ELSEVIER

Journal of Chromatography A, 963 (2002) 205–211

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Chemically facilitated chromium(VI) transport throughout an anion-exchange membrane
Application to an optical sensor for chromium(VI) monitoring

Elianna Castillo[a], Mercè Granados[a], José Luis Cortina[b,*]

[a]*Analytical Chemistry Department, Universitat de Barcelona, Martí i Franquès 1, E-08028 Barcelona, Spain*

[b]*Chemical Engineering Department, ETSEIB, Universitat Politècnica de Catalunya, Diagonal 647, E-08028 Barcelona, Spain*

Abstract

The Raipore R1030 membrane, an anion-exchange membrane containing ammonium groups as ionogenic groups, was evaluated as the interface of an optical sensor for Cr(VI), and the effect of chemical parameters affecting Cr(VI) transport were studied. Good transport features were obtained, demonstrating the suitability of the Raipore R1030 membrane for this application. Thus, an optical sensor for chromium(VI) monitoring in industrial process waters was developed. The sensor is based on the renewable reagent approach and uses the Raipore R1030 membrane as the interface between the sample and the sensor head, which contains 1,5-diphenylcarbazide as spectrophotometric reagent for chromium. Chromium(VI) crosses the membrane and reacts with the reagent inside the sensor head, resulting in changes in the absorption of light. These changes are monitored in situ through a system of optical fibers. The sensor performance was tested by analysing samples from a waste water treatment plant for effluents from electroplating industries.

Keywords: Membranes; Optical sensors; Dialysis; Chromium; Metal complexes

1. Introduction

The determination of chromium(VI) is an application of special interest in environmental [1,2] and industrial control [3,4] due to the high toxicity of the species, even at low concentration [5]. One of the major uses of chromium is in metallurgy, especially in the electroplating and metal finishing industries, where huge volumes of waters containing Cr(VI) are generated in many rinsing operations. These effluents, containing low levels of Cr(VI) ($<$100 mg l^{-1}), are treated by conventional techniques, such as ion-exchange [6] or membrane processes [7], with the aim of removing Cr(VI) and allowing water re-use. Hence, there is a growing demand for systems able to perform in-situ Cr(VI) monitoring, to be used as a process control of the effluent treatment units. Optical sensing based on absorbance measurements arises as a potential approach. Although Cr(VI) shows a characteristic spectrum in the visible range, the use of a chemical reaction for chromium derivatization offers advantages, such as improving selectivity and sensitivity. In the field of optical sensors, different systems have been proposed to immobilise chromogenic reagents onto membranes or onto fiber optic surfaces [8–10]. However, reagent immobilisation limits the range of chemical reactions to reversible reactions, and the stability of the reagent phase can also be limited. An alternative, based on optical sensing reagent renewal, has already shown very promising results in several applications,

*Corresponding author. Fax: +34-93-401-5814.

E-mail address: cortina@eq.upc.es (J.L. Cortina).

0021-9673/02/$ – see front matter
PII: S0021-9673(02)00362-X

i.e. ammonia, free and total chlorine, caustic samples and heavy metal monitoring [11–13]. In the case of renewable reagent sensors the detection reaction holds, through optical fibers, on an optical cell and sampling of the analyte from the sample to the detection cell is achieved by using a membrane [14]. The membrane should allow analyte transport and prevent reagent leakage from the sensor head to the sample.

When an ion-exchange membrane separates a low ionic strength solution (e.g. the sample) from a high ionic strength solution (e.g. the receiving solution), Donnan dialysis takes place. Thus, if an anion-exchange membrane is used, anions from the concentrated solution are transported to the sample solution to meet Donnan equilibrium conditions [15]. Since the membrane is not permeable to cations, anions from the sample must transport to the concentrated solution in order to maintain electroneutrality in both solutions. This transport of anions from the sample solution can even occur against a concentration gradient. If the volume of the receiving solution is smaller than the volume of the sample, preconcentration into the receiving solution can be accomplished.

Chemically facilitated Donnan dialysis (CFDD) can improve the selectivity of conventional Donnan dialysis by using a receiving solution that contains a chemical reagent that selectively reacts with the targeted ion producing a species that is not retained by the membrane. This technique has been applied to chemical analysis and, more recently, to the field of optical sensing [16].

