J. Braz. Chem. Soc., Vol. 11, No. 1, 27-31, 2000.
Printed in Brazil

0103 - 5053 $6.00+0.00

Article

Evaluation of a Fe_2O_3-Based Graphite-Epoxy Tubular Electrode as pH Sensor in Flow Injection Potentiometry

Marcos F. de S. Teixeira, Luiz A. Ramos, Neila M. Cassiano, Orlando Fatibello-Filho e Nerilso Bocchi*

Departamento de Química, Centro de Ciências Exatas e de Tecnologia, Universidade Federal de São Carlos, CP 676, 13.560-970, São Carlos - SP, Brazil

Uma avaliação sistemática de um eletrodo tubular de Fe_2O_3 em grafite epóxi foi realizada através de medições de pH em um sistema de injeção em fluxo de linha única. O eletrodo tubular foi obtido pela deposição de uma mistura de óxido de ferro(III), pó de grafite e resina epóxi no interior de um orifício feito previamente no canal de injeção (de resina poliuretana). O efeito da composição do eletrodo e dos parâmetros do sistema de injeção em fluxo (vazão e volume amostra) sobre a resposta do eletrodo foram avaliados em quintuplicata (limite de confiança de 95%). A melhor resposta potenciométrica (E/mV = 178,2 - 26,5 pH; r = 0,9995) foi obtida no intervalo de pH de 2 a 12 com um eletrodo de composição em massa 30% de Fe_2O_3, 20% de grafite e 50% de resina epóxi, volume de injeção de amostra de 300 µL e vazão de 3,2 mL min^{-1}. A frequência analítica foi 90 h^{-1} e um tempo de vida útil de pelo menos 6 meses (mais de 2000 determinações) foi obtido.

A systematic evaluation of a Fe_2O_3 graphite-epoxy tubular electrode was investigated through pH measurements in a single-channel flow injection system. The tubular electrode was obtained by deposition of a mixture of iron(III) oxide, graphite powder and epoxy resin into a hole previously made in the injection channel (of a polyuretane resin block). The effect of electrode composition and flow injection parameters (flow rate and injection sample volume) on the Fe_2O_3-tubular-electrode response was initially evaluated in quintuplicate (confidence level of 95%). The best potentiometric response (E/mV = 178.2 - 26.5 pH; r = 0.9995) was reached in the pH range 2 to 12 with an electrode composition in mass of 30% Fe_2O_3, 20% graphite and 50% epoxy resin, injection sample volume of 300 µL and a flow rate of 3.2 mL min^{-1}. The frequency rate was 90 h^{-1} and a useful lifetime of at least six months (more than 2000 determinations) was obtained.

Keywords: Fe_2O_3 tubular electrode, graphite-epoxy, pH sensor, flow injection analysis.

Introduction

The pH control of aqueous solutions is an important requirement in routine laboratories, industrial processes, alcoholic fermentation, and in medical and agricultural sciences. For this control, the glass electrode is usually the potentiometric sensor of choice in a wide pH range. Although the glass electrode presents selectivity and sensitivity, it has some limitations such as fragility and difficulties of miniaturization for application in flow injection analysis (FIA).

Several conductometric[1], spectrophotometric[2-5] and amperometric[6,7] flow injection procedures have been reported for pH determinations. More recently, a bulk acoustic wave impedance sensor based on changes in the conductivity of the solution was developed for rapid determination of volatile acids (mainly acetic acid) in a FIA system[8]. There has also been significant interest in the use of indicator electrodes as potentiometric detectors in FIA due to their high selectivity, sensitivity, simplicity and low cost. However, there are only a few reports on pH determination using indicator electrodes in FIA. Tungsten[9,10] and antimony[11] oxides were studied as potentiometric electrodes as pH sensor in flow injection potentiometry. On the other hand, PVC has been used as the matrix and support for immobilization of various neutral carriers and ionophores[12-15] in the construction of electrodes for pH and acidity determination in FIA. Although the combination of ion selective electrodes and flow injection analysis allows the development of systems capable of eliminating interferences, these sensors exhibit small pH response ranges and short lifetimes. The application of Ta_2O_5, ZrO_2, Al_2O_3 and Si_3N_4 films produced on SiO_2-Si substrates (CHEMFETS) as pH-sensitive membranes in FIA has also been described in

