complexation specificity of the receptor involved and the

potentiometric response of the membrane based ion sensor containing a specific ligand that can be used to provide information about the mode of analyte binding as well as insights into the relevant substrate-receptor interactions.

Chromium is required in human body for the digestion of carbohydrates and fat. Its adequate intake for an adult is recommended as 50–200 µg per day [5,6]. On one hand its deficiency may cause cardiovascular diseases and also to diabetes but on the other hand its excessive intake may lead to epigastric pain, toxicity in respiratory tract, nausea, vomiting, diarrhea, hemorrhage and cancer. Chromium is extensively used in various industrial processes like leather tanning, wood treatment, steel manufacturing, metal finishing, and paint and pigment industry etc. The waste from these industries/processes contain appreciable amount of chromium, if not treated properly. Therefore, a quick reliable and online method for selective quantification of chromium is highly desired. Chemical sensors may serve the purpose pretty effectively. Literature survey reveals that some chromium selective sen-

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sors have already been reported by reserachers which take advantage of different types of electroactive materials e.g. 4-dimethylaminoazobenzene [7], 1-(2-(1*H*-imidazole-1-yl)-1-(4-methoxyphenyl)ethylidene)-2-phenyl hydrazine [8], 1-[(2-hydroxy ethyl) amino]-4-methyl-9*H*-thioxanthen-9-one [9], 4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one [10], 2-acetylpyridine [11], *N*-(1-thien-2-ylethylidene)benzene-1,2-diamine [12], 5-amino-1-phenyl-1*H*-pyrazole-4-carboxamide [13], tributylphosphate [14], *N*-(acetoacetanilide)-1,2-diaminoethane and *N*,*N'*-bis(acetoacetanilide)-triethylenetetraammine [15], glyoxal bis(2-hydroxyanil) [16], oxalic acid bis(cyclohexylidine hydrazine) [17], tri-*o*-thymotide [18] and Aurin TCA [19], and *p*-(4-acetanilidazo)calix[4]arene [20]. These compounds are supramolecular receptors which make complexes with specific metal ions and exhibit conformational flexibility and high mobility [21]. Some of these sensors show narrow working concentration range and suffer high interference due to the presence of other metal ions present in the sample. Therefore, the work to develop a better sensor was carried out by using a new synthesized compound i.e. 2-(1-(2-((3-(2-hydroxyphenyl)-1*H*-pyrozol-1-yl)methyl)benzyl)-1*H*-pyrazol-3-yl)phenol which is selective towards Cr(III) ions. The proposed sensor is based on the PVC membranes prepared by incorporating this electroactive compound. During the study optimization of the composition of the membranes was done to obtain the best response characteristics of the proposed sensor. Also, the activities of Cr(III) ions have been determined in the industrial wastes collected from electroplating industries. The obtained results were compared with those obtained by using atomic absorption spectrophotometer.

2 Experimental

2.1 Materials and Methods

2-(1-(2-((3-(2-Hydroxyphenyl)-1*H*-pyrozol-1-yl)methyl)-benzyl)-1*H*-pyrazol-3-yl)phenol was synthesized as described elsewhere [22]. Tetrahydrofuran and EDTA were purchased from (Merck, India). High molecular weight PVC and KClTPB were purchased from (Fluka, Switzerland). Metal solutions were prepared in doubly distilled water and standardized by appropriate methods. Plasticizers NPOE, DBBP, DBP, TEP, TBP, BA, AP, DOS and DOP were obtained from (Mobil, USA), and NaTPB from (BDH, UK). The nitrate and chloride salts of the cations of analytical grade were used without any further purification. Perkin-Elmer 3100 atomic absorption spectrophotometer was used to determine chromium ion concentration in standard solutions as well as in test samples were recorded by using PH 5652 digital millivoltmeter (ECIL, Hyderabad) India.

