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## Research article

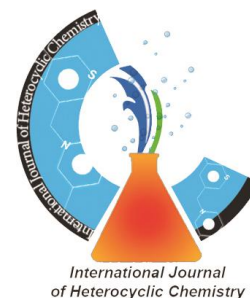
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### Quantitative monitoring of chromium (III) by a selective sensor based on dibenzo-18-crown-6 as a neutral ion carrier

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#### Abstract

In present study a chromium (III) selective sensor based on dibenzo-18-crown-6 as a macrocyclic ionophore was fabricated. The best operation obtained in the membrane including: 5.0 mg dibenzo-18-crown-6 (DB-18C6), 4.0 mg sodium tetraphenylborate (NaTPB), 61.0 mg dioctyl sabacate (DOS) and 30.0 mg polyvinyl chloride (PVC). This electrode has a good selectivity respect to  $\text{Cr}^{3+}$  cation, with a nernstian slope of  $19.6 \pm 0.1$  mV/decade in a linear concentration range of  $1.0 \times 10^{-5}$  M- $1.0 \times 10^{-1}$  M. The detection limit of the electrode is  $8.8 \times 10^{-6}$  M. The proposed sensor has a fast response time of 5 s and good reproducibility. It can be used for a period of 63 days without any significant changes in its potential. The effects of the pH and possible interfering ions were investigated. This electrode was employed as an indicator electrode in potentiometric titrations of chromium cation with EDTA solutions and a sharp break in titration curves around the equivalent point was observed. This sensor was successfully used for the determination of chromium (III) in real samples.

**Keywords:** PVC membrane, chromium (III) selective sensor, dibenzo-18-crown-6, Potentiometry

## Introduction

The need of selective determination of heavy metal ions has increased immensely during the last few decades due to the growing environmental problems. Among heavy metals, the pollution by chromium is of considerable concern, as it is highly toxic and has used in chrome plating, pigment manufacturing, refractory industries, leather tanning, and wood treatment, making steel and other alloys. Chromium is also an essential trace element in human nutrition. It is an essential element required for normal carbohydrate and fat metabolism by potentiating the action of insulin through glucose tolerance factor (GTF) for activating certain enzymes and stabilization of proteins and nucleic acids. Insufficient dietary intake of chromium leads to increases in risk factors associated with diabetes and cardiovascular disease including elevated circulating insulin, glucose, triglycerides, total cholesterol and impaired immune function. The estimated safe and adequate daily dietary intake (ESADDI) for chromium in adults is 50-200  $\mu\text{g}$  per day [1]. Due to vital importance of chromium in biological system and industry, a narrow window of concentration between essentiality and toxicity warrants the determination of chromium.

Potentiometric detection based on ion-selective electrodes (ISEs), as a simple method, offers several advantages such as speed and ease of preparation and procedures, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity, and low cost. These characteristics have inevitably led to sensors for several ionic species, and the list of available electrodes has grown substantially over the last few years [2-6].

Ion-selective electrodes based on neutral carrier ligands are well established for alkali, alkaline earth and transition metal cations [7-9]. Essentially, the neutral carriers have the characteristics of being uncharged, lipophilic and undergoing reversible complexation with selected cations and hence of promoting cation transfer between the aqueous phase and the organic membrane. The selection of suitable neutral carriers for ion sensing can be helped by structure studies on the interaction between carriers and ions. In this respect many cyclic macromolecules have been suggested as electroactive ionophores. Macrocyclic compounds bearing appropriate binding groups act as efficient receptors for complexation of metal ions. Of these; crown compounds have been shown to bind some organic and inorganic cations and anions reversibly and to transport them across organic membranes by carrier translocation [10-12]. Polymeric membrane potentiometric sensors based on these ionophores are found to show excellent

electroactive properties, a near-Nernstian response over a wide range of concentrations and pH, and to display good selectivity. The recognition of specific ions by these receptors is determined by the cavity size, type of functional group and geometry of the molecules. In this paper, we report the use of dibenzo-18-crown-6 (DB-18C6) (Fig. 1) as an excellent neutral ion carrier in construction of a Cr (III) PVC membrane electrode.

