

## Potentiometric Chromate Quantification Based on Interaction with N, N' Butylen Bis (Saliciliden Iminato) Copper (II)

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A new chromate-selective electrode, based on the N, N' butylen bis (saliciliden iminato) copper (II) complex as the membrane carrier, was developed. The electrode exhibited a good Nernstian slope of  $-28.8 \pm 0.5$  mV/decade and a linear range of  $3.0 \times 10^{-6} - 1.0 \times 10^{-1}$  mol.L<sup>-1</sup> for chromate. The limit of detection was  $3.0 \times 10^{-6}$  mol.L<sup>-1</sup>. It had a fast response time of 5-10 sec and could be used for more than three months. The selective coefficients were determined by the Fixed Interference Method (FIM). A chromate-selective electrode could be used in the pH range of 6.5-10.5. It was employed as an indicator electrode for the direct determination of chromate in real samples.

### INTRODUCTION

Chromium is a silvery grey malleable metal. It is a relatively common element with an average concentration of 100 ppm in the earth's crust, occurring primarily in chromite (FeCr<sub>2</sub>O<sub>4</sub>) and krokoite (PbCrO<sub>4</sub>). Chromium (VI) has oxidizing properties. The demand for trace analysis of Cr is particularly high in environmental and biological sciences, as Cr(III) is an essential nutrient, whereas Cr (VI) is toxic to plants, animals and man.

The speciation of Cr determines not only its ecological impact, but also its mobility and transport behavior in the environment. High concentrations of Cr and its related compounds have been found in polluted soil and water bodies, due to its extensive use in dyeing, leather tanning and electroplating industries [1].

Recently, ion-selective electrodes have become one of the most important groups of chemical sensors [2,3]. The development of new types of ISE is of considerable practical interest. Up to now, Cr-responsive ISEs have not been produced commercially. Ion-selective electrodes are well known as being useful in industry and

in clinical, chemical and environmental analyses [4,5]. Many compounds, either organic or inorganic, have been used as electroactive materials [6-10].

As a simple method, Potentiometric detection, based on ion-selective electrodes, offers several advantages, such as speed and ease of preparation and procedures, simple instrumentation, a relatively fast response, a wide dynamic range, reasonable selectivity and low cost [11-14]. Ion-selective electrodes, based on coating polymeric membrane films directly onto the surface of a conducting substance [15-17], are very simple to construct and maintain, since no filling solution is required and, if the membrane is thin enough, such electrodes usually equilibrate much faster with the sample solution. Ion Selective Electrode (ISE) utility and simplicity have replaced other wet analytical methods that were often far slower and more cumbersome to monitor. Solvent polymeric membrane electrodes incorporating ion carriers are known to be very useful tools for chemical, clinical and environmental analyses, as well as in process monitoring. The design of anion receptors is far less developed than the field of cation receptors. Classical liquid membrane electrodes for anions are based on quaternary ammonium salts and their anion responses rely on associated ion exchange. Thus, the selectivity of membrane electrodes, based on the aforementioned ionophores, exhibit a Hofmeister selectivity sequence, based on the analyte lipophilicity. Recently, a series of new anion-selective electrodes have been described, which display a selectivity deviating

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from the Hofmeister sequence as a result of unique interactions between the carriers and the anions. The wide uses of ISE in routine chemical analysis have been accompanied by a search for ionophores that can chemically recognize specific anions and offer either a new or an improved selectivity to different ions.

This paper describes the use of *N, N'* butylen bis (saliciliden iminato) copper (II) [CuL] electroactive material for preparing a chromate-sensitive electrode. The potentiometric response properties, reproducibility and selectivity of the electrodes were evaluated by the response potentials and selectivity coefficients.

## EXPERIMENTAL SECTION

### Reagents

PVC of high relative molecular weight, trioctylmethyl ammonium chloride (TOMAC), and dioctyl phthalate (DOP) were used, as received from Aldrich. Potassium or sodium salts of all anions, tetrahydrofuran (THF) and all other chemicals were of the highest purity available from Merck, and were used without further purification, except THF, which was distilled before use. The ionophore, *N, N'*-butylenbis (salicilideniminato) copper (II) [CuL] (Figure 1), was synthesized and used after purification. All of the solutions were prepared using deionized water. The pH adjustments were made with dilute nitric acid and sodium hydroxide solutions, as required. Wastewater samples were filtered through a filter paper. A stock solution of chromate was prepared by dissolving the appropriate

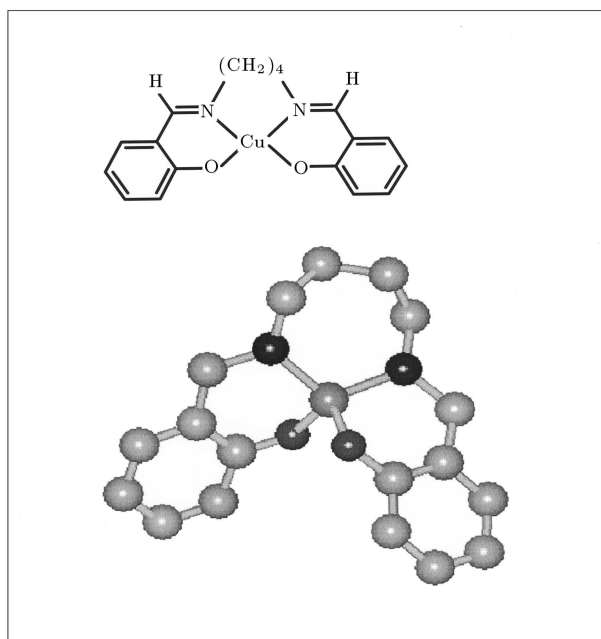
amount of potassium chromate in 100 mL of water. Working solutions were prepared by successive dilutions with water. All of the working solutions were buffered at pH 7.0, using a phosphate buffer solution.

