

## Silsesquioxane 3-*n*-Propylpyridinium Chloride: a New Polymer for the Potentiometric Analysis of Cr(VI) in Electroplating and Leather Industry Wastes

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Um novo polímero, cloreto de 3-*n*-propilpiridínio-silsesquioxano (SiPy<sup>+</sup>Cl<sup>-</sup>), foi utilizado na preparação de um eletrodo. Este eletrodo íon seletivo, formado de um bastão de grafite recoberto pelo polímero, foi construído e avaliado pela determinação de Cr(VI) em amostras de águas residuárias de indústrias de galvanoplastia e de couro. O eletrodo exibiu uma resposta Nernstiana para Cr(VI) entre as concentrações  $3,1 \times 10^{-6}$  e  $1,8 \times 10^{-2}$  mol L<sup>-1</sup> e limite de detecção de  $2,8 \times 10^{-6}$  mol L<sup>-1</sup> (0,15 ppm). A resposta do eletrodo para Cr(VI) foi rápida (15 s) e o potencial independente do pH na faixa de 3,0 a 7,0. Os coeficientes de seletividade para diversos ânions mostram que o eletrodo apresenta um excelente desempenho. O sensor exibe um tempo de vida útil de 6 meses com boa reprodutibilidade. A determinação de Cr(VI) em águas residuárias de indústrias de galvanoplastia e de couro usando o sensor foi realizada com sucesso.

A new polymer, silsesquioxane 3-*n*-propylpyridinium chloride (SiPy<sup>+</sup>Cl<sup>-</sup>), was used in the preparation of an electrode. The polymer coated graphite rod ion selective electrode for Cr(VI) was constructed and evaluated for the determination of Cr(VI) in samples of electroplating and leather industry wastes. This electrode exhibited a Nernstian response for Cr(VI) concentrations between  $3.1 \times 10^{-6}$  and  $1.8 \times 10^{-2}$  mol L<sup>-1</sup> and a detection limit of  $2.8 \times 10^{-6}$  mol L<sup>-1</sup> (0.15 ppm). The response of the electrode for Cr(VI) was fast (15 s) and the independent potential of pH in the range of 3.0 to 7.0. The selectivity coefficients for several anions showed that the electrode presents excellent performance. The sensor exhibits a shelf-life of 6 months with good reproducibility. Determination of Cr(VI) in electroplating and leather wastes using the sensor was successfully achieved.

**Keywords:** chromium, sensors, chromium-selective electrode, silsesquioxane 3-*n*-propylpyridinium chloride

### Introduction

The interest in chromium speciation originates from widespread use of this metal in many industries, such as: metallurgical (steel, ferrous and nonferrous alloys), refractories, and chemical (pigments, electroplating, tanning and others). Due to these industrial processes, large quantities of Cr compounds are discharged as liquid, solid and gaseous wastes into the environment and can, ultimately, have significant adverse biological and ecological effects.

The two common oxidation states of Cr present in the environment, Cr(III) and Cr(VI), are drastically different in charge, physicochemical properties, as well as, chemical and biochemical reactivity. Cr(III) is considered to be a trace element essential for the proper functioning of living

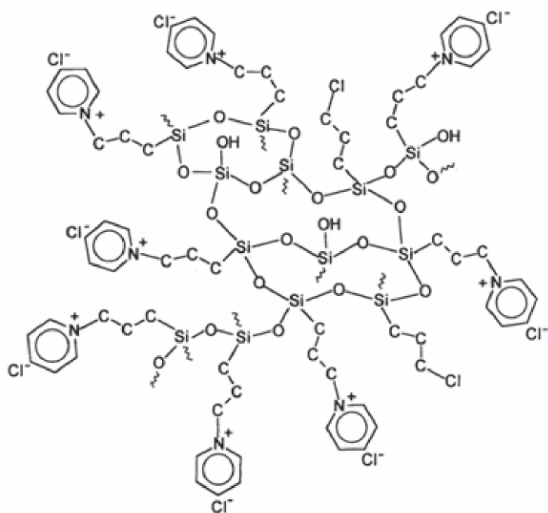
organisms<sup>1-6</sup> while Cr(VI) exerts toxic effects on biological systems. Occupational exposure to hexavalent Cr compounds leads to a variety of clinical problems<sup>7,8</sup> and Cr(VI) compounds toxicity derives from its ability to diffuse through cell membranes and oxidize biological molecules.<sup>9</sup>

