

*Full Paper*

## **Construction of Chromium Potentiometric Sensor by using N-banzoyl-N'(6-methyl-2-pyridyl) thiourea as an Excellent Ionophore**

**Leila Hajiaghababaei\*, Neda Mohamadi and Forogh Adhami**

*Department of Chemistry, College of Science, Yadegar-e-Imam Khomeini (RAH) Branch, Islamic Azad University, Tehran, Iran*

\* Corresponding Author, Tel.: +989125017614; Fax: +982133999022

E-Mail: [lhajiaghababaei@yahoo.com](mailto:lhajiaghababaei@yahoo.com)

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**Abstract-** Ion potentiometric sensors are playing an important role in environmental analysis because of their simplicity and rapidity. In this study, a potentiometric liquid membrane sensor for simple and fast quantification of chromium in various samples was made. N-banzoyl-N'(6-methyl-2-pyridyl) thiourea was selected as a sensing material in the organic phase of the PVC membrane. The wide linear range ( $10^{-6}$ - $10^{-1}$  mol L<sup>-1</sup>), low detection limit ( $3.0 \times 10^{-7}$  mol L<sup>-1</sup>), and fast response time (~5 s) are the characterizations of this electrochemical sensor. The effects of some factors such as internal solution, pH, life time and selectivity were investigated. Finally, it was used for direct determination of chromium and as an indicator electrode in potentiometric titration of chromium ion.

**Keywords-** Potentiometric sensor, Liquid membrane, Chromium, Tea and cocoa samples

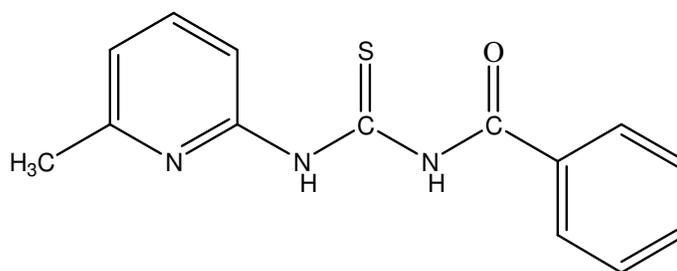
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### **1. INTRODUCTION**

Dissolved chromium is usually found in natural waters in two different oxidation states, chromium(VI) and chromium(III). Both forms of chromium enter the environment from various sources at the effluent discharge of tanning industries, electroplating, oxidative dyeing,

cooling water power, chemical industry and steel works [1,2]. Chromium(III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much chromium(III) can cause health effects as well, for instance skin rashes. Several in vitro studies indicated that high concentrations of chromium(III) in the cell can lead to DNA damage [3]. Cr(VI) is considered to be a toxic material [1,4-6], because of its ability to oxidize other species and its adverse impact on lung, liver and kidney. Since trivalent chromium and hexavalent chromium can interconvert under certain conditions and are both toxic to a certain degree, the detection of trivalent chromium and hexavalent chromium content is of vital importance.

The direct determination of chromium in water may not be possible with sufficient sensitivity by also expensive analytical methods such as inductively coupled plasma atomic emission spectrometry [7] or electrothermal atomic absorption spectrometry [1] because of low concentrations and/or matrix interferences. For this purpose, various separation and pre-concentration methods such as liquid-liquid extraction [1,7], coprecipitation [5,8], ion exchange [9–11] and adsorption [12–15] have been developed. But, most of these preparation methods are lengthy and involve rigid control of conditions. Also, the mentioned methods are elaborate and time consuming and involve sophisticated equipment that might not be available in most analytical laboratories. However, the increasing use of ion sensors in the field of environmental, agriculture, industrial and medicinal analysis is putting more and more pressure on analytical chemists to develop new sensors for the fast, accurate, reproducible, selective and cheap determination of various species.