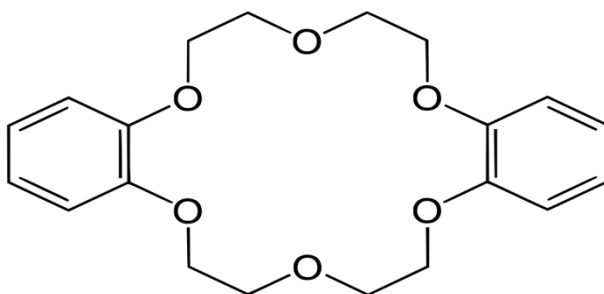


Fig. 1. Structure of ddibenzo-18-crown-6 (DB-18C6).

## Experimental

### Reagents

Reagent grade dibutyl phthalate (DBP), dioctyl sebacate (DOS), nitrobenzene (NB), dioctyl phthalate (DOP), sodium tetraphenylborate (NaTPB), tetrahydrofuran (THF), dbenzo-18-crown-6 (DB-18C6), high relative molecular weight polyvinyl chloride (PVC), ethylenediaminetetraacetic acid disodium salt, nitric acid, sodium hydroxide and nitrate salts of all cations were purchased from Merck chemical company and were of the highest purity available and used as received.

### Electrode preparation

The electrodes were prepared from graphite bars (3 mm diameter and 50 mm long). The graphite bars were polished and put in a concentrated  $\text{HNO}_3$  solution overnight to clean the surface of the electrodes. Then, the bars were rinsed with THF and once again polished and washed with distilled water and allowed to dry. A shielded copper wire was glued to one end of the graphite bar and the bar was inserted into the end of a polyethylene tube.

A mixture of PVC, plasticizer, ionophore and the membrane additive to give a total mass of 100 mg was dissolved in about 2 mL of THF and the solution was mixed well. The graphite bar was coated by dipping into the membrane solution for a few seconds and allowed to dry overnight. The electrode was conditioned for 24 h in  $1.0 \times 10^{-3}$  M chromium (III) nitrate solution and stored in mild concentration solutions of chromium (III) nitrate, when not in use. The coating solutions were stable for several days and could be used for construction of new membranes.

### **Emf measurements**

All the potential measurements were carried out using a 713 pH-mV meter (Metrohm, Switzerland) at laboratory ambient temperature. All the emf measurements were carried out versus an Ag/AgCl double junction reference electrode (Azar electrode, Iran) and were carried out with the following cell assemblies:



The performance of each electrode was investigated by measuring the potential of  $\text{Cr}^{3+}$  solutions with concentrations ranging from  $1.0 \times 10^{-8}$  to  $1.0 \times 10^{-1}$  M by serial dilution of the 0.1 M stock solution. The potential readings recorded when a steady state value was attained. The observed potential versus the logarithm of the  $\text{Cr}^{3+}$  ion concentration was plotted. The pH of the solutions was measured by a conventional glass pH electrode.

## **Results and discussion**

### **Effect of membrane composition on the sensor response and calibration curve**

It is well known that some important features of the PVC-based membranes, such as the nature and amount of the ionophore, the properties of the plasticizer, the plasticizer/PVC ratio and especially the amount of the additives used, significantly influence the sensitivity and selectivity of the ion selective sensors [13,14]. Thus, different aspects of preparation of membranes based on DB-18C6 were investigated and the results are given in Table 1.

Table 1. Optimization of the membrane ingredients.

Electrode no.	Membrane mass composition (%)				Slope (mV/decade)	Linear range (M)
	PVC	Ionophore (DB-18crown6)	Additive (NaTPB)	Plasticizer		
1	30	9.0	—	61.0 (DOS)	14.7±0.6	10 <sup>-3</sup> -10 <sup>-1</sup>
2	30	—	9.0	61.0 (DOS)	12.4±0.9	10 <sup>-3</sup> -10 <sup>-1</sup>
3	30	5.0	4.0	61.0 (DBP)	21.5±0.1	10 <sup>-4</sup> -10 <sup>-1</sup>
4	30	5.0	4.0	61.0 (DOP)	18.6±0.4	10 <sup>-4</sup> -10 <sup>-2</sup>
5	30	5.0	4.0	61.0 (NB)	17.3±0.2	10 <sup>-5</sup> -10 <sup>-1</sup>
6	30	5.0	4.0	61.0 (DOS)	19.6±0.1	10 <sup>-5</sup> -10 <sup>-1</sup>
7	30	4.0	3.0	63.0 (DOP)	15.7±0.3	10 <sup>-5</sup> -10 <sup>-1</sup>
8	30	4.0	3.0	63.0 (DOS)	20.9±0.3	10 <sup>-4</sup> -10 <sup>-1</sup>
9	30	4.0	2.0	64.0 (DOS)	16.0±0.2	10 <sup>-5</sup> -10 <sup>-1</sup>
10	30	6.0	4.0	60.0 (DOS)	18.5±0.2	10 <sup>-5</sup> -10 <sup>-1</sup>
11	30	4.0	2.0	64.0 (DOP)	15.8±0.1	10 <sup>-5</sup> -10 <sup>-1</sup>
12	30	6.0	4.0	60.1 (DOP)	16.9±0.1	10 <sup>-5</sup> -10 <sup>-1</sup>
13	30	6.0	5.0	59.0 (DOS)	17.7±0.1	10 <sup>-5</sup> -10 <sup>-1</sup>
14	30	6.0	5.0	59.0 (DOP)	17.5±0.1	10 <sup>-5</sup> -10 <sup>-2</sup>
15	30	5.2	3.2	62.0 (NB)	18.6±0.6	10 <sup>-4</sup> -10 <sup>-1</sup>
16	30	4.0	2.0	64.0 (NB)	17.3±0.9	10 <sup>-4</sup> -10 <sup>-1</sup>