The Environmental Protection Agency (EPA) has adopted up to 0.01 ppm of total chromium as the maximum contaminant level in community water systems. In Brazil, the Health Ministry Administrative Rule no. MS 518, 03/25/2004 and the Environmental National Agency (CONAMA) Resolution no. 357, 03/17/2005, adopted up to 0.05 ppm of total chromium as the maximum contaminant level in potable water and wastewaters, respectively. Sophisticated techniques as AAS, ICP etc are presently employed for chromium trace amount determination. However, these methods are disadvantageous in terms of cost and also unsuitability for routine analyses of a large number of samples.<sup>10-13</sup>

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Extensive efforts have been made to develop a good sensitive sensor for chromium.<sup>14-22</sup> However, most of the sensors already developed do not allow chromium estimation at lower concentrations (< 1 ppm). They exhibit poor selectivity in the presence of common anions, have a non-Nernstian response or a high response time.

Silsesquioxane 3-*n*-propylpyridinium chloride (Figure 1) is a new water soluble polymer<sup>23</sup> and its most important characteristic is the capacity of forming a stable thin film on substrate surfaces such as aluminum oxide, cellulose fibers, silica gel or glass surfaces.<sup>24,25</sup> The polymer is a strong anionic exchanger and since the immobilized counterion is the pyridinium ion, the exchange reaction does not depend on the solution pH.<sup>26</sup> Considering the excellent capacity of this new anionic exchanger polymer for forming a thin film on the graphite surface,  $\text{HCrO}_4^-$  ion was adsorbed on the resulting modified surface (graphite rod) by an ion exchange reaction at pH 4.0 and investigated for their response towards anions. The results, reported hereby, show that this polymer presents high selectivity towards chromate ions over a large number of anions and could, therefore, be used as a selective sensor for its quantification. To probe the potential usefulness of the modified electrode as a chemical sensor, the studies were extended to analyze chromate ions in electroplating and leather industry wastes around Londrina city (Paraná state).



**Figure 1.** Silsesquioxane 3-*n*-propylpyridinium chloride polymer.

## Experimental

The polymer silsesquioxane 3-*n*-propylpyridinium chloride, referred as  $\text{SiPy}^+\text{Cl}^-$ , was prepared according to a method described elsewhere.<sup>23</sup> All reagents were analytical grade, without further purification and solutions were prepared with water from a Millipore Milli-Q<sub>plus</sub> system.

### Polymer coated graphite

An electrode was made by inserting, under pressure, a spectroscopically pure 8 mm diameter and 15 cm length graphite cylinder in a Teflon bar hole with the same internal diameter. The graphite surface end was polished and the clean surface was immersed in an aqueous solution of polymer  $\text{SiPy}^+\text{Cl}^-$  (2.5 % m/v) for 30 min and, then, dried at room atmosphere.

The infrared spectrum of the thin film on the graphite surface was obtained by using the ATR technique and of the pure polymer as NaBr pellets on a Bomen FT-IR MB series.

The electrode, referred to as  $\text{graph/SiPy}^+\text{Cl}^-$ , was immersed in a  $1.0 \times 10^{-3}$  mol L<sup>-1</sup>  $\text{K}_2\text{Cr}_2\text{O}_7$  solution at pH 4.0 (adjusted with potassium hydrogen phthalate/KOH buffer) for 20 min, rinsed with water and dried at room temperature. The resulting modified electrode is designated ( $\text{graph/SiPy}^+$ )  $\text{HCrO}_4^-$ .

The electrode was previously equilibrated in a solution of  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> Cr(VI) at pH 4.0 (potassium hydrogen phthalate/KOH) for 2-3 h and was stored dry when not in use.

### Sample preparation

Samples of electroplating and leather industry wastes were collected, filtered and stored without any other pretreatment. Suitable aliquots of sample solution were analyzed, after adjustment at pH 4.0. When necessary, appropriate dilutions were done. The analysis were performed by direct potentiometry using calibration plot and the results showed the chromate content in the electroplating and leather industry wastes obtained from triplicate measurements with the sensor ( $\text{graph/SiPy}^+$ )  $\text{HCrO}_4^-$  were found to be in agreement with that determined by spectrophotometric method.<sup>27</sup>

### Potential measurements

The potential measurements were carried out in a thermostated cell at  $25.0 \pm 0.2$  °C. The equipment used was a Hanna HI 9321 Microprocessor pH meter with 0.1 mV resolution. Saturated calomel was used as the reference electrode, with a double junction containing an external saturated  $\text{KNO}_3$  solution.

