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Potentiometric Detection of Cr^{3+} Ions in Solution by a Chromium(III) Electrochemical Sensor Based on Diethyl 2-phthalimidomalonate Doped in Polymeric Membrane

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A new poly(vinyl chloride) membrane sensor that is highly selective to Cr^{3+} ions was prepared by using diethyl 2-phthalimidomalonate (DPM) as a suitable neutral carrier. The best performance was obtained with a membrane composition of 30% poly (vinyl chloride), 62% benzyl acetate (BA), 6% DPM and 2% sodium tetraphenyl borate (NaTBP). The proposed sensor exhibits a Nernstian behavior (with a slope of 20.6±0.2 $mVdecade^{-1}$) for the concentration range of (1.0×10^{-7}–1.0×10^{-2} mol L^{-1}) with a detection limit of 8.6×10^{-8} mol L^{-1}. It illustrates a relatively fast response time in the whole concentration range (~5 s) in a pH range of 2.9–6.1. This sensor revealed a great enhancement in selectivity coefficients for chromium ions in comparison with the previously reported chromium sensors. It was successfully used as an indicator electrode in potentiometric titration of Cr^{3+} against EDTA as well as for the determination of Cr^{3+} in the electroplating industry waste samples.

Keywords: Ion-selective electrode, Sensors, PVC membrane, Potentiometry

1. INTRODUCTION

Chromium is a member of the transition metals, in group 6. It is a steely-gray, lustrous, hard metal that takes a high polish and has a high melting point. It is also odorless, tasteless, and malleable. Chromium compounds are found in the environment, due to erosion of chromium-containing rocks and can be distributed by volcanic eruptions. Chromium was regarded with great interest because of its high corrosion resistance and hardness. A major development was the discovery that steel could be made highly resistant to corrosion and discoloration by adding chromium to form stainless steel. Several chromium compounds are used as catalysts for processing hydrocarbons. For example the Phillips catalysts for the production of polyethylene are mixtures of chromium and silicon dioxide or mixtures of chromium and titanium and aluminium oxide [1]. Furthermore, chromium in hexavalent state is 100–1000 times more toxic than the other. Chromium(VI) is also reported as mutagenic and carcinogenic for the human body, leading to lung cancer, skin allergy and probably to asthma and renal diseases [2, 3]. Due to the necessary need for selective chromium measurements in many copmplex biological systems, environmental, and industrial samples, the search for new selective and sensitive PVC membrane electrodes for its quick measurement is still a challenging goal [4, 5].

Potentiometric determination by ion-selective electrodes (ISEs) offers a simple, low cost and fast analysis procedure without any special equipment. Moreover, this method is nondestructive, without any sample pretreatment requirement [6-20]. There are only a limited number of reports on the development of selective ionophores for chromium [21–25].

We and other researchers have recently introduced a number of PVC-membrane ion selective electrodes for various metal ions [26-50]. In this work, we wish to introduce a highly selective and sensitive Cr^{3+} sensor based on diethyl 2-phthalimidomalonate (DPM) (Figure 1) as a sensing material for the determination of Cr^{3+} ions in sample solutions.

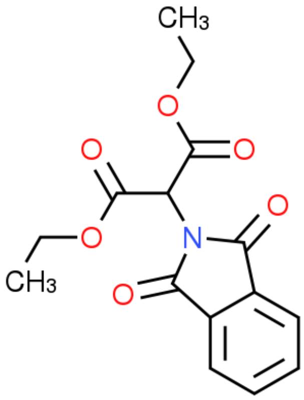


Figure 1. Structure of the ligand DPM.

2. EXPERIMENTAL

2.1. Reagents and materials

Analytical reagent grade diethyl 2-phthalimidomalonate (DPM), dibutyl phthalate (DBP), benzyl acetate (BA), acetophenon (AP), nitrobenzene (NB), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC were purchased from the Merck and the Aldrich Chemical Companies. The nitrate and chloride salts of all cations used (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying. Doubly distilled and deionized water was used throughout.