*E-mail: bocchi@power.ufscar.br
Presented at the XI Simpósio Brasileiro de Eletroquímica e Eletroanalítica, Maragogi - AL, Brazil, April 5-9, 1999. Guest editor: Luis Alberto Avaca.

the literature[16,17]. However, the disadvantages of such sensors are arduous preparation, interference of Na^+ ions and long response time.

A number of electrode designs have been incorporated into flow injection systems. The construction of tubular electrodes with conductive epoxy resin has been proposed by Alegret *et al.*[18,19]. These tubular electrodes have an ideal geometric design for the hydrodynamic flow conditions, avoiding the decrease of the analytic signal by dispersion[20,21]. In the present paper, the results of a systematic evaluation of a Fe_2O_3-based graphite-epoxy tubular electrode as pH sensor in flow injection potentiometry are reported. The electrode is made of graphite as the conductor, iron(III) oxide as the active material and an epoxy resin as the binding agent. The effect of electrode composition and the response characteristics under different flow injection conditions (flow rate and injection sample volume) on the Fe_2O_3-based graphite-epoxy tubular electrode were investigated.

Experimental

Apparatus

An eight-channel model 7618-40 Ismatec (Zurich, Switzerland) peristaltic pump equiped with Tygon pump tubing was used for the propulsion of the fluids. The manifold was constructed with polyethylene tubing (0.8 mm i. d.). Sample injections were performed manually into the carrier stream using a three-piece manual commutator made of Perspex®, with two fixed side bars and a sliding central bar.

The potential difference between the Fe_2O_3-based graphite-epoxy tubular electrode and an Analion (R684 model) Ag/AgCl double-junction reference electrode was measured with a model EA 940 Orion pH/ion meter (USA) with ± 0.1 mV precision and the signals were recorded with a Cole Parmer model CR 53125 recorder.

Reagents and solutions

All solutions were prepared using Millipore Milli-Q water. All chemicals were analytical reagent grade, used without further purification. The reference solutions were prepared from a universal buffer as described by Perrin and Dempsey[22]:

5.7 mmol L^{-1} sodium tetraborate,
20 mmol L^{-1} disodium hydrogen phosphate
13 mmol L^{-1} sodium citrate.

All buffers were adjusted in the pH range 2-12 by addition of HCl or NaOH solution. The evaluation of uncertainty due to the standardization should be 2% because the lack of primary standard solution. The ionic strength of the reference solutions was adjusted to 0.1 mol L^{-1} with KCl.

Fe_2O_3 preparation

The Fe_2O_3 preparation was done following a method reported in the literature[23]. Initially, 5 g of $FeCl_3.6H_2O$ were treated with a 1.0 mol L^{-1} ammonium hydroxide solution. The precipitate was filtered in a 10-15 mm (medium porosity) sintered-glass Gooch filter, washed with distilled water several times and dried at 130ºC for 4 h. Soon after, the mixture was heated in an oven at 600ºC for 4 h, in air, for the total elimination of NH_3.

Construction of the Fe_2O_3-based graphite-epoxy tubular electrode

The composite materials used in the electrodes were prepared by mixing Fe_2O_3, graphite (Ultra Carbon, 10-20 mm particle size) and epoxy resin (a mixture of resin P342 and catalyst from Reforplás, Brazil, in a 5/1 mass ratio) in the following mass proportions (%): a) 20:30:50; b) 25:25:50; c) 30:20:50; e d) 35:15:50. The different Fe_2O_3 graphite-epoxy composites thus obtained were put inside a channel (diameter = 3 mm) of a polyuretane resin block (30 mm × 30 mm × 40 mm) and then dried for 24 h. One of the channel ends was connected to a coaxial cable. After, a channel (diameter = 1 mm) was drilled perpendicularly in the opposing side of the block, through the center of the composite material as shown in Figure 1.