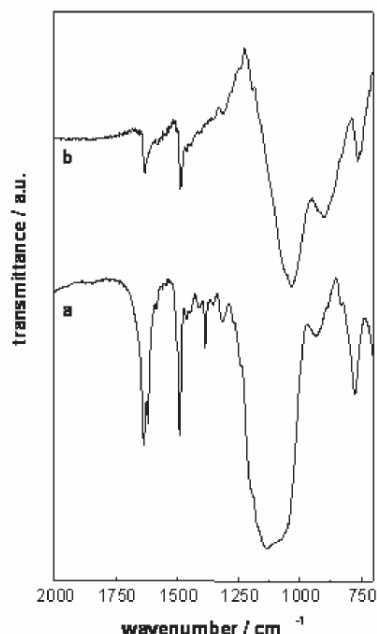
### Determination of the potentiometric selectivity coefficients

The interference in the ( $\text{graph/SiPy}^+$ )  $\text{HCrO}_4^-$  electrode response of most common species found within the sample wastes were evaluated by determining the potentiometric selectivity coefficient  $K_{A,B}^{POT}$  of the membrane following the

“matched potential method” which is independent of the Nicolsky-Eisenman equation and is recommended by IUPAC.<sup>28,29</sup>

## Results and Discussion

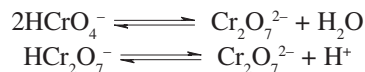
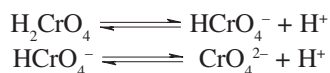
Figure 2a and 2b show the spectra of pure polymer and that of the film on graphite surface, respectively. The bands observed at 1132 cm<sup>-1</sup> corresponding to the Si-O-Si stretching mode and 1630 and 1486 cm<sup>-1</sup> corresponding to the pyridinium ring modes of the pure polymer are observed in the polymer film on graphite surface at 1047, 1630 and 1486 cm<sup>-1</sup>, indicating that the polymer film is adhered on the surface.



**Figure 2** - Infrared spectra of the silsesquioxane 3-*n*-propylpyridinium chloride polymer (a) and silsesquioxane 3-*n*-propylpyridinium chloride polymer coated graphite (b).

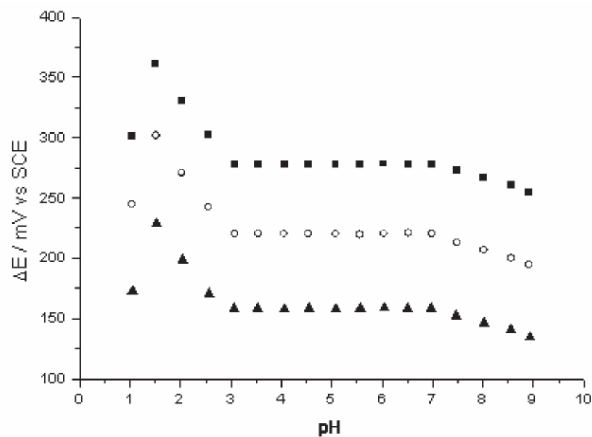
For the development of the potentiometric method using the coated-graphite rod ion-selective electrode, some analytical parameters were studied, such as: stability of the electrode membrane, response time, life time, dependence of the potential as a function of the Cr(VI) concentration and pH of the medium.. The selectivity and the detection limit of the electrode were also evaluated.

In the aqueous phase, chromium(VI) species could be found in different ionic forms (HCrO<sub>4</sub><sup>-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup>, HCr<sub>2</sub>O<sub>7</sub><sup>-</sup>). The distribution of Cr(VI) species is dependent on both the total concentration of Cr(VI) and pH of the equilibrium solution. The following equations describe the distribution of chromium species in aqueous solution.<sup>30-32</sup>