This work presents a new strategy to promote the transport of Cr(VI) through the Raipore R1030 membrane, an anion-exchange membrane which acts as the interface of a renewable reagent optical sensor for chromium(VI) monitoring and uses 1,5-diphenylcarbazide (DPC) as chromogenic reagent. The transport of Cr(VI) through the membrane is facilitated chemically by the selective reaction with DPC inside the sensor head. The chemical reaction consists of two steps: (i) a reduction to Cr(III) and (ii) the formation of an intensely coloured Cr(III) complex. Therefore, the Cr(VI) gradient between both sides of the membrane is kept high while Cr(VI) transport occurs and, moreover, the membrane rejects the positively charged complex and thus prevents any back-diffusion of chromium.

2. Experimental

2.1. Reagents and solutions

A 1 g l^{-1} chromium(VI) standard solution was prepared by dissolving potassium dichromate (Merck, Darmstadt, Germany) in water. 0.25% (w/v) DPC solutions were prepared by dissolving 0.25 g of DPC (Fluka, Buchs, Switzerland) in 10 ml of ethanol (Merck) and diluting to 100 ml with water. Working DPC solutions were prepared by appropriate dilution of 0.25% solutions with sulphuric acid solutions. Chemicals were analytical reagent grade. MilliQ-plus deionized water (Millipore, Molheim, France) of resistivity 18.2 MΩ cm^{-1} was used throughout.

2.2. Membrane

The membrane was a Raipore R1030 (RAI Research Corp., Long Island, NY, USA), an anion-exchange membrane. The R1030 is based on polytetrafluoroethylene with functionalized quaternary ammonium groups grafted by radiation. It is 40 μm thick and its ion-exchange capacity is 1 meq g^{-1} of dry membrane. The membranes were preconditioned with sulphuric/sulphate solutions by immersion for 10–12 h and then transferred into deionized (DI) water for storage until use.

2.3. Apparatus

A HP 8453 (Hewlett-Packard, Waldbronn, Germany) diode-array spectrophotometry (DAD) system equipped with a Fibspec fiber optic transmission probe (Photonetics, Marly-le-Roi, France) was used for chromium spectrophotometric measurements in the stripping phase during batch transport experiments and as the detector device of the optical sensor. Hewlett-Packard software for kinetics applications was used to control the operation of the instrument and collect the spectral data.

A 640 Varian atomic absorption spectrophotometry (AAS) system (Mulgrave, Victoria, Australia) was used for chromium measurements in chromium batch transport experiments. A Metrohm AG 9100 glass combined electrode (Metrohm, Herisau, Switzerland) connected to a Digilab 517 pH meter (Crison, Barcelona, Spain) was used for pH measurements.

2.3.1. Sensor instrumentation

The sensor head is shown in Fig. 1. The head includes the Fibspec fiber optic probe, to deliver and collect the spectroscopic signal, with a reaction chamber (0.75 ml) inside containing the chromogenic reagent, a planar membrane (46 mm^2), which provides a mechanism to sample Cr(VI) from the sample matrix and acts to seal the reagent within the sensor, and a membrane holder. The transmission probe and the membrane holder are made of 316 stainless steel. The support systems external to the sensor head include: (i) a Minipuls 3 peristaltic pump (Gilson, Villiers-le-Bel, France) to flush the reaction/detection cell and provide fresh chromogenic reagent for analysis; (ii) a HP 8453 diode-array spectrophotometer coupled to a fiber optic transmission probe to acquire spectra from the reaction chamber.