Carrier, *N, N'*-butylenbis (salicilideniminato) copper(II) [CuL], was prepared according to the following procedures. The tetradentate Schiff-base ligand; ( $H_2salbn$ ): *N, N'*-butylenebis (salicylideaminato); was prepared from salicylaldehyde by condensation with 1,2-butanediamine, following the standard procedure [18]. For preparation of [Cu( $salbn$ )], a solution of  $Cu(NO_3)_2 \cdot 3H_2O$  (0.489 g, 2 mmol) in methanol (20 mL) was slowly added to a methanolic solution of  $H_2salbn$  (0.176 g, 2 mmol) with constant stirring. A green precipitate was formed in 30 min on stirring the mixture. The product thus obtained was recrystallized from chloroform. Anal. Calcd. for  $C_{18}H_{20}N_2O_2$ : C, 72.95; H, 6.80; N, 9.44. Found: C, 72.81; H, 6.73; N, 9.52%. Anal. Calcd. for  $C_{18}H_{18}N_2O_2Cu$ : C, 60.41; H, 5.07; N, 7.83; Cu, 17.76. Found: C, 60.32; H, 4.93; N, 7.95; Cu, 17.64%.

Significant changes in some important bands from the free Schiff-base ligand were noticed in the IR spectra. For example, free ligand exhibits  $\nu_{C=N}$  stretch at  $1580\text{ cm}^{-1}$ . In complexes, this band shifts to a lower frequency and appears at  $1560\text{ cm}^{-1}$ , indicating the coordination of azomethine nitrogen to the metal. The appearance of two to three bands in the low frequency region (between  $410$  and  $527\text{ cm}^{-1}$ ) indicates the coordination of phenolic oxygen, in addition to azomethine nitrogen. The presence of several bands of medium intensity in the  $2800\text{--}3000\text{ cm}^{-1}$  region indicates the existence of a methyl and butylene group of the amine residue of the ligand. Within the UV spectrum of the ligand, the existence of two absorption bands assigned to the transition  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  at  $241.5$  and  $289.0\text{ nm}$ , respectively, has been observed. Also, these transitions are to be found in the spectra of the complexes, but they are shifted to lower frequencies, confirming the coordination of the ligand to the metal ions [19]. In addition, in the spectra of the complex of  $H_2salbn$  ligand, the new bands observed in the  $390.6\text{--}434.8\text{ nm}$  range can be attributed to the charge-transfer bands (ligand to metal or metal to ligand centre) [19]. The spectrum of the [Cu( $salbn$ )] exhibited one broad band at  $569.8\text{ nm}$  that is attributed to  $d \leftrightarrow d$  transitions. The spectrum of this complex is similar to those reported for Cu(II) complexes [19]. The magnetic moment ( $1.77\text{ BM}$ ) suggests a tetrahedral geometry.

### Electrode Preparation

Membrane ion-selective electrodes were prepared, according to a previously reported method [20]. A mixture of PVC, plasticizer (DOP) and the membrane additive (TOMAC), with a total mass of 200 mg, was



**Figure 1.** Structural representation of *N, N'* butylen bis (saliciliden iminato) copper (II).

dissolved in approximately 10 mL of freshly distilled THF. To this mixture, an electroactive material [CuL] was added and the solution was mixed well. The resulting mixture was poured into a small, flat-bottomed dish with a diameter of 2 cm and covered with a filter paper. The solvent was then allowed to evaporate at room temperature. The resulting membrane (ca. 0.2 mm thick) was then sectioned with a cork borer and mounted across the opening of a PVC tube of about 7 mm i.d. and 1.5 cm length, using a glue of PVC in THF. The PVC tube with the membrane was then filled with an internal solution of  $1.0 \times 10^{-3}$  mol.L<sup>-1</sup> potassium chromate. The filled electrode was conditioned by soaking in  $1.0 \times 10^{-3}$  mol.L<sup>-1</sup> potassium chromate. The first conditioning time was approximately 22 h and, then, 30-40 mins for successive uses. A silver/silver chloride electrode was used as an internal reference electrode.

### Potential Measurement and Calibration

The potential build-up across the membrane electrode was measured using a galvanic cell of the following type: Ag|AgCl|KCl (3M) internal solution ( $1.0 \times 10^{-3}$  mol.L<sup>-1</sup> K<sub>2</sub>CrO<sub>4</sub>)|PVC membrane|test solution || SCE.