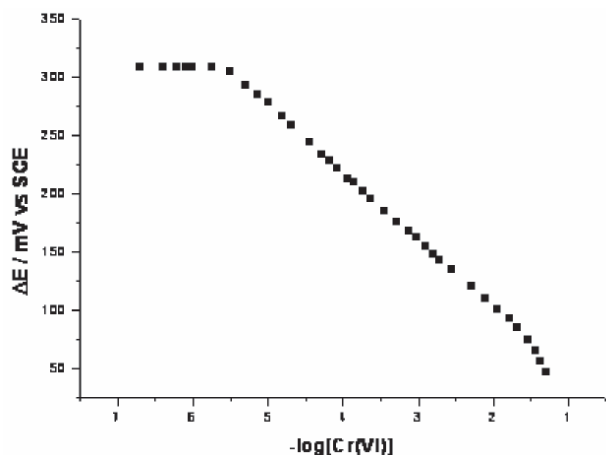
The pH of aqueous 1.0×10<sup>-3</sup>, 1.0×10<sup>-4</sup> and 1.0×10<sup>-5</sup> mol L<sup>-1</sup> solutions were altered by diluted NaOH or HCl solutions and the potential of the solutions was monitored. The results obtained are shown in Figure 3. In every case, the potential was constant in pH range from 3.0 to 7.0. Below pH 1.5, a decrease of the potential was observed, which could be explained by the protonation of the HCrO<sub>4</sub><sup>-</sup> anion<sup>30</sup> forming H<sub>2</sub>CrO<sub>4</sub>, which is leached off from the electrode membrane. For solutions with pH over 7.0, a decrease of the potential was also observed. In alkaline solutions, the hydroxyl ions compete with the adsorbed Cr(VI) anion and by an ion exchange reaction Cr(VI) ions can be leached off from the surface and released to the solution phase. The potential values are drastically changed in pH range from 1.5 to 3.0. This probably corresponds to the decrease in the measurable concentration of HCrO<sub>4</sub><sup>-</sup> and formation of dichromate and polychromate,<sup>33</sup> to which the (graph/SiPy<sup>+</sup>)HCrO<sub>4</sub><sup>-</sup> sensor does not appear to respond in Nernstian manner. The potentiometric measurements were made at pH 4.0 (potassium hydrogen phthalate/KOH buffer) due to better experimental results, such as, response time and reproducibility.

The response time of the electrode for Cr(VI) solutions in the concentration range of 3.1×10<sup>-6</sup> to 1.8×10<sup>-2</sup> mol L<sup>-1</sup> was about 15 s. No potential changes were obtained after 8-9 hours of continuous sampling of a Cr(VI) solution. Also, no memory effect was observed for ten determinations of Cr(VI) solutions alternating the concentrations between 1.0×10<sup>-4</sup> and 5.0×10<sup>-4</sup> mol L<sup>-1</sup>. The electrode showed a life-time of six months, with more than 500 determinations for each polymeric membrane and a potential decrease of only 5-10%, compared to the initial response. The calibration plot (Figure 4) has a linear



**Figure 3.** Effect of the solution pH in the response of the (graph/SiPy<sup>+</sup>)HCrO<sub>4</sub><sup>-</sup> electrode. Cr(VI) concentrations: (■)1.0×10<sup>-5</sup>, (○) 1.0×10<sup>-4</sup> e (▲) 1.0×10<sup>-3</sup> mol L<sup>-1</sup>.

relationship between the electrode potential and the logarithmic concentration of Cr(VI) in the range of  $3.1 \times 10^{-6}$  to  $1.8 \times 10^{-2}$  mol L<sup>-1</sup>, showing linear correlation with the equation represented by  $\Delta E(\text{mV}) = 17.8 - 58.8 \log[\text{Cr(VI)}]$  with  $r = 0.9999$ . The angular coefficient of 58.8 is very close to the 59 mV required for Nernstian behavior. The detection limit calculated was  $2.8 \times 10^{-6}$  mol L<sup>-1</sup> (0.15 ppm).



**Figure 4.** Calibration curve obtained with the polymer coated graphite rod ion selective electrode.

#### Potentiometric selectivity

The interference on the electrode response of the species usually found in electroplating and leather industry wastes, such as: Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, MnO<sub>4</sub><sup>-</sup>, Br<sup>-</sup>, SCN<sup>-</sup>, I<sup>-</sup>, F<sup>-</sup> and CH<sub>3</sub>COO<sup>-</sup>, was verified by determining the  $K_{A,B}^{POT}$  of the membrane, according to the IUPAC recommended “matched potential method”, which is independent of the Nicolsky-Eisenman (N-E) equation.<sup>28,29</sup> To determine the selectivity coefficient, the potential change was measured by changing the primary ion concentration. The interfering ion was then added to an identical reference solution until the same potential change was obtained. The change in the potential must be produced in a constant initial background of the primary ion and must be the same in both cases.<sup>28,29</sup> Table 1 shows the average calculated values, from five determinations for each sample, by using this methodology. The coefficients were very low ( $K_{A,B}^{POT} < 0.001$ ). Therefore, these studies reveal that the developed