2.2. Fabrication of membrane

The viscous solution that was used for the formation of the membrane was prepared by the mixing 30 mg of powdered PVC, 62 mg of BA and 2 mg of additive NaTPB in 5 mL of THF, and 6 mg of DPM. The resulting low-viscosity mixture was thoroughly mixed and transferred into a glass dish of 2 cm diameter and then its solvent was slowly evaporated to gain an oily concentrated mixture. The membrane was then formed on the tip of a Pyrex tube of (3-5 mm o.d.) and by dipping the tube into the mixture for about 5 s, a transparent membrane of about 0.3 mm thickness was formed [51-60]. Then, the tube was removed from the mixture, kept at room temperature for 24 h and then filled with an internal solution (1.0×10^{-3} mol L^{-1} $Cr(NO_3)_3$). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} chromium nitrate solution. A silver/silver chloride electrode was used as an internal reference electrode.

2.3. EMF Measurements

All electromotive force was carried out with the membrane sensor using the following cell assembly:

Ag–AgCl | internal solution, 1.0×10^{-3} mol L^{-1} $Cr(NO_3)_3$ | PVC membrane | test solution | Hg–Hg_2Cl_2, KC1 (satd.)

A Corning ion analyzer (250 pH/mV meter) was used for the potential measurements at 25.0 ºC. The activities were calculated according to the Debye-Hückel procedure [61].

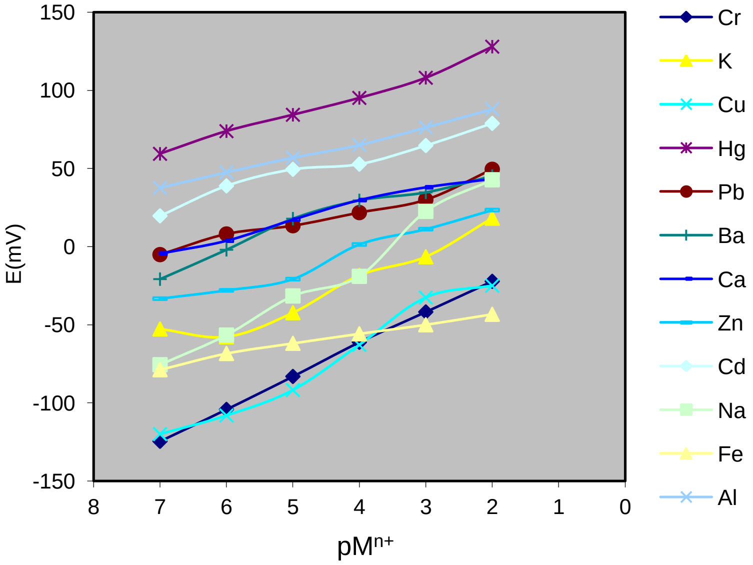
3. RESULTS AND DISCISSION

3.1. Potential response of the Cr^{3+} electrode

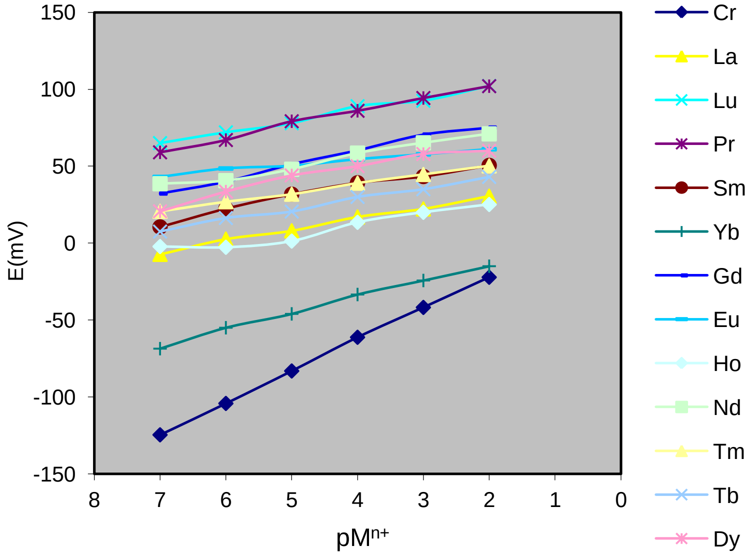
In order to have a clear picture about the selectivity of ligand for various metal ions, it was used as a sensing ionophore in construction of PVC-membrane sensors for a number of metal ions, including alkali, alkaline earth, transition, and heavy metal ions. The potential responses to the ions are shown in Figure 2 (a and b). In each, the electrode was conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} solution of the chloride or nitrate salts of the corresponding cation, to obtain thermodynamically meaningful potential responses and selectivity behaviors. It is noted that the resulting Cr^{3+} potential response showed a Nernstian behavior, while the slopes of the linear parts of the emf responses to other cations were much lower than those expected by the Nernst equation. This behavior may be considered to be the result of the selective tendency of the ionophore against Cr^{3+}, in comparison to other metal ions, and the rapid exchange kinetics of the resulting DPM-Cr^{3+} complex.