All potentials were measured at  $25 \pm 1^\circ\text{C}$  using a digital pH/mV meter (model 691 Metrohm). A saturated calomel electrode (SCE, Metrohm) with a fiber junction was used as the external reference electrode. The activities were calculated according to the Debye-Hückel procedure [21] and, for the calibration curve, the concentration instead of activity was used. The pH of the sample solution was monitored simultaneously with a conventional glass pH electrode (Metrohm).

The performance of the electrode was investigated by measuring its potential in potassium chromate solutions prepared in the concentration range of  $1.0 \times 10^{-7}$ – $1.0 \times 10^{-1}$  mol.L<sup>-1</sup> by serial dilution at constant pH. All solutions were freshly prepared by dilution from the stock standard solution,  $1.0 \times 10^{-1}$  mol.L<sup>-1</sup>, with deionized water. The solutions were stirred and potential readings recorded when they became stable. The data were plotted as observed potential vs. the logarithm of the CrO<sub>4</sub><sup>2-</sup> concentration. The potentiometric titration of a 10 mL of  $1.0 \times 10^{-3}$  mol.L<sup>-1</sup> Pb<sup>2+</sup> solution was carried out with a 0.01 mol.L<sup>-1</sup> CrO<sub>4</sub><sup>2-</sup> solution using the chromate-selective electrode as an indicator electrode, in conjunction with a fiber function SCE electrode.

### Determination of Selectivity Coefficient

The selectivity factor,  $K^{\text{Pot}}$ , is a measure of the preference of the ion-selective electrode for the interfering ion, A, relative to the primary ion chromate to be measured. A selectivity factor below 1 indicates that

the preference is for the primary ion chromate. Selectivities of solvent polymeric membrane ion-selective electrodes are quantitatively related to equilibria at the interface between the sample and the electrode membrane. Selectivity coefficients are determined experimentally using the fixed interference method (FIM). The fixed interference method has advantages such as: a) Accurate for a larger variety of systems than separate solutions; b) Relatively simple to perform for a reasonable set of potential interfering ions of interest; c) More accurate than separate solutions; d) Gives good data for most real world systems and e) Coefficients translate fairly well to selectivity performance in many observed applications. Also, it has disadvantages such as: a) Does not account for all multiple ion-ion interactions, only interfering ion-analyte interference and b) has a poor match of performance for most physiological fluids [22,23].

### RESULTS AND DISCUSSION

In preliminary experiments, membranes with and without carriers were constructed. The membranes with no carrier displayed insignificant selectivity toward chromate and its response was not reliable, whereas, in the presence of the proposed carrier, the optimized membrane demonstrated a Nernstian response and a remarkable selectivity for chromate over several common inorganic and organic anions. The preferential response toward CrO<sub>4</sub><sup>2-</sup> is believed to be associated with the coordination of chromate with the central metal ion of the carrier.

### Influence of Membrane Composition

A polymer matrix provides the mechanical stability of the membrane, chemical stability, a clean surface of the resulting membrane, chemical inertness and can be adjusted to extra requirements, i.e. physiological fluid samples, biocompatibility, adhesion etc.

Several membrane compositions were investigated by varying the ratio of PVC, plasticizer and the membrane active material, [CuL] complex (Table 1). The optimized composition of the membrane was 6% (w/w) ionophore, 61% (w/w) membrane solvent, 32.6% (w/w) PVC and 0.4% additive (w/w). The potentiometric response of the membrane was greatly improved in the presence of lipophilic cationic additive, (TOMAC). It is known that lipophilic salts not only reduce membrane resistance, but also enhance response behavior and selectivity and reduce interferences from sample anions [24,25]. The presence of lipophilic ionic sites is beneficial for both neutral carrier and charged carrier based ion-selective electrodes [26,27]. Neutral carrier based cation-selective electrodes require lipophilic ionic sites with a charge sign opposite to that of the primary

**Table 1.** Evaluation of different membrane composition of chromate-selective electrode.

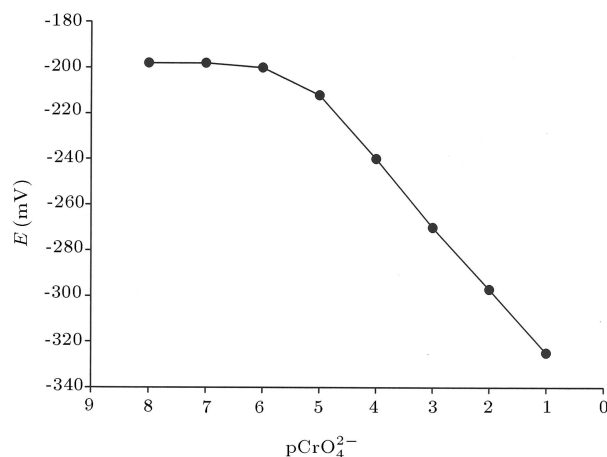
No	PVC%	Plasticizer %	Ionophore%	Additive%	Slope (mVdecade <sup>-1</sup> )	Linear Range (mol.L <sup>-1</sup> )
1	32	62	6	0	-23.8	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$
2	33	61	6	0	-22.5	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$
3	31.5	63	5	0.5	-35.6	$5.0 \times 10^{-6} - 1.0 \times 10^{-1}$
4	32	61	6	1.0	-46.0	$5.0 \times 10^{-6} - 1.0 \times 10^{-1}$
5	32.6	61	6	0.4	-28.8	$3.0 \times 10^{-6} - 1.0 \times 10^{-1}$
6	33.6	61	5	0.4	-24.4	$5.0 \times 10^{-6} - 1.0 \times 10^{-1}$
7	32.8	61	6	0.2	-26.6	$5.0 \times 10^{-6} - 1.0 \times 10^{-1}$

ion for obtaining Nernstian responses [28,29]. However, for the charged carrier based ion-selective electrodes, the charge sign of the ionic sites that gives the highest potentiometric selectivity depends on the charge of the ionophore and of the primary and interfering ions, as well as on the stoichiometry of their complexes with the ionophore [30].