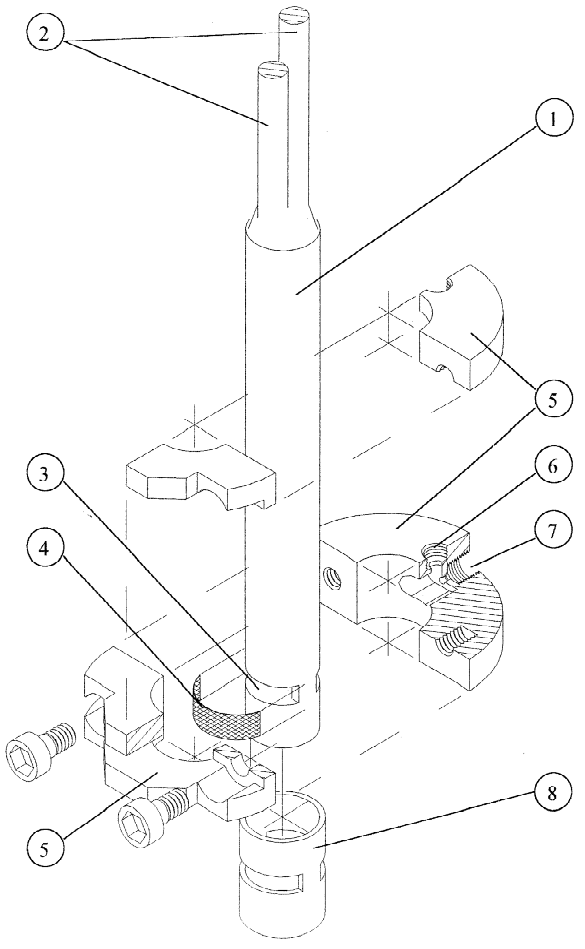


Fig. 1. Scheme of the optical sensor. 1, Stainless steel fiber optic probe; 2, fibers from the light source and to the DAD system; 3, reaction chamber; 4, anion-exchange membrane; 5, stainless steel membrane holder; 6, reagent outlet; 7, reagent inlet; 8, silicone ring to fix the membrane.

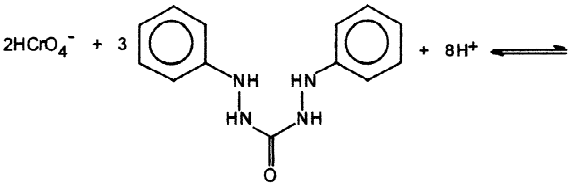
2.4. Transport experiments

The batch transport experiments were carried out in a permeation cell consisting of two compartments made of methacrylate and separated by the membrane. In one compartment the feed solution, i.e. the Cr(VI) solutions, simulated the sample, whereas in the other compartment the stripping solution, i.e. DPC in H_2SO_4 medium, simulated the chromogenic solution in the sensor head. After chromium diffusion across the membrane, the reaction of Cr(VI) with DPC in the stripping phase produces a violet complex, which is the basis of the optical sensing. In fact, the sensor transduction mechanism of the analyte can be described by the following transport and chemical reactions steps:

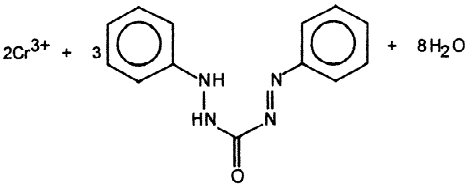
(a) Cr(VI) (feed solution)⇒Cr(VI) (membrane). Cr(VI) anions (either $HCrO_4^-$ or CrO_4^{2-}) are extracted into the membrane by ion-exchange reactions with HSO_4^- ions from the membrane phase.

(b) Cr(VI) (membrane)⇒Cr(III) (stripping solution). This is accomplished by the combination of Cr(VI) stripping from the membrane to the receiving phase and the following chemical reactions [17]:

(i) Cr(VI) reduction step:



DPC



DPCO

(ii) Complexation step:

$$Cr^{3+} + DPCO \Leftrightarrow CrDPCO^{(3-n)+} + nH^{+}$$

where n is the number of protons released in complex formation.

The geometrical membrane area in the permeation cell was 19.50 cm^2 and the volume of the feed and stripping solution was 200 ml. The experiments were performed at 20 °C at a mechanical stirring speed of 1300 rpm in both the feed and the stripping phases.

The chromium concentration in both phases was monitored by periodical sampling, and chromium was analysed, after appropriate dilution, by atomic absorption spectrophotometry. In some experiments, monitoring of the chromium concentration changes in the stripping phase was also carried out by following changes in the Vis spectra of the stripping solution due to the appearance of the Cr(III)–DPC violet complex by use of a fiber optic probe.

Chromium transport was evaluated in terms of the recovery factor (RF). The RF is defined according to the equation

$$RF = 1 - \frac{C_f}{C_f^0}$$

where C_f and C_f^0 are the total chromium concentration and the initial total chromium concentration, both in the feed phase. Thus, the RF is an indicator of the driving force of the stripping solution: an RF close to 1 indicates that there is effective pumping from the feed to the stripping solution, whereas an RF close to 0 reveals that poor transport is achieved.