2.2 Preparation of the Electrode and Cell Setup

Varying weight ratios of synthesized ionophore, as sensing material and PVC as inert support matrix were dissolved in 5 mL of tetrahydrofuran solvent. The mixture was shaken vigorously in a shaker to get a homogeneous solution. It took maximum 30 minutes for the same. The electrode membrane was prepared by dropping 10 µL of the membrane solution cocktail on a thoroughly cleaned and polished graphite electrode covered in teflon. The solution was allowed to evaporate for 24 h in a closed cabinet at room temperature. Many such sensors were prepared and equilibrated in a solution having constant activity of a particular metal ion. The time of contact between electrode and the solution, ratio of membrane ingredients were optimized after a good deal of experimentation to obtain the membranes, which generated stable and reproducible results. Plasticizers are known to improve the response of membrane by providing a smooth surface and homogeneity. Anion excluders suppress the interference caused by the undesired passing of anions through the membrane and ensure the permselectivity. The effect of the addition of plasticizers namely NPOE, DBP, DOP, DBBP, TBP, DOS, BA, AP and TEP; and anion excluders namely NaTPB and KClTPB was studied after adding them as membrane ingredients.

The cell was composed of graphite electrode/Test solution/External reference electrode (Ag-AgCl). The activity of the metal ion in the test solutions varied from 1.0×10^{-8} to 1.0×10^{-1} M. the observed potential values were plotted against negative log values of cation activities to plot the calibration curves. This is to note that the sensors were stored in 0.1 M chromium(III) solution when not in use to avoid cracking of PVC based membranes.

3 Results and Discussion

3.1 Complexation Study

To determine the maximum selectivity of the ionophore towards a metal ion, distribution coefficient values were calculated. The experiments were based on titration of standard EDTA solution firstly with 20 mL 0.1 M solution of particular metal ion taking one ion at a time; namely Cr^{3+}, Li^+, K^+, Na^+, Ni^{2+}, Hg^{2+}, Co^{2+}, Cu^{2+}, Sr^{2+}, Ba^{2+}, Cs^+, Pb^{2+}, Zn^{2+}, Mg^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+}, and La^{3+}; and then with the same solution after it remained in contact with 0.2 g of ionophore for 24 h. Distribution coefficient values were calculated by using the formula

$$K_d = (I - F)/F \ V/W$$

where I is the volume of EDTA required by the metal ion solution before the interaction with the ligand, F is the volume of EDTA required by the metal ion solution after interaction with the ligand, V is the initial volume of the metal ion solution, and W is the initial dry mass of ion exchanger.

After calculations, the distribution coefficient value for Cr^{3+} was obtained as 36.2 while for all other metal ions it remained between 12.2 and 23.7. It shows that the ionophore is selective for Cr^{3+} ions. Therefore, the ionophore

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is explored as neutral ionophore for the fabrication of Cr^{3+} selective and sensitive electrode.