Ionophores for use in sensors should have rapid exchange kinetics and adequate complex formation constants in the membrane. Also, they should be well soluble in the membrane matrix and have a sufficient lipophilicity to prevent leaching from the membrane into the sample solution. In addition, the selectivity of the neutral carrier-based ISEs is known to be governing by stability constant of the neutral carrier-ion complex and its partition constant between the membrane and sample solution [15]. As is shown in Table 1, 5.0 mg of

DB-18C6 was chosen as the optimum amount of the ionophore in the PVC-membrane (membrane No. 6). In the absence of DB-18C6, a non-Nernstian slope (12.4 mV/decade) was observed.

Solvent polymeric membrane ion selective electrodes are usually based on a matrix of the solvent mediator/PVC ratio of about 2. Polymeric films with such a plasticizer/PVC ratio will result in optimum physical properties and high enough mobility of their constituents. In this study, a plasticizer/PVC ratio of about 2 was found to be the most suitable. It is reported that the selectivity and working concentration range of membrane sensors are affected by the nature and amount of the plasticizer used. This is due to the influence of the plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands [13]. As is obvious from Table 1, among the four different plasticizers used, DOS (61.2 mg) resulted in the best sensitivity (membrane No. 6). The presence of lipophilic anions in cation selective membrane electrodes is advantageous for decreasing the ohmic resistance and anion interference, and for enhancing the response behavior, selectivity and sensitivity of the membrane electrodes. In addition, lipophilic anions induce permselectivity of the PVC membrane electrodes [16]. The potential response of the  $\text{Cr}^{3+}$ -ISE containing a lipophilic anion additive was investigated to examine the effect of the additive content (Table 1). The results revealed that the potential response of the electrode in the absence of additives led to weak sensitivity with a diminished slope of 14.7 mV/decade over a linear range from  $1.0 \times 10^{-3}$  to  $1.0 \times 10^{-1}$  M. The sensitivity was greatly improved by increasing the amount of lipophilic anion, which led to the best performance with a Nernstian slope. As is shown in Table 1, it is evident that the amount of additive influence the performance of the membrane sensor. Thus, the addition of 4.0 mg sodium tetraphenylborate (membrane No. 6) significantly increased the sensitivity of the response of the  $\text{Cr}^{3+}$  sensor. Thus, the best response was observed with the membrane composed of the following ingredients: 30.0 mg PVC, 61.0 mg DOS, 5.0 mg DB-18C6 and 4.0 mg NaTPB (membrane No. 6). The characteristic properties of this optimized coated membrane were studied and the calibration curve for  $\text{Cr}^{3+}$  cation is shown in Fig. 2. Over the concentration range from  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-1}$  M of the cation, the electrode potential response was linear with the logarithm of chromium cation concentration. The slope of the calibration curve was found to be:  $19.6 \pm 0.1$  mV/decade. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was  $8.8 \times 10^{-6}$  M.