2.5. Optical sensing experiments

The sensor, with fresh reagent solution, was immersed in the sample, and the spectrum of the sensor chamber was acquired through the optical fibers, each for 120 s. Data acquisition for each sample during the optimisation of experimental conditions lasted for about 30 min, whereas under the selected conditions, in a typical sensor performance, one measurement took 16 min. Before a new analysis, the reagent solution inside the sensor chamber was flushed with fresh solution for 10 min by means of a peristaltic pump, to recover the baseline signal.

Prior to processing the data for Cr(VI) quantitation, and in order to reduce the noise of the raw signal from the spectrometer, filtering of the spectra by Fourier transform was performed. Thus, for each sample the filtered spectrum from a fixed analysis time (16 min) was used to predict the chromium(VI) concentration. A least-squares regression using the absorbance values of a series of Cr(VI) standards at the maximum of the Cr(III)–DPCO complex spectrum ($\lambda = 543$ nm) corresponding to 16 min was used to calculate Cr(VI) concentrations.

For the wastewater samples from the electroplating industry, the reference values were determined by atomic absorption spectrophotometry.

3. Results and discussion

3.1. Chromium(VI) transport evaluation

The effect of chemical parameters that can influence Cr(VI) transport through the membrane was studied in order to find conditions that favour effective Cr(VI) pumping. A second reason for this was to check the suitability of the Raipore R1030-DPC system as the basis of a Cr(VI) optical sensor. The considered parameters were DPC concentration in the stripping solution, and pH and Cr(VI) concentration in the feed solution. This series of experiments was carried out using the permeation cell and batch methodology described in Section 2.4.

In this particular case there were constraints on the chemical composition of the stripping phase, determined by the spectroscopic detection of Cr(VI) in the optical sensor format. Thus, the stripping solution consisted of a DPC solution in 0.1 mol l^{-1} sulphuric acid medium. The chemical reactions between Cr(VI) and DPC (see Section 2.4) facilitate Cr(VI) transport. In this study, the DPC concentration was varied between 0 and 0.01%. Experiments with no DPC provided RF values close to 0.6, while in the experiments with DPC, the RF values increased to 0.9. The RF vs. time curves corresponding to 0.005 and 0.01% DPC were almost coincident (Fig. 2), which indicates that, at these DPC concentrations, the facilitated transport does not depend on the DPC concentration. To check how the composition of the sample could affect the sensor response, two vari-

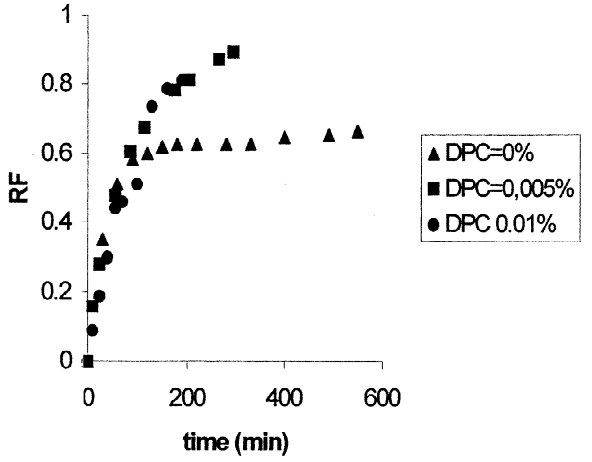


Fig. 2. Effect of DPC concentration on the recovery factor curves. Feed phase: [Cr(VI)] = 15 mg l^{-1}, pH 3.0. Stripping solution: DPC in 0.1 mol l^{-1} H_2SO_4.

ables concerning the feed solution were considered: the pH and the chromium concentration. Thus, to analyse the influence of pH, a set of experiments covering the range from 1.8 to 10.0 was performed, and no significant differences were observed in the range assayed (Fig. 3). This points to the fact that Cr(VI) transport is not dependent on the sample pH. Finally, an evaluation was made to determine if there was any effect of Cr(VI) concentration on transport. The Cr(VI) concentration in the feed solution was varied between 15 and 100 mg l^{-1}, and it was found that, up to 50 mg l^{-1}, the RF vs. time curves were coincident (Fig. 4), but the curve corresponding to 100 mg l^{-1} exhibited RF values significantly lower,