3.2 Response Characteristics of the Sensor

The sensors were prepared by using PVC membrane containing 2-(1-(2-((3-(2-hydroxyphenyl)-1H-pyrozol-1-yl)-methyl)benzyl)-1H-pyrazol-3-yl)phenol (Figure 1) as an electroactive material and were tried for potential response for different metal ions namely Cr^{3+}, Li^+, K^+, Na^+, Ni^{2+}, Hg^{2+}, Co^{2+}, Cu^{2+}, Sr^{2+}, Ba^{2+}, Cs^+, Pb^{2+}, Zn^{2+}, Mg^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+}, and La^{3+}. The best results were obtained for chromium(III) ions. Lower potential values were observed for Al^{3+} and Fe^{3+} ions while Cd^{2+} and Mg^{2+} also exhibited response with very less slope values. It shows the selective behavior of the ionophore towards Cr^{3+} in comparison to the other metal ions and the rapid exchange kinetics of the resulting ligand-metal ion complex. This is important to mention that for the sake of uniformity, the potential values for 0.1 M metal ion concentrations are adjusted to zero in all the cases. It was observed that the generated potentials remained stable for about three minutes and the value start to decrease very slowly. The weight ratio of the ionophore was varied and it was observed the membranes prepared by using only ionophore and PVC in the composition I: PVC; 15:85 (w/w) exhibited the best response. Solvent mediators, if added into the membrane ingre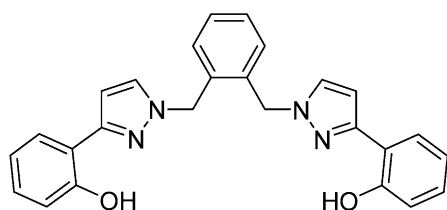dients provide a smooth surface. These compounds can also improve the potential response of the sensor by facilitating the movement of ionophore and its metal complex [23]. Also some additives like anion excluder improve the selectivity and sensitivity of cation selective membranes by ensuring the Donnan exclusion of co-ions and thus preventing the interference offered by anions [24]. Therefore, the effect of the addition of anion excluder KClTPB, and NaTPB; and plasticizers like TBP, DOS, BA, AP, DBP, DOP, TEP, NPOE, and DBBP on the performance of the fabricated sensors was also studied (Table 1). The membrane containing only 2-(1-(2-((3-(2-hydroxyphenyl)-1H-pyrozol-1-yl)methyl)benzyl)-1H-pyrazol-3-yl)phenol in the PVC matrix exhibited a linear response of 4.0×10^{-5}–1.0×10^{-1} M with a slope of 18.0 mV/decade of activity. After adding the anion excluder KClTPB and NPOE as a plasticizer, the sensor exhibited the best results (sensor no. 12). This sensor displayed linear potential response over concentrations range of 1.2×10^{-7}–1.0×10^{-1} M with the slope of 20.1 mV/decade of activity (Figure 2). Repeated monitoring of potentials (10 measurements) on the same sample gave a standard deviation of 0.5 mV while the deviation in slope values was 0.5–1.0 mV which suggested good reproducibility.

3.3 Response Time and Life Time

The time required to achieve 95% of the final potential change after successive immersion of the sensor in a series of metal ion solutions is known as response time of that sensor. The response time of the membranes containing only ionophore and PVC was recorded between 90 and 120 s at higher activity levels of test solution and 120–180 s at lower activity levels i.e. below 10^{-4} M. The addition of plasticizers reduced the response time significantly. The quickest time was 10 s displayed by the membrane no. 12, containing NPOE as a plasticizer (Table 1). The results with DOP, DOS and AP were also found good (20–40 s).

To determine the life time of the sensor, its response was recorded daily. The results were observed as fairly

Fig. 1. Structure of ionophore 2-(1-(2-((3-(2-hydroxyphenyl)-1H-pyrozol-1-yl)methyl)benzyl)-1H-pyrazol-3-yl)phenol (I).

Table 1. Composition of PVC based membranes of 2-(1-(2-((3-(2-hydroxyphenyl)-1H-pyrozol-1-yl)methyl)benzyl)-1H-pyrazol-3-yl)-phenol and performance characteristics of Cr(III) selective all solid state sensors based on them.