The critical response characteristics of the proposed electrode were investigated according to IUPAC recommendations [31,32]. The membrane with a composition of 6% ionophore, 61% DOP, 32.6% PVC and 0.4% TOMAC generated a stable potential response in solutions containing chromate, after conditioning for 22 h in a  $1.0 \times 10^{-5}$  mol.L<sup>-1</sup> CrO<sub>4</sub><sup>2-</sup> solution.

### Response Characteristics of the Electrode

Figure 2 shows the calibration curve of the chromate selective electrode with the optimum membrane composition. The linear response range covers from  $3.0 \times 10^{-6}$  mol.L<sup>-1</sup> to  $1.0 \times 10^{-1}$  mol.L<sup>-1</sup> chromate. This curve has a slope of  $-28.8 \pm 0.5$  per decade of concentration of chromate ion. The detection limit was established, as described by IUPAC recommendations [31]. The practical limit of detection, defined as the concentration of chromate ion obtained from the intersection of two extrapolated segments of the calibration graph, was  $3.0 \times 10^{-6}$  mol.L<sup>-1</sup>. The optimum equilibration time (conditioning time) of the chromate-selective electrode for  $1.0 \times 10^{-5}$  mol.L<sup>-1</sup> potassium chromate was 22 h, after which the electrode would generate stable



**Figure 2.** Potentiometric response of the chromate-selective electrode to chromate using optimized membrane electrode.

potentials in contact with chromate solutions (Table 2). The practical characteristic properties of the optimized membrane are summarized in Table 3.

The precision of the assay was investigated, with respect to repeatability. The standard deviation of 20 replicate measurements at  $1.0 \times 10^{-3}$  and  $1.0 \times 10^{-4}$  mol.L<sup>-1</sup> CrO<sub>4</sub><sup>2-</sup> were  $\pm 0.57$  and  $\pm 0.64$  mV, respectively. The long-term stability of the electrode was studied by periodically re-calibrating in standard solutions and calculating the response slope over the range of  $3.0 \times 10^{-6} - 1.0 \times 10^{-1}$  mol.L<sup>-1</sup>. The detection system was very stable and could be used over a

**Table 2.** Conditioning time for chromate-ISE.

Conditioning (Time/h)	Slope (mVdecade <sup>-1</sup> )	Linear Range (mol.L <sup>-1</sup> )	Correlation Coefficient (R <sup>2</sup> )
5	-24.1	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	0.994
8	-26.2	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	0.998
12	-28.1	$5.0 \times 10^{-6} - 1.0 \times 10^{-1}$	0.997
22	-28.8	$3.0 \times 10^{-6} - 1.0 \times 10^{-1}$	0.998
26	-28.6	$5.0 \times 10^{-6} - 1.0 \times 10^{-1}$	0.997
30	-28.2	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	0.997

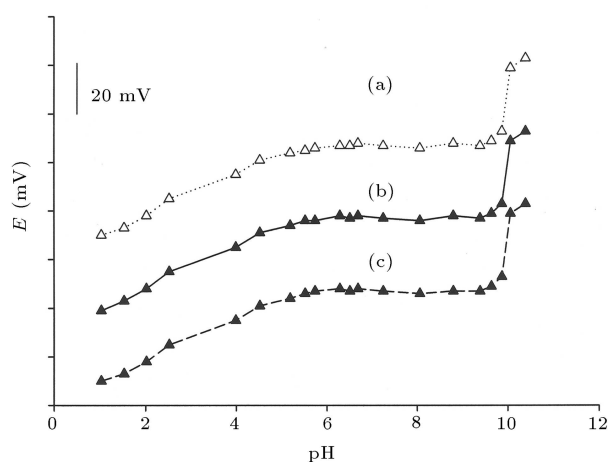
**Table 3.** Characteristics of optimized chromate-ISE.

<b>Linear Range (mol.L<sup>-1</sup>)</b>	$3.0 \times 10^{-6} - 1.0 \times 10^{-1}$
<b>Slope (mVdecade<sup>-1</sup>)</b>	-28.8
<b>pH Range</b>	6.5-10.5
<b>Precision</b>	At concentrations of $1.0 \times 10^{-3}$ and $1.0 \times 10^{-4}$ mol.L <sup>-1</sup> CrO <sub>4</sub> <sup>2-</sup> standard deviations were of $\pm 0.57$ and $\pm 0.64$ mV, respectively.
<b>Detection Limit (mol.L<sup>-1</sup>)</b>	$3.0 \times 10^{-6}$
<b>Life Time (month)</b>	> 2
<b>Response Time (s)</b>	5-10

period of more than 3 months without observing any detectable loss of performance characteristics.