3.2. The effect of the membrane composition

It is well known that some important features of the PVC-based membranes, such as the nature and amount of ionophore, the properties of the plasticizer, the plasticizer/PVC ratio and, especially, the nature of additives used, significantly influence the sensitivity and selectivity of the ion-selective electrodes [62-72]. Thus, different aspects of membrane preparation based on DPM were optimized and the results are given in Table 1. As seen, among the four different plasticizers used, BA found to be the most effective solvent mediator in preparing the Cr^{3+} ion-selective electrode. It is reported that, the selectivity and working concentration range of membrane sensor are affected by the nature and amount of plasticizer used. The nature of plasticizer is known to influence both the dielectric constant of the membrane and the mobility of the ionophore and its cation complex [73-80]. Moreover, 6% of DPM was chosen as the optimum amount of the ionophore in the PVC-membrane (no. 6).



(a)



(b)

Figure 2. Potential responses of various PVC membrane sensors based on DPM.

Table 1. Optimization of the membrane ingredients.

Sensor No.	Composition of the membrane (wt, %)				Slope / $mVdecade^{-1}$	Dynamic Linear range / $molL^{-1}$
	PVC	Plasticizer	DPM	NaTPB		
1	30	NB, 66	2	2	16.3 ± 0.4	1.0×10^{-6}-1.0×10^{-2}
2	30	AP, 66	2	2	15.5 ± 0.2	1.0×10^{-6}-1.0×10^{-2}
3	30	BA, 66	2	2	17.4 ± 0.3	1.0×10^{-7}-1.0×10^{-2}
4	30	DBP, 66	2	2	14.6 ± 0.5	1.0×10^{-6}-1.0×10^{-3}
5	30	BA, 64	4	2	18.8 ± 0.4	1.0×10^{-7}-1.0×10^{-2}
6	30	BA, 62	6	2	20.6 ± 0.2	1.0×10^{-7}-1.0×10^{-2}
7	30	BA, 60	8	2	18.3 ± 0.6	1.0×10^{-7}-1.0×10^{-2}
8	30	BA, 64	6	0	12.4 ± 0.3	1.0×10^{-7}-1.0×10^{-2}
9	30	BA, 63	6	1	15.6 ± 0.5	1.0×10^{-7}-1.0×10^{-2}
10	30	BA, 61	6	3	17.9 ± 0.4	1.0×10^{-7}-1.0×10^{-2}

As is seen from Table 1, addition of 2% NaTPB (membrane No. 6) will increase the sensitivity of the electrode response to a great extent. In fact, it has been demonstrated that the presence of lipophilic anions in the composition of cationic-selective membrane sensors improves the potentiometric behavior of certain selective electrodes not only by reducing the ohmic resistance and improving the potential behavior and selectivity, but also, in poor extraction capacities, increases the sensitivity of the membrane electrodes has long been known [80-85]. The data given in Table 1 revealed that in the absence of a proper additive, the sensitivity of the PVC membrane based on DPM is low (no. 8 with slope of 12.4 $mVdecade^{-1}$). However, the presence of 2% NaTPB as a suitable lipophilic additive will improve the sensitivity of the Cr^{3+} sensor considerably (no. 6 with slope 20.6 $mVdecade^{-1}$).

3.3. Calibration curve

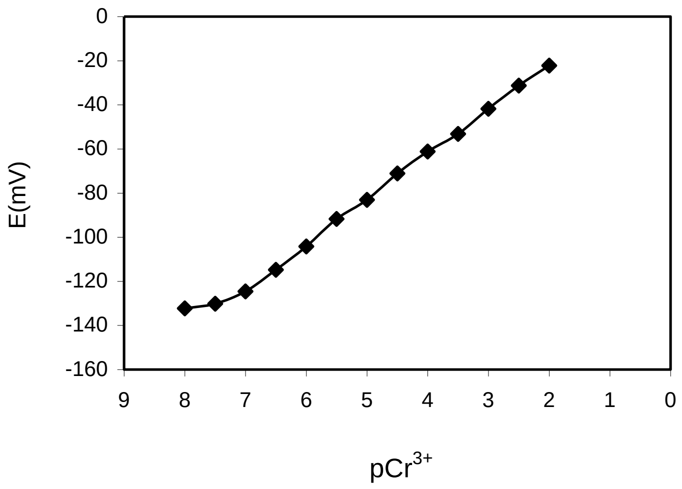


Figure 3. Calibration curve of the Cr^{3+} sensor based on DPM in the range of 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} Cr^{3+} ions.