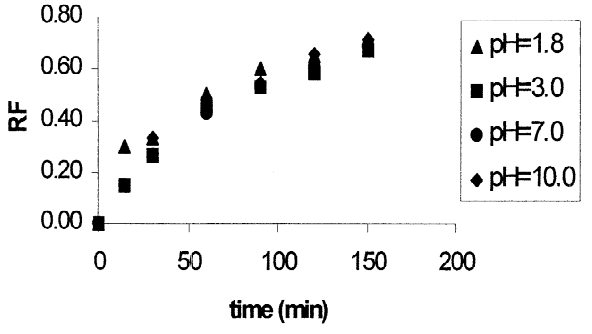


Fig. 3. Effect of the pH of the feed solution on the recovery factor curves. Feed phase: [Cr(VI)] = 15 mg l^{-1}. Stripping solution: 0.01% DPC in 0.1 mol l^{-1} H_2SO_4.

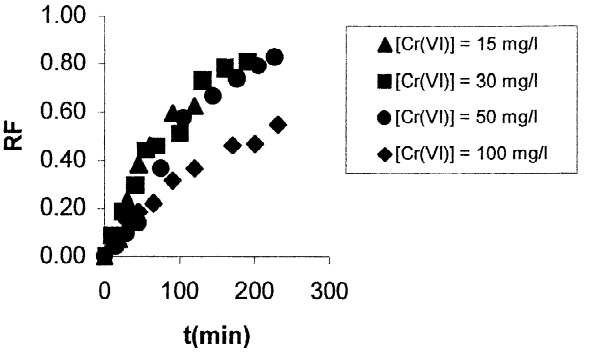


Fig. 4. Effect of Cr(VI) concentration on the recovery factor curves. Feed phase: pH 3. Stripping solution: 0.01% DPC in 0.1 mol l^{-1} H_2SO_4.

because there was insufficient excess of DPC. This behaviour showed that, below 50 mg l^{-1}, Cr(VI) transport was a function of time, but not of Cr(VI) concentration, i.e. for a fixed time, Cr(VI) recovery does not depend on the Cr(VI) concentration.

These results from the transport experiments indicate that the Raipore R1030-DPC system could form the basis of an optical sensor. There is Cr(VI) transport through the membrane, and a violet-coloured species is formed in the stripping solution, which can easily be detected by means of absorbance measurements.

3.2. Chromium(VI) optical sensor feasibility studies

Preliminary experiments were performed with the optical sensor (see Sections 2.3.1 and 2.5) to adjust the chemical parameters that could affect the sensor signal. The effect of DPC concentration on the detector response was investigated. Since optical detection requires an acidic medium, in all the experiments the chromogenic solution was 0.1 mol l^{-1} H_2SO_4. DPC was varied between 0.01 and 0.05%, and a clear improvement in sensor signal was observed when DPC was varied from 0.01 to 0.025% (Fig. 5), but a further increase of the concentration did not lead to significant changes on the optical response.

The effect of the ionic strength of the chromogenic solution was also evaluated. Thus, experiments were performed with a chromogenic solution containing

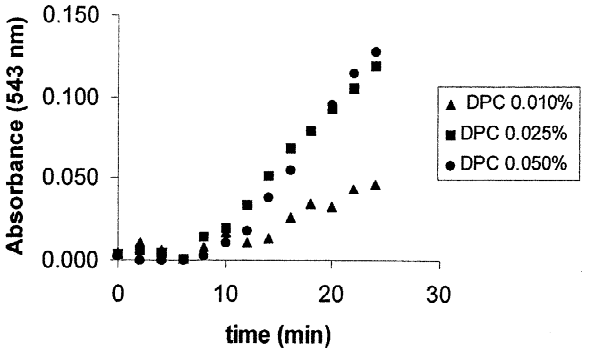


Fig. 5. Effect of DPC concentration on the sensor signal. Sample: [Cr(VI)]=5 mg l^{-1}, pH 3.0. Reagent solution: DPC in 0.1 mol l^{-1} H_2SO_4.