| S.N.	(I)	PVC	Plasticizer	Anion excluder	Working concentration range (M)	Slope (mV/activity dec.)	Response time (s)
1.	15	85			4.5×10^{-5}–1.0×10^{-1}	18.0	90–120
2.	15	45	40 (DBP)		8.5×10^{-6}–1.0×10^{-1}	18.6	40
3.	15	50	35 (DBBP)		1.0×10^{-6}–1.0×10^{-1}	18.5	40
4.	15	45	40 (TEP)		4.0×10^{-6}–1.0×10^{-1}	18.5	45
5.	15	60	25 (TBP)		1.7×10^{-6}–1.0×10^{-1}	18.5	45
6.	15	60	25 (DOP)		9.0×10^{-7}–1.0×10^{-1}	19.4	22
7.	15	55	30 (DOS)		1.0×10^{-6}–1.0×10^{-1}	19.4	20
8.	15	60	25 (BA)		9.0×10^{-6}–1.0×10^{-1}	18.5	30–40
9.	15	45	40 (AP)		3.0×10^{-6}–1.0×10^{-1}	19.5	25–35
10.	15	45	40 (NPOE)		3.6×10^{-7}–1.0×10^{-1}	20.0	12–15
11.	15	42	40 (NPOE)	3 (NaTPB)	2.0×10^{-7}–1.0×10^{-1}	20.0	10
12.	15	42	40 (NPOE)	3 (KClTPB)	1.2×10^{-7}–1.0×10^{-1}	20.1	10
13.	13	44	40 (NPOE)	3 (KClTPB)	2.8×10^{-7}–1.0×10^{-1}	20.1	10
14.	16	41	40 (NPOE)	3 (KClTPB)	1.2×10^{-7}–1.0×10^{-1}	20.1	10
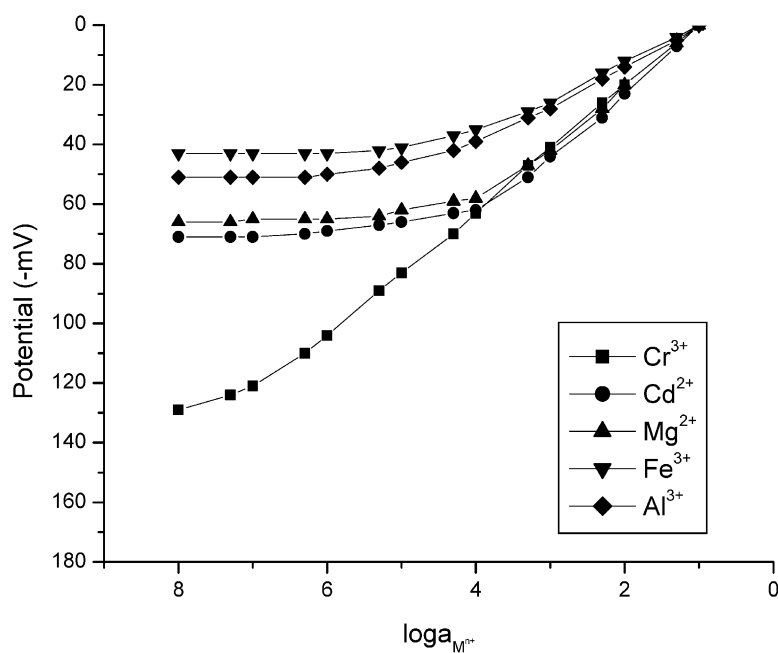
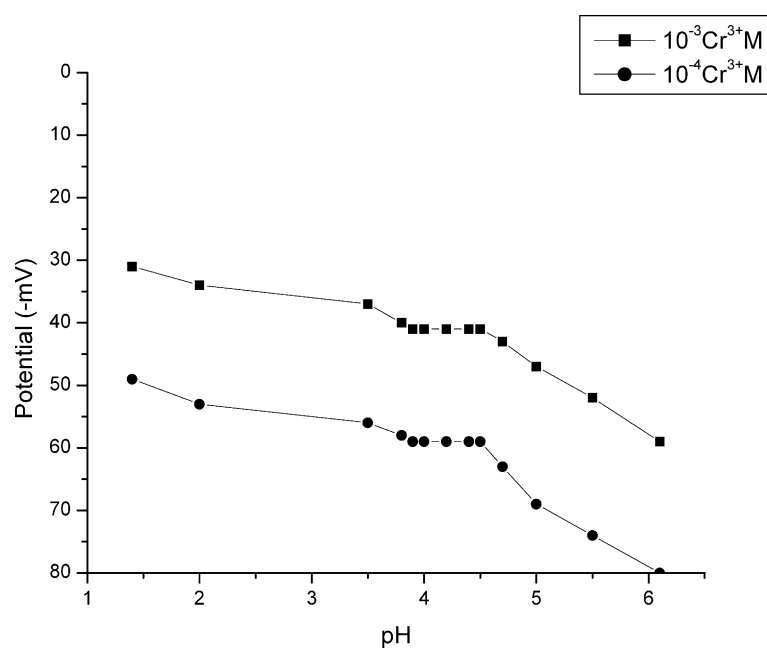Fig. 2.   Calibration graph of the proposed Cr(III)-selective sensor (composition no. 12).