The optimum equilibration time for the membrane electrode in the presence of 1.0×10^{-2} mol L^{-1} chromium nitrate was 12 h, after which it would generate stable potentials in contact with Cr^{3+} solution. The electrode shows a linear response to the concentration of Cr^{3+} ions in the range of 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} (Fig. 3). The slope of calibration graph was 20.6±0.2 $mVdecade^{-1}$. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 8.6×10^{-8} mol L^{-1} [86]. The standard deviation of eight replicate measurements was ± 0.6 mV.

3.4. The pH influence

The influence of pH on the response of the proposed sensor over a pH range from 1.0 to 10.0 (for a 1.0×10^{-3} $molL^{-1}$ of Cr^{3+}) was studied, and the results are shown in Figure 4. The pH of the solutions was adjusted by either HNO_3 or NaOH solutions. As seen, the potential remained constant from pH 2.9 to 6.1. Beyond this range, a gradual change in potential was detected. The observed decreased potential drift at higher pH values could be due to the formation of some hydroxyl complexes of Cr^{3+} in solution. At lower pH, the potentials increased, indicating that the membrane sensor responds to hydrogen ions.

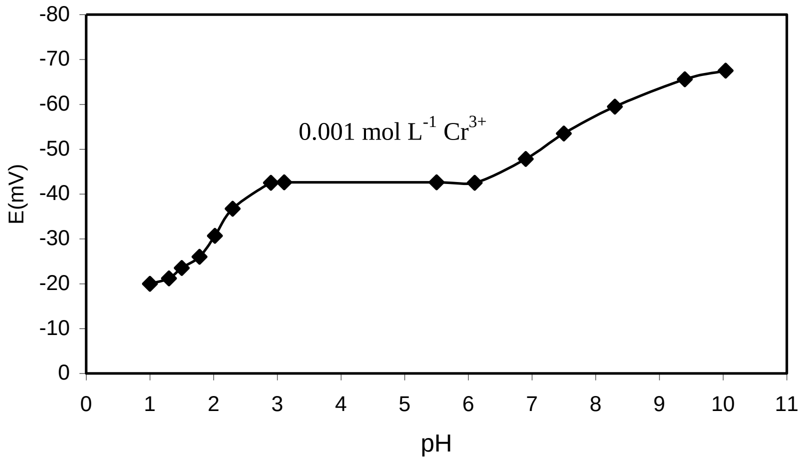


Figure 4. Effect of the pH of test solution (1.0×10^{-3} $molL^{-1}$ of Cr^{3+}) on the potential response of the Cr^{3+} sensor based on DPM.

3.5. Dynamic response time

Dynamic response time is an important factor for any ions elective electrode. In this study, the practical response time of the proposed electrode was recorded by changing the Cr^{3+} concentration in solution over a concentration range of 1.0×10^{-7} to 1.0×10^{-2} $molL^{-1}$. The potentials versus time traces are shown in Figure 5. As can be seen, over the entire concentration range, the membrane sensor reaches its equilibrium responses in a very short time (~5 s). This is most probably due to the fast exchange kinetics of the complexation-decomplexation of the Cr^{3+} ion with the ionophore at the test solution membrane interface.