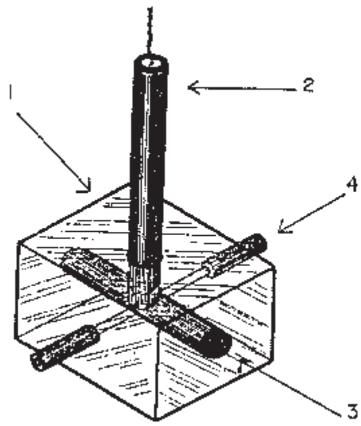

Figure 1. Schematic diagram of the Fe_2O_3-based graphite-epoxy tubular electrode used in the potentiometric measurement of pH in a flow injection system. 1 - polyuretane resin block; 2 - electric connection; 3 - hole (3 mm i. d.) where the composite electrode is deposited and 4 - hole (1 mm i. d.) through which the solution flows.

Flow injection system

Figure 2 shows the flow injection system used for the evaluation of the Fe_2O_3-based graphite-epoxy tubular electrode. The carrier (C) was a buffer solution of pH 7, the analytical path was of 50 cm and the whole FI system was maintained at 25°C.

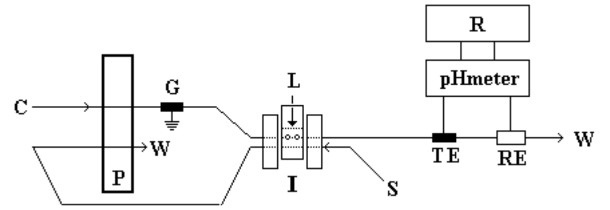

Figure 2. Schematic diagram of the flow system used for the evaluation of the Fe_2O_3-based graphite-epoxy tubular electrode. The central bar of the manual injector-commutator (I) shows the injection position after commutation. P - peristaltic pump; S - reference solutions; L - sample loop; C - carrier solution (pH = 7); G - earthed stainless-stell tube; TE - tubular electrode; RE - Ag/AgCl reference electrode; R - recorder and W - waste.

Results and Discussion

Effect of the electrode composition

The potentiometric response of the Fe_2O_3-based graphite-epoxy tubular electrode in aqueous solutions of different pH is determined by a charge transfer reaction at the Fe_2O_3/aqueous solution interface. The mechanism by which the surface charge is established may be viewed qualitatively as a two-step process: surface hydration followed by dissociation of the surface hydroxide[24]. This mechanism may be represented schematically as shown in Figure 3. The surface reactions involved in the establishment of a surface charge may be represented formally by the following equations:

$$Fe(OH)_2{}^{+}{}_{(surface)} + 2H_2O_{(l)} \rightleftharpoons Fe(OH)_{3(surface)} + H_3O^{+}(aq) \quad (1)$$

$$Fe(OH)_{3(surface)} \rightleftharpoons FeO_2{}^{-}{}_{(surface)} + H_3O^{+}(aq) \quad (2)$$

where $Fe(OH)_3$ (surface) represents the uncharged surface site which by adsorbing a proton becomes positive [$Fe(OH)_2{}^{+}$] or by desorbing a proton becomes negative . By adding equations (1) and (2) the equilibrium represented by the following equation is obtained:

$$Fe(OH)_2{}^{+}{}_{(surface)} + 2H_2O_{(l)} \rightleftharpoons FeO_2{}^{-}{}_{(surface)} + 2H_3O^{+}{}_{(aq)} \quad (3)$$