**Fig. 1.** The structure of ligand

Therefore, in this work, we report a novel potentiometric sensor to chromium determination by using a new ligand (Fig.1) [N-banzoyl-N' (6 methyl-2-pyridyl) thiourea] (NBMPT) as an excellent ionophore. To the best our knowledge, this is the first application of this ionophore for determination of chromium ions.

## 2. EXPERIMENTAL

### 2.1. Apparatus

A Corning ion analyzer 250 pH/mV meters was used for the potential measurements at  $25.0 \pm 0.1$  °C. Two Ag/AgCl reference electrodes (Azar-Electrode, Iran) were used as the internal and external reference electrodes.

### 2.2. Reagents and Materials

Reagent grade dibutyl phthalate (DBP), high relative molecular weight polyvinyl chloride (PVC), sodium tetraphenyl borate (NaTPB), oleic acid (OA) and tetrahydrofuran (THF) were purchased from Merck and used as received. N-banzoyl-N'(6-methyl-2-pyridyl) thiourea was synthesized and purified as described elsewhere [16]. Nitrate salts of the cations used (from Merck and Aldrich) were all of the highest purity available, and used without any further purification except for vacuum drying over P<sub>2</sub>O<sub>5</sub>. Doubly distilled deionized water was used throughout.

### 2.3. Electrode Preparation

The general procedure to prepare the PVC membrane was as followed: Different amounts of the ionophore (NBMPT) along with appropriate amounts of additive were weighed. Then, known amounts of PVC and plasticizer were added to the mixture. The mixture was dissolved in 2 mL of tetrahydrofuran (THF), and the solution was mixed well. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3-5 mm o.d.) was dipped into the mixture for about 10 s so that a transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 24 h. The tube was then filled with an internal filling solution ( $1.0 \times 10^{-3}$  mol L<sup>-1</sup> Cr<sup>3+</sup>). The electrode was finally conditioned for 24 h by soaking in a  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> Cr<sup>3+</sup> solution.

### 2.4. Emf Measurements

The following cell was assembled for the conduction of the emf (electromotive force) measurements;

Ag–AgCl, KCl (satd.) | internal solution,  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> Cr(NO<sub>3</sub>)<sub>3</sub> | PVC membrane | sample solution | Ag–AgCl, KCl (satd.)

These measurements were preceded using calibration of the electrodes with several standard solutions. Activities were calculated according to the Debye- Huckel procedure.

### 3. RESULTS AND DISCUSSION

#### 3.1. Membrane Composition Effect on the Potential Response of the Sensor

Because the degree of sensitivity and selectivity for a certain ionophore is greatly related to the membrane ingredients [17,18], the influence of membrane composition on the potential responses of the  $\text{Cr}^{3+}$  sensor was inspected. In this study, different membrane compositions, as shown in Table 1, were tested. As can be seen, the membrane with the composition of 30% PVC, 10% NBMPT, 2% NaTPB and 58% DBP (No. 5) was the optimum one in the development of this sensor.

**Table 1.** The optimization of the membrane ingredients

Membrane No.	Composition (%)					Slope (mV per decade)
	PVC (% wt.)	DBP (% wt.)	Ionophore (% wt.)	NaTPB (% wt.)	OA (% wt.)	
1	30	70	---	---	---	5.9±0.2
2	30	63	7	---	---	10.5±0.4
3	30	61	7	2	---	15.8±0.2
4	30	60	8	2	---	17.4±0.3
5	30	58	10	2	---	19.7±0.3
6	28	58	12	2	---	12.6 ± 0.2
7	28	60	10	---	2	10.7±0.3
8	28	57	10	---	5	13.5±0.4

Besides the critical role of the nature of the ionophore in preparing membrane-selective electrodes, some other important features of the PVC membrane such as the amount of ionophore, the nature of the solvent mediator, the plasticizer/PVC ratio and, especially, the nature of additives used are known to significantly influence the sensitivity and selectivity of ion-selective electrodes. Thus, different aspects of membrane preparation based on the ligand NBMPT for  $\text{Cr}^{3+}$  ion were optimized and results are given in Table 1. From Table 1, it was obvious that in the absence of ionophore (No. 1), the response of the recommended electrode was low (slope of 5.9±0.2 mV per decade). The sensitivity of the electrode response increases with increasing ionophore content until a value of 10% is reached. It shows the affinity of the