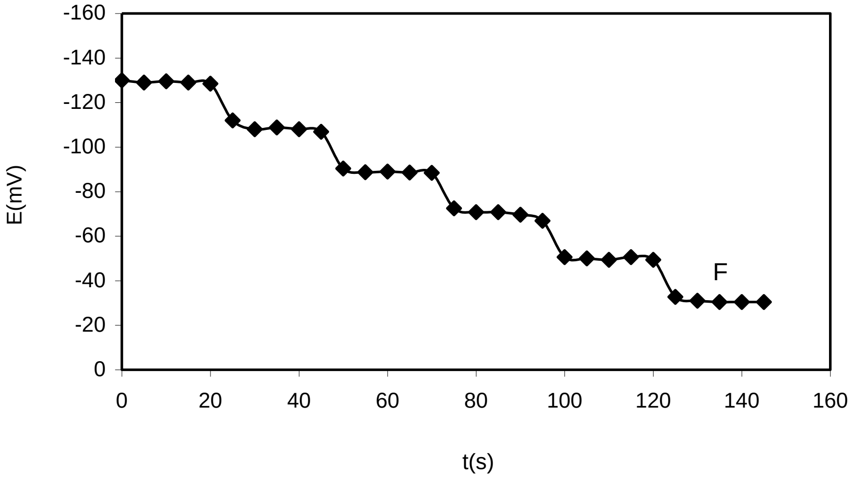


Figure 5. Dynamic response time of the Cr^{3+} sensor for step changes in the Cr^{3+} concentration: A) 1.0×10^{-7} $molL^{-1}$, B) 1.0×10^{-6} $molL^{-1}$, C) 1.0×10^{-5} $molL^{-1}$, D) 1.0×10^{-4} $molL^{-1}$, E) 1.0×10^{-3} $molL^{-1}$, F) 1.0×10^{-2} $molL^{-1}$.

3.6. Potentiometric selectivity

Table 2. Selectivity coefficients of the developed Cr^{3+} electrode.

Interfering Ion	K^{MPM}
Dy^{3+}	5.8×10^{-4}
Nd^{3+}	2.6×10^{-3}
Ho^{3+}	6.9×10^{-4}
Lu^{3+}	6.3×10^{-4}
Tm^{3+}	2.5×10^{-3}
Er^{3+}	1.0×10^{-3}
Eu^{3+}	7.7×10^{-4}
Tb^{3+}	2.3×10^{-3}
Pr^{3+}	3.0×10^{-3}
Fe^{3+}	6.3×10^{-4}
Na^{+}	7.3×10^{-4}
K^{+}	3.8×10^{-4}
Ca^{2+}	6.7×10^{-4}
Co^{2+}	1.0×10^{-4}
Ni^{2+}	8.5×10^{-4}
Pb^{2+}	4.5×10^{-4}
Concentration Range (mol L^{-1})	1.0×10^{-7}-1.0×10^{-2}
Detection Limit (mol L^{-1})	8.6×10^{-8} mol L^{-1}
pH Range	2.9-6.1
Slope ($mVdecade^{-1}$)	20.6 ± 0.2
Response Time (s)	~5 s

Potentiometric selectivity coefficients, describing the preference of the DPM-based membrane sensor for an interfering ion, B, relative to chromium ions, A, were determined by the matched potential method [87-91]. According to the MPM, the selectivity coefficient is defined as the activity (concentration) ratio of the primary ion and the interfering ion, which gives the same potential change in a reference solution. Subsequently, the potential change should be measured upon changing the primary ion activity. Then, the interfering ion would be added to an identical reference solution until the same potential change would be obtained. The MPM selectivity coefficient, K^{MPM}, is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $K^{MPM} = a_A/a_B$. The experimental conditions employed and the resulting values are given in Table 2. As it is seen, for the monovalent and the divalent metal ions used, the selectivity coefficients are in the order of 8.5×10^{-4} or smaller, indicating they would not disturb the functioning of the chromium sensor. The selectivity coefficients for the Fe^{3+} and the lanthanide ions are relatively small (3.0×10^{-3} to 7.7×10^{-4}), that indicating they would not very significantly disturb the functioning of the Cr^{3+} sensor. Therefore, the electrode could be used for the Cr^{3+} ions detection in the presence of certain interfering ions.

Table 3 compares the selectivity coefficient values, linear range and detection limit of the Cr^{3+} sensor with those of the best Cr^{3+} electrodes previously reported in the literature by other researchers [21-25]. It becomes apparent that the newly developed sensor is superior to the formerly reported Cr^{3+} sensors in terms of selectivity, detection limit and dynamic concentration range.

Table 3. Comparison of selectivity coefficients, linearity range and detection limit of the proposed Cr^{3+} sensor and the previously reported Cr^{3+} ion-selective electrodes.