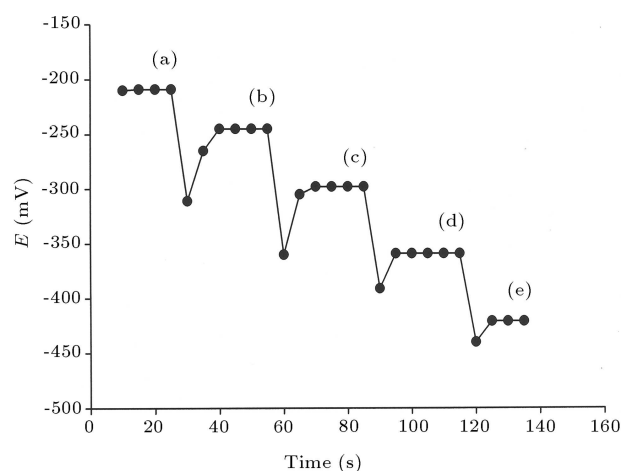
The influence of the pH of the test solution on the potential response of the membrane sensor was tested by recording the emf of a cell that contained chromate adjusted to the appropriate pH. As illustrated in Figure 3 for  $1.0 \times 10^{-4}$ ,  $1.0 \times 10^{-3}$  mol.L<sup>-1</sup> and  $1.0 \times 10^{-2}$  mol.L<sup>-1</sup> chromate, the potentials remain constant from pH of about 6.5–10.5. The results show that the sensor is suitable for chromate determination in a wide pH range of 6.5–10.5. In high pH media, OH<sup>-</sup> will probably compete with the chromate ion. It was supposed that the chromate and OH<sup>-</sup> ions coordinate competitively with the CuL complex and at higher pH values. Under pH 6.5, the free chromate ion was decreased in a stronger acidity solution (decrease of chromate, increase of dichromate), which caused a deterioration in potentiometric responses.

The influence of the concentration of the internal


**Figure 3.** The pH response of the membrane electrode at a)  $1.0 \times 10^{-4}$ ; b)  $1.0 \times 10^{-3}$  and c)  $1.0 \times 10^{-2}$  mol.L<sup>-1</sup> chromate concentration.

solution of the PVC electrode was studied as follows. Three similar membranes were prepared under optimal membrane composition and each electrode was filled with an internal solution of varying CrO<sub>4</sub><sup>2-</sup> concentrations of  $1.0 \times 10^{-3}$ ,  $1.0 \times 10^{-4}$  and  $1.0 \times 10^{-5}$  mol.L<sup>-1</sup>CrO<sub>4</sub><sup>2-</sup>. The electrodes were then conditioned for 22 h by soaking in the same solutions of CrO<sub>4</sub><sup>2-</sup>. Finally, the emf versus pCrO<sub>4</sub><sup>2-</sup> plot for each electrode was constructed in a pCrO<sub>4</sub><sup>2-</sup> range of 1-6. As can be seen from Table 4, the concentration of the internal filling solution has a negligible effect on the potential response of the electrode, except for an expected change in the intercept of the resulting plots. A  $1.0 \times 10^{-5}$  mol.L<sup>-1</sup> concentration was found to be appropriate for a Nernstian response.

An important characteristic of a potentiometric indicator electrode is the response time. The average time for the chromate-selective electrode to reach a potential within  $\pm 1$  mV of its final equilibrium value was measured after successive immersion of the electrode in a series of chromate solutions, each having a 10-fold increase in chromate concentration from  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-1}$  mol.L<sup>-1</sup> (Figure 4). The static response time for the PVC membrane electrode obtained was 5 sec for  $1.0 \times 10^{-1}$  mol.L<sup>-1</sup> chromate concentration. At lower concentrations, the response time was delayed and reached 10 sec. Response times inherent in ion-selective electrodes are only measurable if the overall response time of the potentiometric system is governed by the properties of the membrane electrode, i.e. if the time constant of the response function of the electrode is much larger than the time constants of the electrochemical cell and the electronic EMF-measuring device. Thus, the overall response time, necessarily, not only reflects the properties of the membrane electrode, but also expresses features of the measuring technique


**Figure 4.** Response time of the membrane electrode for chromate with change of concentration from  $1.0 \times 10^{-6}$  mol.L<sup>-1</sup> (a) to  $1.0 \times 10^{-1}$  mol.L<sup>-1</sup> (e).