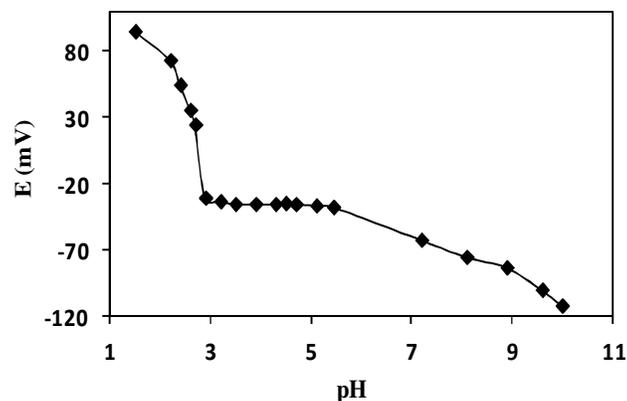
NBMPT toward  $\text{Cr}^{3+}$  ion. Further addition of ionophore will, however, result in diminished response of the sensor, most probably due to some inhomogeneities and possible saturation of the membrane [19].

The second factor which helps the extraction of the  $\text{Cr}^{3+}$  ion is plasticizer. It should be noted that the nature of plasticizer influences both the dielectric constant of the membrane and the mobility of ionophore and its complex. The data given in table 1 revealed that DBP is the effective solvent mediator in preparing the  $\text{Cr}^{3+}$  ion-selective electrode in a suitable DBP/PVC ratio (No. 5).

The presence of lipophilic anions in a cation-selective membrane was also considered. Actually, the presence of such anions in a cation-selective membrane, which is based on a neutral carrier, decreases the ohmic resistance and improves the response behavior and selectivity. Furthermore, when the extraction capability is poor, it increases the membrane electrode sensitivity [20-22]. The data given in table 1 revealed that in the absence of a proper additive (No. 2) and in the presence of 2% and 5% OA, the sensitivity of the PVC membrane based on NBMPT is quite low (Nos. 7,8). However, the presence of 2% NaTPB as suitable lipophilic additive will improve the sensitivity of the  $\text{Cr}^{3+}$  sensor considerably (No. 5). In fact, it helps to the ion-exchange of the analyte from aqueous solution to organic layer of the membrane.

### 3.2. pH Effect on the Electrode Response

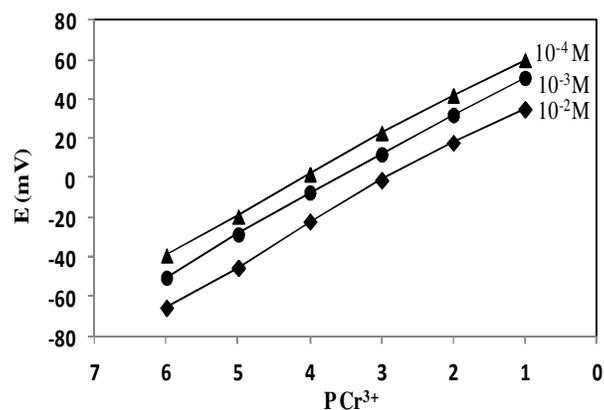
The influence of the pH of the test solution on the potential response of  $\text{Cr}^{3+}$  sensor investigated at  $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ Cr}^{3+}$  concentration, in the pH value of 2.0 up to 10.0 (concentrated NaOH or HCl solutions were employed for the pH adjustment). It is clear from Fig. 2 that the potentials remained constant from the pH range 3.0 to 5.5 for this sensor. Therefore, the pH range 3.0 to 5.5 was taken as the working pH range of the sensor. Beyond this range, relatively noteworthy fluctuations in potential were observed. The variations in potentials above the pH value of 5.5 might be justified by the formation of the  $\text{Cr}^{3+}$  ion hydroxy complexes in the solution. On the other hand, the fluctuations below the pH value of 3.0 were attributed to the partial protonation of the employed ionophore [23]. This ionophore has N and S atoms which are donor and soft atoms. Therefore, charge-dipole interaction between  $\text{Cr}^{3+}$  ions and nitrogen and sulfur atoms of ionophore is stronger than interaction between  $\text{H}^+$  ions and these atoms. If  $\text{H}^+$  concentration is much more than  $\text{Cr}^{3+}$ , then  $\text{H}^+$  ions can compete with  $\text{Cr}^{3+}$  ions for making complex with ionophore. In pH between 3-5.5,  $\text{H}^+$  concentration is not enough for competing with  $\text{Cr}^{3+}$  ions (because ionophore has more trend to  $\text{Cr}^{3+}$  ions in compare to  $\text{H}^+$  ions), but in below pH of 3,  $\text{H}^+$  concentration is enough to overcome on  $\text{Cr}^{3+}$  and employed ionophore can be protonated. Consequently, the behavior of the membrane electrode towards the  $\text{Cr}^{3+}$  ion concentration was found to be inaccurate beyond the pH range of 3.0 to 5.5.