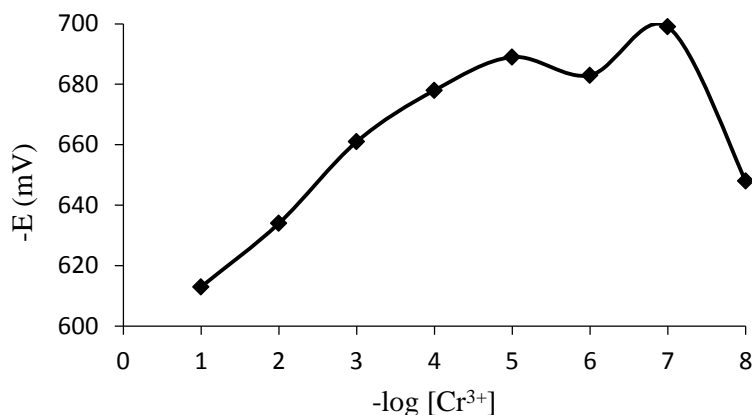


Fig. 2. Calibration curve for optimum  $\text{Cr}^{3+}$  selective sensor.

### Response time of the sensor

The response time is an important factor for ion selective sensors. The static response time of the sensor was studied by plotting the potential response vs. time, at  $1.0 \times 10^{-3}$  M and  $1.0 \times 10^{-2}$  M of  $\text{Cr}^{3+}$  ion solutions (Fig. 3). As is evident in this figure, in the whole concentration range, the sensor reaches its equilibrium response in a short time (5 s) and potentials stay constant for about 3 min. This is most probably due to the fast exchange kinetics of complexation-decomplexation of  $\text{Cr}^{3+}$  cation with the ion carrier at the test solution-membrane interface.

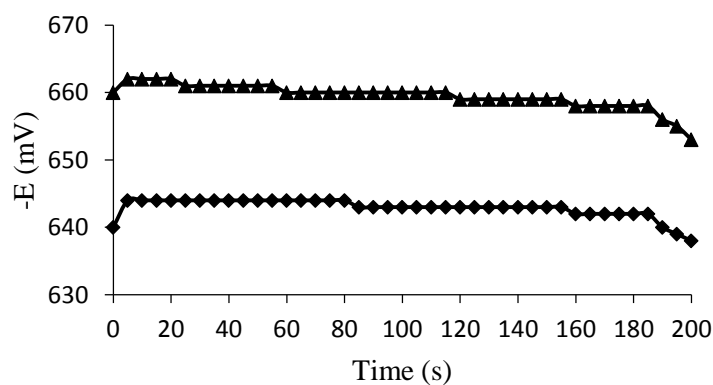


Fig. 3. The response time curves of the optimum  $\text{Cr}^{3+}$  selective sensor (◆  $1.0 \times 10^{-2}$  M, ▲  $1.0 \times 10^{-3}$  M).

In addition, dynamic response time of the sensor has been recorded by changing solutions with different  $\text{Cr}^{3+}$  concentrations. The measurement sequence was from the lower ( $1.0 \times 10^{-5}$  M) to the higher ( $1.0 \times 10^{-1}$  M) concentrations and the results are shown in Fig. 4.

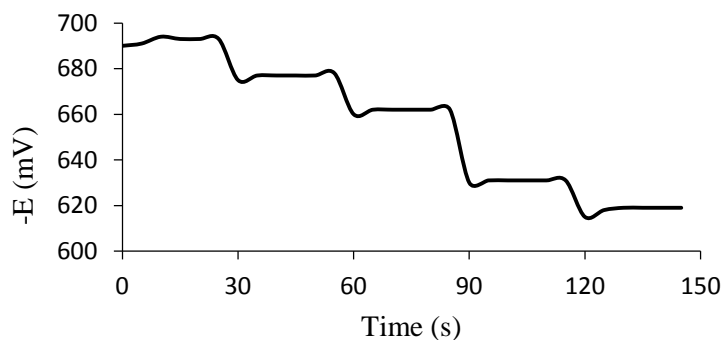


Fig. 4. Dynamic response of the optimum  $\text{Cr}^{3+}$  selective sensor for step changes in concentration of  $\text{Cr}^{3+}$  cations from  $1.0 \times 10^{-5}$  M to  $1.0 \times 10^{-1}$  M.

#### Lifetime of the sensor

The lifetime and stability of the proposed sensor was investigated by measuring potentials over a period of 11 weeks. The performances with respect to slope and linear range were measured and results are summarized in Table 2. During this time, the sensor could be used without any significant change in slope and linear concentration range. Thus, the response characteristics of the sensor remained almost constant. The divergence in slope and linear concentration range concluded that the sensor was used practically for 63 days.