Fig. 3.   Effect of pH of the test solution on the potentiometric response of the sensor no 12.

constant over a period of four months when NaTPB was used as an anion excluder in the membrane. The life time of the sensor was increased about two weeks when KClTPB was used instead of NaTPB. After this period a drift in potentials was observed then the membrane was discarded. Relatively short life time of the sensor containing NaTPB as membrane ingredient may be due to the less lipophilicity of NaTPB.

3.4 pH and Non-Aqueous Effect

The effect of pH on the performance of the sensor was studied at two concentrations of the test solutions i.e. 1.0×10^{-3} and 1.0×10^{-4} M Cr^{3+}. The pH of these solutions were varied from 1.0–8.0 by using hexamine and nitric acid. The potential remained unaffected of the pH of the test solution over the pH range of 3.8–4.5 (Figure 3). The drift in potential values below pH 3.8 may be caused by H^+ co-fluxing and above pH 4.5 may be due to hydrolysis

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Table 2. The working concentration range and slope values recorded per week. No 6 keeps on changing day by day.

No. of months	Working concentration range (M)	Slope (mV/activity decade)
1	1.2×10^{-7}–1.0×10^{-1}	20.1
2	1.2×10^{-7}–1.0×10^{-1}	20.1
3	1.2×10^{-7}–1.0×10^{-1}	20.0
4	1.8×10^{-7}–1.0×10^{-1}	19.9
5	9.5×10^{-7}–1.0×10^{-1}	18.1
6	3.3×10^{-5}–1.0×10^{-1}	15.5

Table 3. Effect of presence of non-aqueous content on the performance of the proposed all solid state potentiometric sensor for the determination of Cr(III) ions.

Percentage of non-aqueous content	Working concentration range (M)	Slope (mV/decade of activity)
Methanol		
10	1.2×10^{-7}–1.0×10^{-1}	20.1
15	1.2×10^{-7}–1.0×10^{-1}	20.1
20	3.0×10^{-7}–1.0×10^{-1}	19.8
25	9.0×10^{-7}–1.0×10^{-1}	19.4
Acetone		
10	1.2×10^{-7}–1.0×10^{-1}	20.1
15	1.2×10^{-7}–1.0×10^{-1}	20.1
20	5.5×10^{-7}–1.0×10^{-1}	19.5
25	1.8×10^{-6}–1.0×10^{-1}	19.0

of Cr^{3+} ions. It was made sure that the pH of the standard solutions of Cr(III), used for calibration of the electrode, remains within the above written pH range.

Partially non-aqueous mediums i.e. methanol-water, and acetone-water mixtures were used to investigate the performance of the sensor in these mediums (Tables 2 and 3). Sensor no. 12 could tolerate the nonaqueous content only up to 15 % (v/v). The working concentration range decreased sharply when the non-aqueous content exceeds this volume percentage (Tables 2 and 3).

3.5 Selectivity

Selectivity is the most important parameter of the sensor which is determined in terms of potentiometric selectivity coefficient values ($K_{Cr^{3+},B^{pot}}$). Potentiometric selectivity coefficient values are evaluated by using a modified form of the fixed interference method as well as by matched potential method (MPM) [25,26]. MPM is recommended by International Union of Pure and Applied Chemistry, which gets rid of the limitation of the corresponding methods based on Nicolsky–Eisenman equation used for the same purpose. According to MPM the selectivity coefficient is the activity ratio of the primary ion (A) and the interfering ion (B) that exhibits the same potential change in a reference solution of Cr(III) ions. The interfering ion should be added to an identical reference solution until the same potential change is reached.