**Fig. 2.** Effect of pH on potential response of the chromium ion sensor

### 3.3. Internal Solution

The concentration of the internal solution ( $\text{Cr}(\text{NO}_3)_3$ ) of the electrode was changed from  $1.0 \times 10^{-2} \text{ mol L}^{-1}$  to  $1.0 \times 10^{-4} \text{ mol L}^{-1}$  and the potential response of the  $\text{Cr}^{3+}$  ion selective electrode was obtained (Fig. 3). It was found that the variation of concentration of the internal solution does not cause any significant differences in potential response, except for an expected change in the intercept of the resulting Nernstian plot. A  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  concentration  $\text{Cr}(\text{NO}_3)_3$  solution is quite appropriate for smooth functioning of the electrode system.



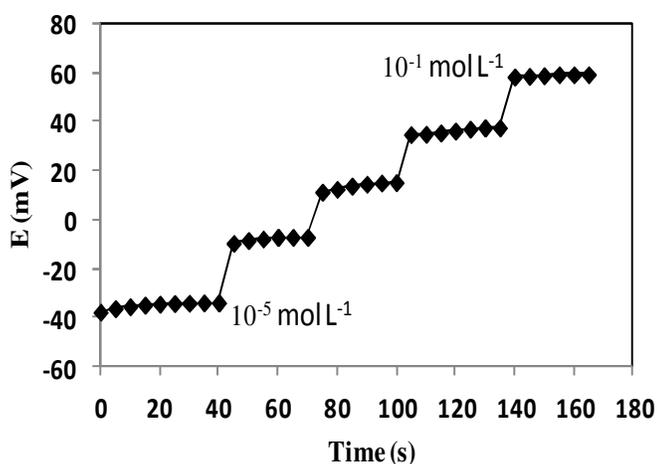
**Fig. 3.** The effect of internal reference solution concentration on the electrode response

### 3.4. Response Time

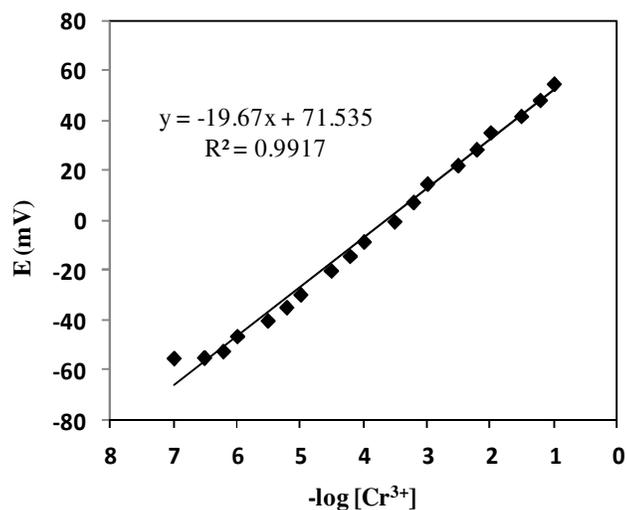
The response time of an electrode is evaluated by measuring the average time required to achieve a potential within  $\pm 0.1 \text{ mV}$  of the final steady-state potential, upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration. It is notable that the experimental conditions-like the stirring or flow rate, the ionic