**Table 3** - Comparison of the proposed sensor with reported electrodes

S. No.	Reference No.	Detection limit/ppm	Response time/s	Life time/month	Selectivity
1	19	2.0	nm	nm	Good
2	20	0.4	30	6 weeks	Very good
3	21	2.9	20	12	Good
4	22	0.3	20	5	Very good
5	23	0.2	60	5	Very good
6	(graph/SiPy <sup>+</sup> )HCrO <sub>4</sub> <sup>-</sup> sensor	0.15	15	6	Excellent

NM: not mentioned.

**Table 1.** Potentiometric selectivity coefficients for the Cr(VI) (graph/SiPy<sup>+</sup>)HCrO<sub>4</sub><sup>-</sup> electrode  $K_{A,B}^{POT}$  determined by the IUPAC recommended method<sup>29</sup>

Interferent ion (B)	Selectivity coefficients ( $K_{A,B}^{POT}$ )
Cl <sup>-</sup>	0.0009
NO <sub>3</sub> <sup>-</sup>	0.0004
HPO <sub>4</sub> <sup>2-</sup>	0.0007
SO <sub>4</sub> <sup>2-</sup>	0.00002
NO <sub>2</sub> <sup>-</sup>	0.0003
CH <sub>3</sub> COO <sup>-</sup>	0.00005
MnO <sub>4</sub> <sup>-</sup>	0.00001
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	0.0005
F <sup>-</sup>	0.0008
SCN <sup>-</sup>	0.0003
Br <sup>-</sup>	0.0006
I <sup>-</sup>	0.00005

(graph/SiPy<sup>+</sup>)HCrO<sub>4</sub><sup>-</sup> sensor is selective over the commonly present interfering ions.

#### Analytical application

The proposed Cr(VI) sensor has been used for determining Cr(VI) in electroplating and leather industry wastes. Sixteen samples from a local electroplating and

**Table 2.** Determination of Cr(VI) in electroplating and leather waste water using diphenylcarbazine method and (graph/SiPy<sup>+</sup>)HCrO<sub>4</sub><sup>-</sup> sensor

Samples	Cr(VI) <sup>a</sup> /ppm	
	Spectrophotometry	Potentiometry
1	35.1 ± 0.2	34.9 ± 0.2
2	30.5 ± 0.2	30.1 ± 0.3
3	27.4 ± 0.1	26.2 ± 0.2
4	12.3 ± 0.2	10.7 ± 0.3
5	11.2 ± 0.2	11.0 ± 0.3
6	40.7 ± 0.2	40.2 ± 0.4
7	58.6 ± 0.1	57.7 ± 0.2
8	22.3 ± 0.2	22.1 ± 0.2
9	77.5 ± 0.2	77.4 ± 0.3
10	11.1 ± 0.2	11.1 ± 0.4
11	23.6 ± 0.2	23.2 ± 0.4
12	29.4 ± 0.2	28.9 ± 0.2
13	17.6 ± 0.2	17.5 ± 0.4
14	15.4 ± 0.1	15.4 ± 0.4
15	5.6 ± 0.2	4.9 ± 0.3
16	32.9 ± 0.2	32.5 ± 0.3

<sup>a</sup> Assay values represent the average of three (n=3) determinations.

leather unit were collected. The analyses were performed by direct potentiometry using calibration plot. The results showed the Cr(VI) content in the samples obtained from triplicate measurements with the sensor were in agreement with those determined by spectrophotometric method (diphenylcarbazide)<sup>27</sup> (Table 2). Table 3 compares (graph/SiPy<sup>+</sup>)HCrO<sub>4</sub><sup>-</sup> sensor characteristics with other electrodes reported in the literature.

## Conclusions

The electrode prepared with silsequioxane 3-*n*-propylpyridinium chloride, for the quantification of Cr(VI), proved to be very selective regarding the low detection limit (0.15 ppm) and with fast response time (15 s). The developed sensor is fast, stable, and reproducible. It is easily constructed and presents selective response over a prolonged period. A comparison of the proposed sensor with reported electrodes presented in Table 3, indicates that this sensor is superior not only in the working concentration range and response time, but also with regard to its construction.

## Acknowledgments

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