Table 4. Potentiometric selectivity coefficient values ($K_{Cr^{3+},B^{pot}}$), obtained for various interfering ions.

Interfering ion	Fixed interference method	Matched potential method
Na^+	1.3×10^{-3}	8.7×10^{-3}
Li^+	3.2×10^{-3}	6.2×10^{-3}
K^+	5.0×10^{-3}	1.3×10^{-3}
Cs^+	6.5×10^{-3}	5.4×10^{-3}
Co^{2+}	8.0×10^{-3}	7.5×10^{-3}
Sr^{2+}	1.0×10^{-2}	6.6×10^{-3}
Ni^{2+}	3.5×10^{-3}	2.7×10^{-3}
Cu^{2+}	2.0×10^{-3}	7.1×10^{-3}
Hg^{2+}	6.9×10^{-3}	5.5×10^{-3}
Zn^{2+}	1.0×10^{-2}	6.2×10^{-3}
Ba^{2+}	7.6×10^{-3}	3.8×10^{-3}
Cd^{2+}	4.0×10^{-2}	9.0×10^{-2}
Pb^{2+}	5.0×10^{-3}	8.5×10^{-3}
Mg^{2+}	3.7×10^{-3}	4.6×10^{-3}
La^{3+}	5.7×10^{-3}	5.2×10^{-3}
Al^{3+}	2.0×10^{-3}	8.0×10^{-3}
Fe^{3+}	9.0×10^{-3}	7.8×10^{-3}

$$K_{Cr^{3+},B^{pot}} = \frac{a'_{Cr} - a_{Cr}}{a_B}$$

a_{Cr} represents the initial primary ion Cr^{3+} activity and a'_{Cr} is the primary ion activity in the presence of interfering ion B while a_B is the activity of interfering ion. The data is presented in Table 4 clearly indicate that the electrode is selective towards Cr^{3+} over a number of cations as the selectivity coefficient values are of the order of 10^{-2}. The smaller values of selectivity coefficient suggest that the response of the sensor will remain unaffected of the presence of other cations in the test samples. Relatively increased selectivity coefficient values were observed in case of Cd(II) ions. Therefore, to determine the maximum tolerable activity of Cd^{2+} ions, some mixed run studies were carried out. The sensor could tolerate Cd^{2+} ions up to 1.0×10^{-4} M. But if Cd^{2+} activity is increased further, the sensor could be used to determine Cr^{3+} over a reduced concentration range only. In the presence of 1.0×10^{-3}, and 1.0×10^{-2} M Cd^{2+}, the electrode assembly

Table 5. Cr(III) activity as determined by the proposed all solid state potentiometric sensor as well as by atomic absorption spectrophotometer.

Sample no.	pH found	pH adjusted at	Cr(III) activity as determined by the proposed sensor (ppm)	Cr(III) concentration as determined by AAS (ppm) (± 0.2)
1	2.7	4.0	12.6	12.9
2	2.3	4.0	11.3	11.2
3	2.0	4.0	9.0	9.2
4	2.2	4.0	7.8	7.8
5	4.7	4.0	17.5	17.6
6	5.1	4.0	18.2	17.9
7	4.5	4.0	14.3	14.3
8	4.7	4.0	16.6	16.8

Table 6. Comparison of proposed chromium(III)-selective electrode with some of the earlier reported electrodes.