concentration and composition of the test solution, the concentration and composition of the solution to which the electrode was exposed before experiment measurements were performed, any previous usages or preconditioning of the electrode, and the testing temperature have an effort on the experimental response time of a sensor [24].

In this work, dynamic response time was obtained by changing the  $\text{Cr}^{3+}$  concentration in solution, over a concentration range of  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-1} \text{ mol L}^{-1}$ . The actual potential versus time traces is shown in Fig. 4. As can be seen, in whole concentration range the electrode reaches its equilibrium response in a relatively short time ( $\sim 5 \text{ s}$ ). This is most probably due to the fast exchange kinetics of complexation-decomplexation of  $\text{Cr}^{3+}$  ion with the ionophore at the test solution-membrane interface.



**Fig. 4.** Dynamic response of chromium ion sensor for step changes in concentration of  $\text{Cr}^{3+}$  ion



**Fig. 5.** The calibration curve of the chromium ion sensor

### 3.5. Measuring Range and Detection Limit

The measuring range of an ion-selective electrode includes the linear part of the calibration graph as shown in Fig. 5. The applicable measuring range of the proposed sensor is between  $5 \times 10^{-7}$  and  $1 \times 10^{-1}$  mol L<sup>-1</sup>.

In practice, detection limits for the most selective electrodes are in the range of  $10^{-5}$ – $10^{-6}$  mol L<sup>-1</sup>. In this work the detection limit of the proposed membrane sensor was  $3 \times 10^{-7}$  mol L<sup>-1</sup> which was calculated by extrapolating the two segments of the calibration curve.

### 3.6. Selectivity

The potentiometric selectivity coefficients of the Cr<sup>3+</sup> sensor were evaluated by the matched potential method (MPM) [25]. The resulting values of the selectivity coefficients are given in Table 2. The selectivity coefficients clearly indicate that the electrode is more selective to Cr<sup>3+</sup> than to a number of other metal ions. A value of  $K_{\text{MPM}} = 1.0$  indicates equal response to primary and interfering ions. Further, the smaller the value of the selectivity coefficient, the higher is the selectivity of the sensor.

**Table 2.** The selectivity coefficients of various interfering cations for the membrane

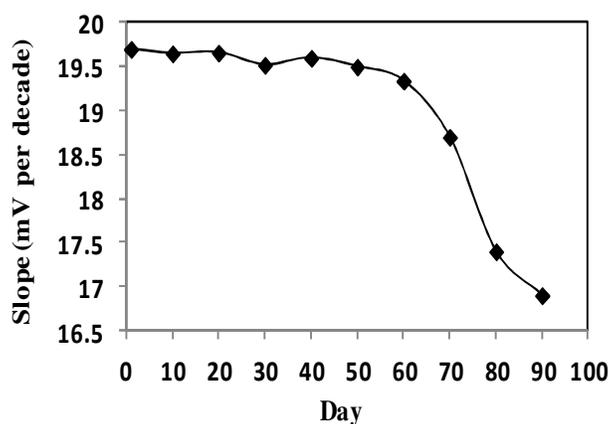
Ion	$K_{\text{MPM}}$
K <sup>+</sup>	$2.0 \times 10^{-3}$
Mg <sup>2+</sup>	$1.0 \times 10^{-2}$
Co <sup>2+</sup>	$2.0 \times 10^{-4}$
Pb <sup>2+</sup>	$4.0 \times 10^{-2}$
Ni <sup>2+</sup>	$5.0 \times 10^{-3}$
Cu <sup>2+</sup>	$4.0 \times 10^{-4}$
Zn <sup>2+</sup>	$2.0 \times 10^{-3}$
Cd <sup>2+</sup>	$6.5 \times 10^{-3}$
Ag <sup>+</sup>	$6.0 \times 10^{-2}$