**Table 4.** Optimization of conditioning concentration solution.

Internal Solution (mol.L <sup>-1</sup> )	External Solution (mol.L <sup>-1</sup> )	Time (h)	Slope (mV decade <sup>-1</sup> )	Linear Range (mol.L <sup>-1</sup> )	Detection Limit (mol.L <sup>-1</sup> )
1.0 × 10 <sup>-1</sup>	1.0 × 10 <sup>-1</sup>	4	-29	1.0 × 10 <sup>-5</sup> – 1.0 × 10 <sup>-1</sup>	7.9 × 10 <sup>-6</sup>
1.0 × 10 <sup>-2</sup>	1.0 × 10 <sup>-2</sup>	7	-28.9	1.0 × 10 <sup>-5</sup> – 1.0 × 10 <sup>-1</sup>	6.6 × 10 <sup>-6</sup>
1.0 × 10 <sup>-3</sup>	1.0 × 10 <sup>-3</sup>	10	-28.9	1.0 × 10 <sup>-5</sup> – 1.0 × 10 <sup>-1</sup>	5.4 × 10 <sup>-6</sup>
1.0 × 10 <sup>-4</sup>	1.0 × 10 <sup>-4</sup>	16	-28.8	5.0 × 10 <sup>-6</sup> – 1.0 × 10 <sup>-1</sup>	5.0 × 10 <sup>-6</sup>
1.0 × 10 <sup>-5</sup>	1.0 × 10 <sup>-5</sup>	22	-28.8	3.0 × 10 <sup>-6</sup> – 1.0 × 10 <sup>-1</sup>	3.0 × 10 <sup>-6</sup>

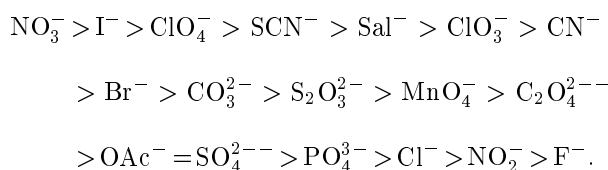
or properties of the electronic equipment. This time interval can span from milliseconds to minutes or hours and depends on many conditions, e.g. concentration of the measuring ion, speed of stirring, temperature, history and pretreatment of the indicator electrode and so on.

**Interferences in Potentiometric Measurements**

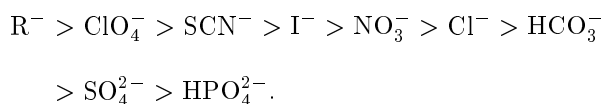
The fixed interference method is amongst the most commonly employed for its good mix of realism and simplicity. The method of determining the selectivity coefficient by fixed interfering ion activity, developed by Moody and Thomas [33], is also recommended by IUPAC [34]. Here, the electrode potential is measured in a solution with a fixed activity of the interfering ion and varying activities of the measured ion.

Selectivity is the most important characteristic of the ISE membrane, describing its specificity towards the primary ion in the presence of interfering ions. For polymer membranes, interference by other sample ions is mainly dictated by their competitive extraction into the membrane phase. The selectivity coefficient patterns clearly indicate that the electrode is highly selective to chromate over a number of other anions (Table 5). It is interesting to note that the observed selectivity pattern for the CrO<sub>4</sub><sup>2-</sup>-ISE significantly differs from the so-called Hofmeister selectivity sequence. The

interfering effect of the ions is in the following order:



The sequence is characterized by the Hofmeister series:



The reason that the selectivity coefficients proposed chromate electrode do not comply with the Hofmeister series can be due to the specific interaction of the anions with the metal center in the carrier (CuL) [35] used in this study, i.e. chemical recognition of the anions, and especially of chromate by the complex.

As can be seen from Table 5, the most interfering anions to the electrode are I<sup>-</sup> and NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>.

**Analytical Applications**

To assess the applicability of the proposed electrodes to real samples, an attempt was made to determine chromate in industrial wastewater samples, using the standard addition method. The concentration of chromate

**Table 5.** Selectivity of coefficients determined by use of the fixed interference method for chromate-ISE.

Interferent Ion	logK <sub>CrO<sub>4</sub><sup>2-</sup>,A-}^pot</sub>	Interferent Ion	logK <sub>CrO<sub>4</sub><sup>2-</sup>,A-}^pot</sub>
F <sup>-</sup>	-5.5	CO <sub>3</sub> <sup>2-</sup>	-3.3
Cl <sup>-</sup>	-4.3	ClO <sub>4</sub> <sup>-</sup>	-1.2
Br <sup>-</sup>	-3.1	ClO <sub>3</sub> <sup>-</sup>	-2.7
I <sup>-</sup>	-1.1	SO <sub>4</sub> <sup>2-</sup>	-4.0
CN <sup>-</sup>	-3.0	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	-3.6
NO <sub>3</sub> <sup>-</sup>	-1.2	PO <sub>4</sub> <sup>3-</sup>	-4.2
Acetate	-4.0	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	-3.9
NO <sub>2</sub> <sup>-</sup>	-4.5	SCN <sup>-</sup>	-1.8
Salicylate	-2.4	MnO <sub>4</sub> <sup>-</sup>	-3.8

in the resulting solution was determined by the Atomic Absorption Spectroscopy (AAS) method, adopted as the reference technique. A sample was analyzed ( $n = 10$ ) using the proposed electrode and the obtained results indicated a very good correspondence between the two values obtained by the spectrophotometer and the proposed electrode (Table 6). The results indicate that the proposed electrode can be successfully applied to the determination of chromate at concentrations normally present in some water samples.