Ionophore used	Working concentration range (M)	Detection limit (M)	Working pH range	Interference	Response time (s)	Reference
4-Dimethyl aminobenzene	1.66×10^{-6}–1.0×10^{-2}	8.0×10^{-7}	3.0–5.5	Cu^{2+}, Ag^+, Fe^{3+}	10	[3]
N,N'-Bis(acetoacetanilide)	8.3×10^{-7}–1.0×10^{-1}	6.3×10^{-7}	2.0–5.5	No interference	22	[11]
Triethylenetetraamine glyoxal bis(2-hydroxyanil)	3.0×10^{-6}–1.0×10^{-2}	6.3×10^{-7}	2.7–6.5	Zn^{2+}	20	[12]
Oxalic acid bis(cyclohexylidine hydrazide	1.0×10^{-7}–1.0×10^{-2}	6.3×10^{-7}	1.7–6.5	Cd^{2+}, Ni^{2+}	20	[13]
Tri-o-thymotide	4.0×10^{-6}–1.0×10^{-1}	2.0×10^{-7}	2.8–5.1	Na^+, Cd^{2+}	15	[14]
p-(4-Acetanilidazo) calix[4]arene	9.8×10^{-7}–1.0×10^{-1}	7.3×10^{-7}	2.8–5.7	No interference	14	[15]
Aurin TCA	7.0×10^{-6}–1.0×10^{-1}	Not mentioned	3.5–6.5	Na^+, Zn^{2+}, Pb^{2+}	10	[16]
1-[(2-Hydroxy ethyl) amino]-4-Methyl-9H-thioxanthen-9-one	3.2×10^{-7}–1.0×10^{-1}	1.6×10^{-7}	4.8–6.3	NM	10	[5]
4-Amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one	1.0×10^{-6}–1.0×10^{-1}	5.8×10^{-7}	2.7–6.6	NM	8	[6]
N-(1-Thien-2-ylethylidene)benzene-1,2-diamine	1.0×10^{-6}–1.0×10^{-1}	7.0×10^{-7}	3.0–6.6	NM	15	[8]
2-(1-(2-((3-(2-Hydroxyphenyl)-1H-pyrozol-1-yl)methyl)benzyl)-1H-pyrazol-3-yl)phenol	1.2×10^{-7}–1.0×10^{-1}	8.6×10^{-8}	3.8–4.5	Cd^{2+}	10	This work

could be used in the concentration ranges of 2.7×10^{-5}–1.0×10^{-1}, and 9.0×10^{-5}–1.0×10^{-1} M respectively.

3.6 Analytical Application

The developed sensor has been successfully used to determine the activity of chromium ions in real samples. Four samples were collected from a lather tanning industry at the interval of seven days and another four samples from an electroplating industry in a similar fashion. The samples were collected, filtered, and stored in PET bottles and were analyzed within 2 h of their collection. pH of these solutions was adjusted at 3.0 by using 0.1 M HNO_3 and hexamine. Cr(VI) ions were converted to Cr(III) ions, if present any, by following the reported procedure [27]. The results presented in Table 5 are the average values of four results obtained for the same sample. There is good agreement between the results obtained by using the developed sensor, and those obtained by using the atomic absorption spectrophotometer as a standard method.

To assess the performance of the proposed sensor, the results were compared with the existing sensors. This sensor shows better working concentration range [7,9,10,12,15–20], better selectivity [7,10,16,17,18,20] and better response time [15–19]. Therefore, the proposed sensor is a good addition in the existing list of Cr(III) selective sensors (Table 6).

4 Conclusions

The results obtained for a new all solid state sensor, selective towards Cr(III) ions have been presented here. The developed sensor contains synthesized N_2O_2-donor ligand i.e. 2-(1-(2-((3-(2-hydroxyphenyl)-1H-pyrazol-1-yl)methyl)benzyl)-1H-pyrazol-3-yl)phenol as an ionophore, NPOE as plasticizer and KClTPB as anion excluder in

a PVC matrix in the weight ratio [15:40:3:42]. It was successfully used to determine Cr^{3+} ions in the concentration range 1.2×10^{-7}–1.0×10^{-1} M with a detection limit of 8.6×10^{-8} M. it works satisfactorily in the pH range 3.8–4.5 and most of the metal ions do not cause any interference in the estimation of chromium (III) ions. Its response remains unaffected even in the presence of upto 15% (v/v) nonaqueous content. Also, real samples were successfully tested for the determination of Cr(III) ion activity by using the developed sensor.

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