It is seen from the table that the selectivity coefficient values are much smaller than 1.0 indicating that they exhibit sufficient selectivity towards Cr<sup>3+</sup> over all the interfering ions

studied. The selectivity coefficients seem to indicate negligible interferences in the performance of the electrode assembly.

### 3.7. Lifetime

It is well established that the loss of plasticizer, carrier, or ionic site from the polymeric film due to leaching into the sample is a primary reason for the limited lifetimes of the sensors. The average lifetime for most of the reported ion-selective sensors is in the range of 4–10 weeks. The average lifetime of this sensor was investigated by monitoring the changes in sensor slope with time. The sensors were tested for 90 days, during which time the electrodes were used extensively (one hour per day). Fig. 6 shows the changes in the slope of this sensor with time. The proposed sensors can be used for 60 days. There is a slight gradual decrease in the slopes during 60 days (from 19.7 to 19.3 mV per decade), but after it, a significant change in slope is observed (from 19.3 to 16.9 mV per decade). In PVC membrane electrodes after several time of usage, the membrane ingredients leak from the organic layer and affect the membrane response.



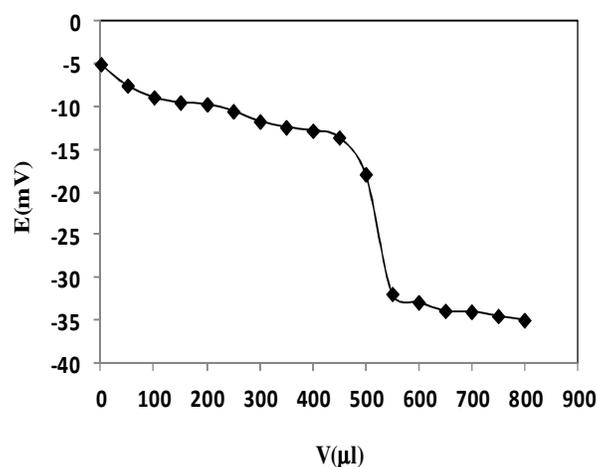
**Fig. 6.** The lifetime of the chromium ion sensor

### 3.8. Analytical Application

The practical utility of the proposed membrane sensor was tested by its use as an indicator electrode for the titration of 50.0 mL of  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> of Cr<sup>3+</sup> solution with EDTA  $1.0 \times 10^{-2}$  mol L<sup>-1</sup>. The resulting titration curve is shown in Fig. 7. As can be seen, the amount of Cr<sup>3+</sup> ions in solution can be accurately determined with the electrode.

To assess the applicability of proposed electrode in real samples an attempt was made to determine Cr<sup>3+</sup> ions in black tea and cocoa powder sample. A 1.0 g black tea and cocoa powder was taken in a beaker and dissolved in concentrated HNO<sub>3</sub> (10 mL) and HClO<sub>4</sub> (4

mL) with heating. The solution was cooled, neutralized with NaOH solution, diluted and filtered. The filtrate was made to 100 ml with water in a calibrated flask.



**Fig. 7.** Potentiometric titration curve of  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> Cr<sup>3+</sup> solution (50 ml) with  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> EDTA using the proposed sensor as an indicator electrode.

**Table 3.** Determination results of Cr<sup>3+</sup> ions in various samples

Sample	Measured by FAAS (mg L <sup>-1</sup> )	Measured by proposed sensor (mg L <sup>-1</sup> )
Black tea	0.95 (±0.9) <sup>a</sup>	1.0 (±1.8)
Cocoa powder	1.20 (±1.1)	1.3 (±1.4)

<sup>a</sup> % RSD based on three replicate analysis

An aliquot of the sample solution was taken and a Cr<sup>3+</sup> ion was determined by the calibration procedure by proposed electrode and flame atomic absorption spectroscopy (FAAS). The results are given in Table 3. As seen the results obtained by the proposed method and FAAS are in satisfactory agreement.