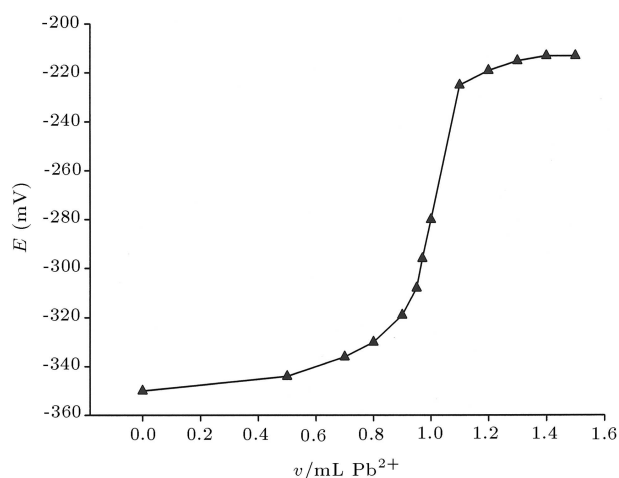
In addition, the sensor was used for potentiometric titration determination of  $\text{CrO}_4^{2-}$  with  $\text{Pb}^{2+}$ . Typical results for titration of 10 mL of  $0.001 \text{ mol.L}^{-1} \text{ Pb}^{2+}$  with  $0.01 \text{ mol.L}^{-1}$  chromate had a very good inflection point, showing perfect stoichiometry as observed in the titration plot (Figure 5). As seen, the amount of chromate ion in the solution can be accurately determined with the electrode.

## CONCLUSIONS

The high degree of copper selectivity by the electrode makes it potentially useful for monitoring concentration levels of chromate in real samples. The proposed sensor has been shown to have good operating characteristics (sensitivity, stability, response time, detection limit and a wide linear range) and is easy to prepare and use.

**Table 6.** Determination of chromate in real sample by chromate-ISE and atomic absorption spectroscopy methods.

Sample	AAS (mg/L)	ISE (mg/L)
Wastewater	$11.80 \pm 0.20$	$11.45 \pm 0.50$



**Figure 5.** Titration curve using chromate-selective electrode as indicator electrode, 10 mL of  $1.0 \times 10^{-3} \text{ mol.L}^{-1} \text{ Pb}^{2+}$  with  $1.0 \times 10^{-2} \text{ mol.L}^{-1}$  chromate.

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## REFERENCES

- Palmer, C.D. and Wittbrodt, P.R. "Processes affecting the remediation of chromium-contaminated sites", *Environ. Health Perspect*, **92**, pp 25-40 (1991).
- Puhlmann, P., Pretsch, E. and Bakker, E. "Carrier-based ion-selective electrodes and bulk optodes. 2. ionophores for potentiometric and optical sensors", *Chem. Rev.*, **98**, pp 1593-1681 (1998).
- Kristiansen, J., Christensen, J.M. and Byrialsen, K. "A DANREF certified reference material for chromate in cement", *Analyst*, **122**, pp 1155-1159 (1997).
- Moody, G.J., Saad, B.B. and Thomas, J.D.R. "The development of polymer matrix membranes for ion-selective electrodes", *Sel. Electrode Rev.*, **10**, pp 71-74 (1998).
- Li, Z.Q., Liu, G.D., Duan, L.M. and Shen, G.L. "Sulfate-selective PVC membrane electrodes based on a derivative of imidazole as a neutral carrier", *Anal. Chimica Acta*, **382**, pp 165-170 (1999).
- Rudoi, V.M., Makarenko, M.Y., Novikov, A.E. and Yaroslavtesva, O.V. "Membrane electrode for determining chromium(VI)", *J. Anal. Chem.*, **53**, pp 144-146 (1998).
- Linder, E., Toth, K. and Pungor, E. "Lead selectiveneutral carrier based liquid membrane electrode", *Anal. Chem.*, **56**, pp 1127-1131 (1984).
- Shen, S.R. and Shin, J. "Lead(II) ion-selective electrodes based on crown ethers", *Analyst*, **117**, pp 1691-1697 (1992).
- Kamata, S. and Onoyama, V. "Lead-selective membrane electrode using methylene bis(diisobutyldithiocarbamate)neutral carrier", *Anal. Chem.*, **63**, pp 1295-1298 (1991).
- Srivastava, S.K., Gupta, V.K. and Jain, S. "Determination of lead using a poly(vinyl chloride)-based crown ether membrane", *Analyst*, **120**, pp 495-498 (1995).
- Meyerhaw, M.E. and Opdyche, M.N., *Adv. Din. Chem.*, **25**, p 1 (1986).
- Singh, A.K., Ponwar, A., Kumar, S. and Baniwal, S. "Chromium(III)-selective electrode based on a macrocyclic compound", *Analyst*, **124**, pp 521-527 (1999).
- Srinivasan, K. and Rechnitz, G.A. "Selectivity studies on liquid membrane, ion-selective electrodes", *Anal. Chem.*, **41**, pp 1203-1208 (1969).
- Tavakkoli, N. and Shamsipur, M. "Lead-selective membrane electrode based on dibenzopyridino-18-crown-6", *Anal. Lett.*, **29**, pp 2269-2273 (1996).