0.4 mol l^{-1} sodium sulphate in addition to 0.025% DPC and 0.1 mol l^{-1} H_2SO_4, and no significant differences were observed when compared with the sensor response when no sulphate was added to the reagent solution.

The pH of the sample solution was another parameter investigated. Solutions containing 5 mg l^{-1} of Cr(VI) and adjusted to pH 2.8, 7.0, and 10.0 were measured with the sensor (Fig. 6). The absorbance curves were almost coincident; therefore, the sensor response does not depend on the sample pH. This is an important point because it indicates

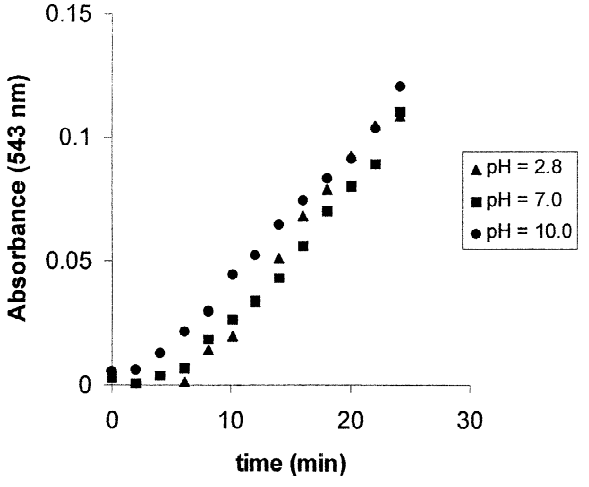


Fig. 6. Effect of the pH of the sample on the sensor signal. Sample: [Cr(VI)]=5 mg l^{-1}. Reagent solution: 0.025% DPC in 0.1 mol l^{-1} H_2SO_4.

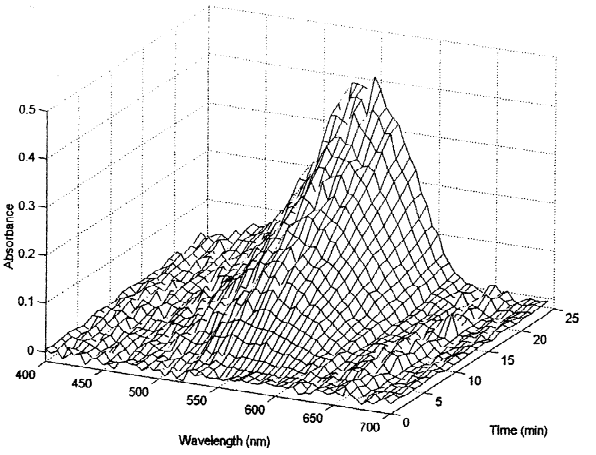


Fig. 7. Typical sensor response. Sample: [Cr(VI)]=15.6 mg l^{-1}. Reagent solution: 0.025% DPC in 0.1 mol l^{-1} H_2SO_4.

that the pH of the standards used for calibration does not need to match that of the samples.

A typical sensor response is shown in Fig. 7. As Cr(VI) permeates the membrane it reacts with the reagent solution to form the violet Cr(III)–DPCO complex and its spectrum is detected by means of the optical fibers. The sensor signal increases with time as chromium ions migrate across the membrane. For quantitation purposes the analysis time was fixed at 16 min, and the analytical signal was the absorbance corresponding to the maximum of the absorption spectrum, i.e. 543 nm.

3.3. Chromium(VI) optical sensor performance

The calibration graph was linear up to the maximum concentration assayed, 16 mg l^{-1} ($A=0.003+0.0247$ [Cr(VI)] (mg l^{-1}), $r=0.998$). The detection limit was 0.75 mg l^{-1}, and the relative standard

Table 1
Determination of chromium(VI) in wastewater samples from electroplating industries

Sample	[Cr(VI)] (mg l^{-1})[a]		Recovery (%)
	Optical sensor	AAS	
1	5.3 (0.4)	5.1 (0.2)	103
2	7.8 (0.2)	8.2 (0.2)	95
3	12.5 (1.0)	12.0 (0.1)	104
4	14.5 (1.0)	15.2 (0.4)	95

[a] Mean value±SD ($n=3$).

deviation from six successive analyses of a 5 mg l^{-1} Cr(VI) solution was 9%.