### 3.9. Comparison of the proposed Cr<sup>3+</sup> sensor and some of the best previously reports

The Nernstian slope, detection limit, linearity range, response time and selectivity of proposed Cr<sup>3+</sup> sensor with some of the best previously reports are compared in Table 4. As is obvious, the results clearly indicate that the proposed sensor is superior to the previously reported ones in: response time and selectivity coefficients. In linearity range, proposed sensor is better than the most previously reports. In Nernstian slope and detection limit, proposed sensor is not superior but is closed to the most previously reports.

**Table 4.** Determination results of Cr<sup>3+</sup> ions in various samples

Ionophore	Slope (mV per decade)	Linear range (mol L <sup>-1</sup> )	Detection limit (mol L <sup>-1</sup> )	Response time (s)	Interfer- ences ions	Ref.
Glyoxal bis (2-hydroxyanil)	19.8	3.0×10 <sup>-6</sup> -1.0×10 <sup>-2</sup>	6.3×10 <sup>-7</sup>	20	Cu <sup>2+</sup> , Cr <sup>2+</sup> , Zn <sup>2+</sup> , Co <sup>2+</sup>	[26]
N- (1- thien-2-ylethylene) benzen-1,2-diamine	19.9	10 <sup>-6</sup> -10 <sup>-1</sup>	7.0×10 <sup>-7</sup>	12	Fe <sup>3+</sup>	[27]
4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one	19.7	10 <sup>-6</sup> -10 <sup>-1</sup>	5.8×10 <sup>-7</sup>	10	La <sup>3+</sup> , Ce <sup>3+</sup> , Al <sup>3+</sup>	[28]
5-amino-1-phenyl-1H-pyrazole-4-carboxamide	19.6	10 <sup>-6</sup> -10 <sup>-1</sup>	5.3×10 <sup>-7</sup>	10	Fe <sup>3+</sup> , Al <sup>3+</sup> , La <sup>3+</sup>	[29]
2-acetylpyridine and nanoporous silica gel	19.8	10 <sup>-8</sup> -10 <sup>-3</sup>	8.0×10 <sup>-9</sup>	55	Ce <sup>3+</sup> , Pb <sup>2+</sup> , Ni <sup>2+</sup>	[30]
1-[(2- hydroxy ethyl) amino]-4-methyl-9H-thioxanthen-9-one	20.51	3.2×10 <sup>-7</sup> -1.0×10 <sup>-1</sup>	1.6×10 <sup>-7</sup>	8	Zn <sup>2+</sup> Ni <sup>2+</sup>	[31]
N-banzoyl-N'(6-methyl-2-pyridyl) thiourea]	19.7	3×10 <sup>-7</sup> -1.0×10 <sup>-1</sup>	3×10 <sup>-7</sup>	5	---	This work

#### 4. CONCLUSION

Ion-selective electrodes tend to be; low in cost, simple to use, easily automated for rapid sampling, with low interferences from the matrix and can be applied to small volumes. These characteristics make them an ideal choice for environmental measurements.

As a consequence, the design of a new and selective chromium ion sensor was based on the selection of a suitable ionophore. The Cr<sup>3+</sup> potentiometric membrane sensor was constructed by N-banzoyl-N'(6-methyl-2-pyridyl) thiourea. This electrode exhibits a fast response time of 5 s, a lower detection limit of 3×10<sup>-7</sup> mol L<sup>-1</sup>, pH independent potential responses across the range of 3.0–5.5 and relatively long lifetime of 60 days. Its selectivity towards the chromium ions was not influenced by the presence of the common alkali, alkaline earth, or transition and heavy metal ions, since the interference of these substances was low.

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