	Ref. 21	Ref. 22	Ref. 23	Ref. 24	Ref. 25	This work
Linearity rang (mol L^{-1})	1.7×10^{-6}-1.0×10^{-1}	3.0×10^{-6}-1.0×10^{-2}	1.6×10^{-6}-1.0×10^{-1}	1.0×10^{-6}-1.0×10^{-1}	4.0×10^{-6}-1.0×10^{-1}	1.0×10^{-7}-1.0×10^{-2}
Detection limit (mol L^{-1})	___	6.3×10^{-7}	___	5.8×10^{-7}	2.0×10^{-7}	8.6×10^{-8}
Selectivity coefficients	FIM	MPM	MPM	MPM	FIM	MPM
Na^+	-0.91	-2.48	-0.76	-3.39	-3.39	-3.14
K^+	-0.90	-2.62	___	-3.55	___	-3.42
Ca^{2+}	-1.87	-2.44	-1.85	-3.37	-3.37	-3.17
Pb^{2+}	-1.95	-2.22	-2.85	-3.20	-1.08	-3.35
Co^{2+}	-1.75	-2.16	___	-3.15	-3.15	-4.00
Ni^{2+}	-2.05	-2.92	-2.49	-3.07	-1.88	-3.07
Fe^{3+}	-3.18	___	-3.65	-3.25	-1.34	-3.20
Dy^{3+}	___	___	___	___	___	-3.24
Nd^{3+}	___	___	___	___	___	-2.59
Ho^{3+}	___	___	___	___	___	-3.16
Lu^{3+}	___	___	___	___	___	-3.20
Tm^{3+}	___	___	___	___	___	-2.60
Er^{3+}	___	___	___	___	___	-3.00
Eu^{3+}	___	___	___	___	___	-3.11
Tb^{3+}	___	___	___	___	___	-2.64
Pr^{3+}	___	___	___	___	___	-2.52

3.7. Analytical application

3.7.1. Titration with EDTA

The developed Cr^{3+} PVC-membrane sensor was successfully applied as an indicator electrode in the titration of Cr^{3+} (1.0×10^{-4} mol L^{-1}) with a standard EDTA solution (1.0×10^{-2} mol L^{-1}). The resulting titration curve is shown in Figure 6. As seen, the amount of chromium ion can be accurately determined by the proposed sensor.

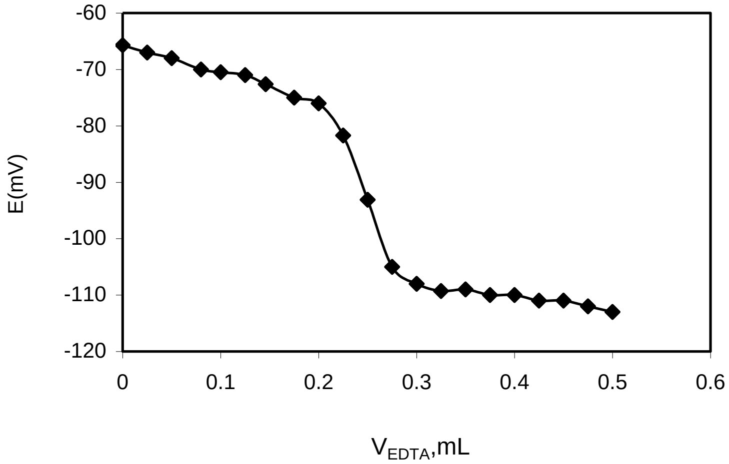


Figure 6. Potential titration curve of 25.0 mL from a 1.0×10^{-4} $molL^{-1}$ Cr^{3+} solution with 1.0×10^{-2} $molL^{-1}$ of EDTA.

3.7.2. Chromium(III) determination in electroplating industry waste samples

To assess the practical applicability of the sensor in real samples an attempt was made to determine Cr^{3+} in the three electroplating industry waste samples. 10.0 mL of each sample were taken and diluted with 10.0 mL of buffer acetic acid/sodium acetate (pH 8.0) and distilled water in a 100.0 mL flask. The results are given in Tables 4. With the use of the membrane sensor's calibration plot, the chromium content in the electroplating industries obtained from triplicate measurements with electrode was found to be in satisfactory agreement with that determined by atomic absorbtion spectrometry.

Table 4. Analysis of three electroplating industry waste samples by using AAS and the constructed Cr^{3+} sensor.