Table 2. Lifetime study for optimum Cr (III) selective sensor.

<i>Period (days)</i>	<i>Slope (mV/decade)</i>	<i>Linear range (M)</i>
1	$19.6 \pm 0.1$	$10^{-5} - 10^{-1}$
7	$19.6 \pm 0.2$	$10^{-5} - 10^{-1}$
14	$19.6 \pm 0.2$	$10^{-5} - 10^{-1}$
21	$19.6 \pm 0.2$	$10^{-5} - 10^{-1}$
28	$19.6 \pm 0.4$	$10^{-5} - 10^{-1}$
35	$19.8 \pm 0.3$	$10^{-5} - 10^{-1}$



42	18.7±0.4	10 <sup>-5</sup> -10 <sup>-1</sup>
49	18.5±0.5	10 <sup>-5</sup> -10 <sup>-1</sup>
56	18.6±0.4	10 <sup>-5</sup> -10 <sup>-1</sup>
63	18.3±0.3	10 <sup>-5</sup> -10 <sup>-1</sup>
70	15.5±0.3	10 <sup>-4</sup> -10 <sup>-1</sup>
77	14.0±0.5	10 <sup>-4</sup> -10 <sup>-1</sup>

### Effect of pH

The pH dependence of the proposed sensor potential for  $1.0 \times 10^{-2}$  and  $1.0 \times 10^{-3}$  M of  $\text{Cr}^{3+}$  was examined over the pH range 1.0-12.0, where the pH was adjusted with  $\text{HNO}_3$  or  $\text{NaOH}$  solutions as required. The results are shown in Fig. 5. It can be seen from this figure that the potentials are independent of pH in the range of 1.0-9.0. The observed changes of potential at higher pH values could be due to the protonation of the ion carrier and formation of some hydroxyl complexes of  $\text{Cr}^{3+}$  ion in solution.

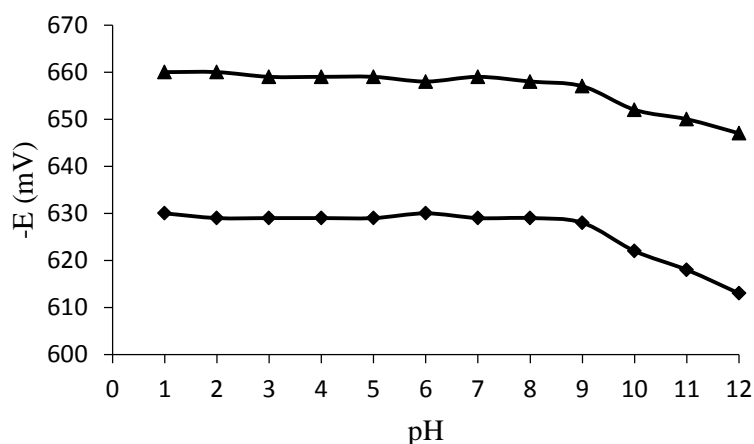


Fig. 5. Effect of pH on potential response of the optimum  $\text{Cr}^{3+}$  selective sensor (◆  $1.0 \times 10^{-2}$  M, ▲  $1.0 \times 10^{-3}$  M).

### Selectivity

The potentiometric selectivity of an electrode as one of the most important characteristics is defined by its relative response for the primary ion over other ions present in the solution [17-

20]. In this study, the potentiometric selectivity coefficients of the proposed sensor were determined by the Separate Solution Method (SSM). The selectivity coefficient ( $K_{Crj}^{Pot}$ ) of mono-, di- and trivalent cations were measured and the results are summarized in Table 3. As it is evident from the data in Table 3, most of the selectivity coefficients of interfering ions are low (less than  $1.0 \times 10^{-3}$ ) indicating no significant interference in the performance of the sensor (except for  $Cu^{2+}$ ) and the sensor can, therefore, be used for  $Cr^{3+}$  determination in the presence of several other ions. From the data presented in this table, it is obvious that DB-18C6 interacts relatively strongly with  $Cr^{3+}$  ion and can be used successfully as a sensing agent for chromium (III) selective sensor.

Table 3. Selectivity coefficients ( $K_{Crj}^{Pot}$ ) of various interfering ions for optimum Cr (III) selective sensor.