The sensor was tested to analyse Cr(VI) in effluents from the electroplating industry. To calibrate the sensor, six Cr(VI) standard solutions, ranging from 3 to 16 mg l^{-1}, were used. The results obtained were compared with those determined by AAS (Table 1). Very good agreement between both sets of data was obtained, demonstrating the suitability of the sensor.

4. Conclusions

The results demonstrate the usefulness of the R1030 anion-exchange membrane employed in chemically facilitated Donnan dialysis for effective Cr(VI) transport. The chemical reaction of Cr(VI) with DPC, which facilitates Cr(VI) permeation through the membrane, leads to the formation of a cationic complex, which is rejected by the membrane. This complex, which is the support of classical spectrophotometric methods for Cr(VI) analysis [18], is the basis of the optical detection of Cr(VI) through a system of optical fibers in a sensor using the anionic R1030 membrane as interface. The sensor avoids the limitations associated with the irreversibility of the chemical reaction between Cr(VI) and DPC by using the renewable reagent approach. The analysis of Cr(VI) in rinsing solutions from electroplating industries demonstrated the suitability of the sensor.

Acknowledgements

The authors are very grateful for the design and fabrication expertise of R. Bermudez and I. Minero of the ETSEIB Machine Shop (UPC). We thank Galvagestió for kindly supplying water samples and L.K. Moore and L.W. Burgess, Center for Process Analytical Chemistry (University of Washington), for suggestions. We gratefully acknowledge J.A. Cortina for the sensor drawing. This work was supported by CICYT projects AMB98-0327, QUI99-0749-CO3-02 and HY99-1147-CO2-01, and the SGR99-00049 project of the Generalitat de Catalunya.

References

[1] K.B. Olsen, J. Wang, R. Setladji, J.M. Lu, Environ. Sci. Technol. 28 (1994) 2074.
[2] J. Wang, K. Ashley, E. Kennedy, C. Neumeister, Analyst 122 (1997) 1307.
[3] B.R. James, R.J. Bartlett, J. Environ. Qual. 12 (1983) 173.
[4] O. Egorov, J. Ruzicka, Analyst 120 (1995) 1959.
[5] C.T. Dillon, P.A. Lay, A.M. Bonin, N.E. Dixon, T.J. Collins, K. Kostka, Carcinogenosis 14 (1993) 1875.
[6] A. Miret, J. Ruffo, A.M. Sastre, J.L. Cortina, in: N. Piccinini, R. Delorenzo (Eds.), Chemical Industry and Environment, Vol. 1, 1996.
[7] I.J. Youn, P.J. Harrington, G.W. Stevens, Sol. Extr. Ion Exch. 18 (2000) 933.
[8] W.R. Seitz, CRC Crit. Rev. Anal. Chem. 19 (1988) 135.
[9] O.S. Wolfeis, in: O.S. Wolfeis (Ed.), Fiber Optic Chemical Sensors and Biosensors, Vol. II, CRC Press, Boca Raton, FL, 1991, p. 267.
[10] M. Zevin, R. Reisfeld, I. Oehme, O. Wolfeis, Sensors Actuators B 38/39 (1997) 235.
[11] L.K. Moore, D.J. Veltkamp, J.L. Cortina, Z. Lin, L.W. Burgess, Sensors Actuators B 38/39 (1997) 130.
[12] R.J. Berman, G.D. Christian, L.W. Burgess, Anal. Chem. 62 (1990) 2066.
[13] R. Berman, L.W. Burgess, in: R.A. Lieberman, M.T. Wlodarczyk (Eds.), Proc. SPIE 1172 (1990) 206.
[14] M. Granados, E. Castillo, J.L. Cortina, Quim. Anal. 19 (2000) 68.
[15] F.G. Donnan, Chem. Rev. 1 (1925) 73.
[16] Z. Lin, L.W. Burgess, Anal. Chem. 66 (1994) 2544.
[17] G.J. Willems, N.M. Blaton, O.M. Peeters, C.J. de Ranter, Anal. Chim. Acta 88 (1977) 345.
[18] K.L. Cheng, K. Ueno, T. Imamura (Eds.), Handbook of Organic Analytical Reagents, CRC Press, Boca Raton, FL, 1982, p. 277.