Sample No.	ISE (ppm)	AAS (ppm)
1	1.47 ± 0.07	1.42 ± 0.05
2	3.57 ± 0.06	3.49 ± 0.07
3	4.75 ± 0.04	4.66 ± 0.03

a. Results are based on three measurements

3.7.3. Chromium(III) determination in mixture of different ions

The high degree of chromium selectivity, exhibited by the DPM-based sensor, makes it potentially useful for the recovery of Cr^{3+} ions in mixtures of various different ions. The reported values of Table 5 demonstrate that the recovery of the Cr^{3+} ions in all mixtures is satisfactory.

4. CONCLUSION

The combination of the diethyl 2-phthalimidomalonate (DPM) with the plasticizer BA demonstrates a Nernstian behavior (slope 20.6±0.2 mV decade^{-1}) with the best response characteristics within the Cr^{3+} concentration range of 1.0×10^{-7}-1.0×10^{-2} mol L^{-1} and the response time of 5 s. The sensor have a good selectivity coefficient with respect to alkaline, alkaline earth, and heavy metal ions and could be used over a pH range of 2.9–6.1. The Cr^{3+} sensor can be used for the determination of this ion in the presence of considerable concentrations of common interfering ions. The proposed sensor was used for the determination of Cr^{3+} ions in the electroplating industry waste samples.

Table 5. Determination of Cr^{3+} ions in mixtures of different ions.

Serial no.	Composition	Observed content (mol L^{-1})
1	0.000010 mol L^{-1} $Cr(NO_3)_3$ + 0.0001 mol L^{-1} $Tm(NO_3)_3$ + 0.0001 mol L^{-1} $Yb(NO_3)_3$ + 0.0001 mol L^{-1} $Er(NO_3)_3$	0.0000097
2	0.000010 mol L^{-1} $Cr(NO_3)_3$ + 0.0001 mol L^{-1} $Eu(NO_3)_3$ + 0.0001 mol L^{-1} $Nd(NO_3)_3$ + 0.0001 mol L^{-1} $La(NO_3)_3$	0.0000096
3	0.000010 mol L^{-1} $Cr(NO_3)_3$ + 0.0001 mol L^{-1} $Dy(NO_3)_3$ + 0.0001 mol L^{-1} $Tm(NO_3)_3$ + 0.0001 mol L^{-1} $Sm(NO_3)_3$	0.0000102
4	0.000010 mol L^{-1} $Cr(NO_3)_3$ + 0.0001 mol L^{-1} $Gd(NO_3)_3$ + 0.0001 mol L^{-1} $Tb(NO_3)_3$ + 0.0001 mol L^{-1} $Lu(NO_3)_3$	0.0000103
5	0.000010 mol L^{-1} $Cr(NO_3)_3$ + 0.0001 mol L^{-1} $Er(NO_3)_3$ + 0.0001 mol L^{-1} $Pr(NO_3)_3$ + 0.0001 mol L^{-1} $Ho(NO_3)_3$	0.0000098
6	0.000010 mol L^{-1} $Cr(NO_3)_3$ + 0.0001 mol L^{-1} $Sm(NO_3)_3$ + 0.0001 mol L^{-1} $Gd(NO_3)_3$ + 0.0001 mol L^{-1} $Dy(NO_3)_3$	0.0000096
7	0.000010 mol L^{-1} $Cr(NO_3)_3$ + 0.0001 mol L^{-1} $Cu(NO_3)_2$+ 0.0001 mol L^{-1} $Fe(NO_3)_3$ + 0.0001 mol L^{-1} $Ni(NO_3)_2$	0.0000104
8	0.000010 mol L^{-1} $Cr(NO_3)_3$ + 0.0001 mol L^{-1} $Co(NO_3)_2$+ 0.0001 mol L^{-1} $Ca(NO_3)_2$ + 0.0001 mol L^{-1} $NaNO_3$	0.0000101
9	0.000010 mol L^{-1} $Cr(NO_3)_3$ + 0.0001 mol L^{-1} $Hg(NO_3)_2$+ 0.0001 mol L^{-1} $Cd(NO_3)_2$ + 0.0001 mol L^{-1} KNO_3	0.0000098
10	0.000010 mol L^{-1} $Cr(NO_3)_3$ + 0.0001 mol L^{-1} $Pb(NO_3)_2$+ 0.0001 mol L^{-1} $Ni(NO_3)_2$ + 0.0001 mol L^{-1} $Co(NO_3)_2$	0.0000098

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