15. Mazloum, M., Salavati Niassary, M., Mirhoseini Chahoki S.H. and Amini, M.K. "Silver-selective coated-wire electrode based on resorc[4] arene neutral carrier", *Electroanalysis*, **14**, pp 376-381 (2002).
16. Catrall, R.W. and Chin-Poh Pui "Coated wire ion-selective electrodes for determination of mercury (II)", *Anal. Chem.*, **48**, pp 552-556 (1976).
17. Khalil, S. "Ion-selective electrode for the determination of trazodone in tablets", *Analyst*, **124**, pp 139-143 (1999).
18. Mazloum Ardakani, M., Pourhakak, P. and Salavati-Niasari, M. "Bis(2-hydroxy acetophenone)ethylenediimine as a neutral carrier in a coated-wire membrane electrode for lead(II)", *Anal. Sci.*, **22**, pp 865-871 (2006); Zare, H.R., Salavati-Niasari, M., Memarzadeh, F., Mazloum, M. and Nasirizadeh, N. "Coated wire silver-ion selective electrode based on a N,N'-Bis(2-thienylmethylene)-1,2-diaminobenzen", *Anal. Sci.*, **20**, pp 815-821 (2004).
19. Salavati-Niasari, M., Hassani-Kabutarakhani, M. and Davar, F. "Alumina-supported Mn(II), Co(II), Ni(II) and Cu(II) N,N-bis(salicylidene)-2,2-dimethylpropane-1,3-diamine complexes: Synthesis, characterization and catalytic oxidation of cyclohexene with tert-butylhydroperoxide and hydrogen peroxide", *Catal. Commun.*, **7**, pp 955-962 (2006); Salavati-Niasari, M. "Synthesis, characterization and catalytic oxidation of cyclohexene with molecular oxygen over host (montmorillonite-K10)/guest (nickel(II) complexes of 12- and 13-membered diaza dioxo Schiff-base macrocyclic ligand) nanocatalyst (HGN)", *J. Mol. Catal. A: Chem.*, **263**, pp 247-252 (2007).
20. Mazloum, M., Salavati, M. and Sadeghi, A. "Novel selective thiocyanate PVC membrane electrode based on new Schiff base complex of 2.2-[(1,3-dimethyl-1,3-propanediylidene)dinitrilo]bis-benzenethiolato cadmium(II)", *New. J. Chem.*, **28**, pp 595-599 (2004).
21. Kamata, S., Bhal, A., Fakunaga, Y. and Marata, A. "Copper(II)-selective electrode using thiuram disulfide neutral carriers", *Anal. Chem.*, **60**, pp 2464-2467 (1988).
22. Umezawa, Y., Umezawa, K. and Sato, H., *Pure & Appl. Chem.*, **67**, p 507 (1995).
23. Patko, T., *Ion Selective Sensors Overview*, website: [www.astisensor.com](http://www.astisensor.com), pp 1-9 (2003).
24. Morf, W.E., Khar, G. and Simon, W. "Reduction of the anion interference in neutral carrier liquid-membrane electrodes responsive to cations", *Anal. Lett.*, **7**, pp 9-22 (1974).
25. Huser, M., Gehrlg, P.M., Morf, W.E., Simon, W., Lindner, C., Jeney, J., Toth, K. and Pungor, E. "Membrane technology and dynamic response of ion-selective liquid-membrane electrodes", *Anal. Chem.*, **63**, pp 1380-1386 (1991).
26. Schaller, U., Bakker, E., Spichiger, U.E. and Pretsch, E. "Ionic additives for ion-selective electrodes based on electrically charged carriers", *Anal. Chem.*, **66**, pp 391-398 (1994).
27. Bakker, E., Malinowska, E., Schiller, R. D., Meyerhoff, M.E. "Anion-selective membrane electrodes based on metalloporphyrins: The influence of lipophilic anionic", *Talanta*, **41**, p 881 (1994).
28. Bühlmann, P., Yajima, S., Tohda, K., Umezawa, K., Nishizawa, S. and Umezawa, Y. "Studies on the phase boundaries and the significance of ionic sites of liquid membrane ion-selective electrodes", *Electroanalysis*, **7**, pp 811-816 (1995).
29. Yajima, S., Tohda, K., Bühlmann, P. and Umezawa, Y. "Donnan exclusion failure of neutral ionophore-based ion-selective electrodes studied by optical second-harmonic generation", *Anal. Chem.*, **69**, pp 1919-1924 (1997).
30. Amemiya, S., Bühlmann, P., Pretsch, E., Rusterholz, B. and Umezawa, Y. "Cationic or anionic sites? Selectivity optimization of ion-selective electrode based on charged ionophore", *Anal. Chem.*, **72**, pp 1618-1631 (2000).
31. Buck, R.P. and Lindner, E. "Recommendations for nomenclature of ion-sensitive electrodes", *Pure Appl. Chem.*, **66**, pp 2527-2536 (1994).
32. Srinivasan, K. and Rechnitz, G.A. "Selectivity study of liquid membrane, ion-selective electrodes", *Anal. Chem.*, **41**, pp 1203-1208 (1969).
33. TR, Y. and GL, J., *Electrochemical Methods in Soil and Water Research*, Pergammon Press, Oxford (1993).
34. Guilbault, G.G. "Recommendations for publishing manuscripts on ion-selective electrodes", *Pure Appl. Chem.*, **53**, pp 1907-1912 (1981).
35. Daunert, S., Wallace, S., Florido, A. and Bachas, L.G. "Anion-selective electrodes based on electropolymerized porphyrin films", *Anal. Chem.*, **63**, pp 1676-1679 (1991).