<i>Interfering ions</i>	<i>Selectivity coefficients (<math>K_{Crj}^{Pot}</math>)</i>
$K^+$	$< 10^{-6}$
$Ni^{2+}$	$2.5 \times 10^{-4}$
$Pb^{2+}$	$3.5 \times 10^{-5}$
$Cd^{2+}$	$3.5 \times 10^{-4}$
$Cu^{2+}$	$5.7 \times 10^{-2}$
$Zn^{2+}$	$2.5 \times 10^{-5}$
$Fe^{3+}$	$< 10^{-6}$
$Ce^{3+}$	$6.5 \times 10^{-4}$

### **Analytical Applications**

The practical utility of the proposed sensor was tested by using it as an indicator electrode for the titration of 25 mL  $1.0 \times 10^{-3}$  M and 25 mL  $1.0 \times 10^{-4}$  M of  $Cr^{3+}$  ions with  $1.0 \times 10^{-2}$  M and  $1.0 \times 10^{-3}$  M of EDTA solutions, respectively. The resulting titration curves are shown in Figs. 6. As can be seen, the amount of chromium (III) ions in solution can be accurately determined with the sensor. Very good inflection points, showing a perfect stoichiometry and efficiency of the sensor in the potentiometric determination of  $Cr^{3+}$  cation in solutions.

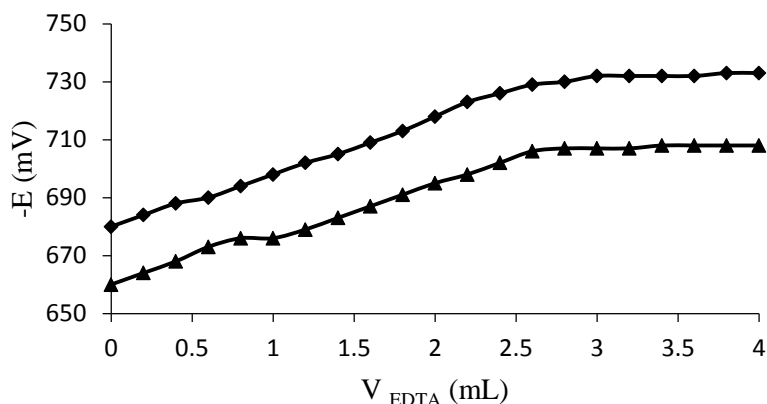


Fig. 6. Potentiometric titration curves for 25 mL of ▲  $1.0 \times 10^{-3}$  M  $\text{Cr}^{3+}$  with  $1.0 \times 10^{-2}$  M EDTA and 25 mL of ◆  $1.0 \times 10^{-4}$  M  $\text{Cr}^{3+}$  with  $1.0 \times 10^{-3}$  M EDTA.

#### Determination of $\text{Cr}^{3+}$ ion in real samples

The proposed sensor was successfully applied to the determination of chromium (III) ions in real samples using standard addition method and the results are shown in Table 4. The recoveries of the method were in the range of 92.0-96.0%. Results indicate that the composition of the real samples do not interfere significantly the detection of  $\text{Cr}^{3+}$  ions. In fact, chromium (III) selective sensor seems to provide an alternative device for the quantitative determination of  $\text{Cr}^{3+}$  ions in real samples.

Table 4. Determination of  $\text{Cr}^{3+}$  ion in real samples using the optimum chromium (III) selective sensor.

<i>samples</i>	<i>Added <math>\text{Cr}^{3+}</math> concentration (M)</i>	<i>Found <math>\text{Cr}^{3+}</math> concentration (M)</i>	<i>Recovery (%)</i>
Tap water (Mahshahr city, Iran)	$4.0 \times 10^{-3}$	$3.8 \times 10^{-3}$	95.0
Tap water (Abadan city, Iran)	$9.0 \times 10^{-4}$	$8.7 \times 10^{-4}$	96.6
Karoon river water	$5.0 \times 10^{-3}$	$4.6 \times 10^{-3}$	92.0

## Conclusion

The selective chromium (III) sensor based on DB-18C6 shows a Nernstian slope of  $19.6 \pm 0.1$  mV/decade with a dynamic range from  $1 \times 10^{-5}$  to  $1 \times 10^{-1}$  M of chromium (III) cation and has fast response time (5 s). It can be used in pH range 1-9. The sensor response is stable for 63 days. It exhibits a good selectivity for chromium (III) cation over many of the other ions. Also it was successfully applied as an indicator electrode in potentiometric titrations and in chromium (III) measurement in real samples.

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