The effect of the electrode composition on the potentiometric response of the Fe_2O_3-based graphite-epoxy tubular electrode was evaluated in quintuplicate (confidence level of 95%) by measuring its operational potential in universal buffer solutions of different pH (see Figure 4). As shown in this figure, the potential of the tubular electrode decreases linearly as the pH of the buffer solution is increased for all the electrode compositions studied. The negative slope (mV/pH) of the straight lines also increases as the electrode Fe_2O_3 content is increased up to 30%; at a composition higher than 30% the slope decreases. The dependence of these slopes with the electrode Fe_2O_3 content is shown in Figure 5, where the error bars are the average standard deviations of three slope values obtained from straight lines as those in Figure 4. The reproducibility of the measurements is not very good only for the two extreme electrode compositions; for the intermediate compositions the average standard deviation is smaller than 1%. The best potentiometric response (-26.5 + 0.3 mV/pH) was reached for an electrode composition of 30% Fe_2O_3, 20% graphite and 50% epoxy resin. This tubular electrode was stable for a wide range of flow hydrodynamic conditions. It is important to point out that a slope lower than 59 mV/pH (predicted by the Nernst equation) was also found for other metal oxide/aqueous electrolyte interfaces such as SiO_2, TiO_2, Al_2O_3, ZnO and α-Fe_2O_3. Instead of the classical Nernst equation, another equation was proposed to describe the electrode potential with the electrolyte pH[25].

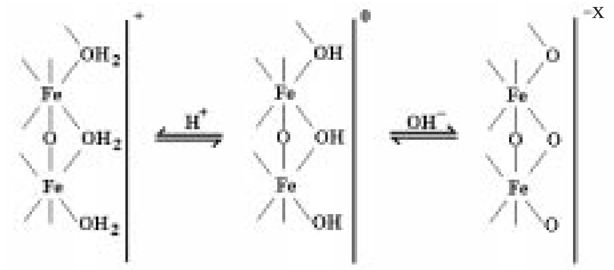

Figure 3. Schematic illustration of the surface hydration and dissociation of the surface hydroxide in the ferric oxide.

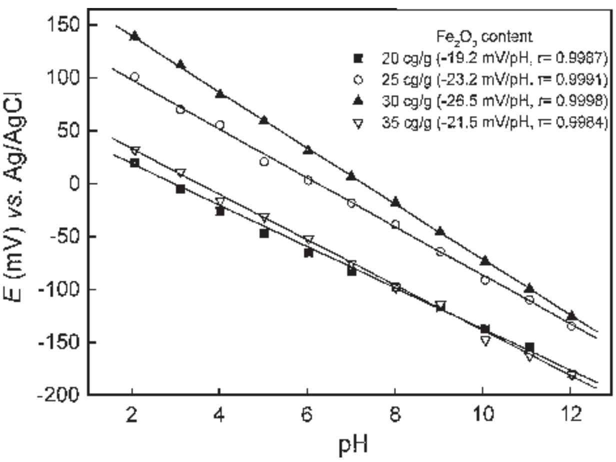

Figure 4. pH dependence of the operational potentials (at 25°C) of Fe_2O_3-based graphite-epoxy tubular electrodes with different compositions.

Flow injection parameters and tubular electrode characteristics

Preliminary studies were carried out to establish the best flow injection parameters and tubular electrode char-

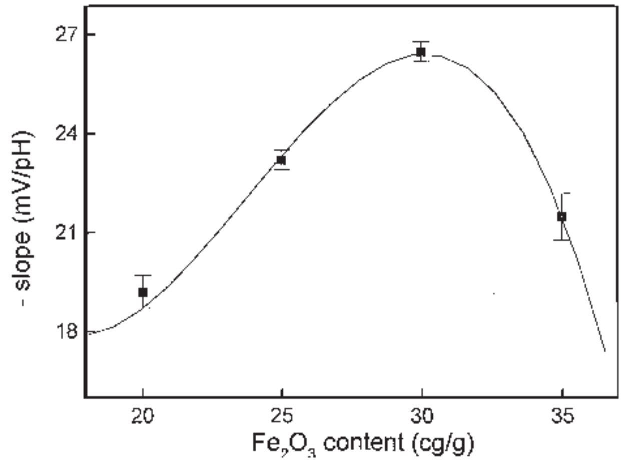

Figure 5. Electrode composition dependence of the slopes of lines such as the ones shown in Figure 4. The error bars are the average standard deviations of three slope values.

acteristics. A carrier solution of low buffer capacity (pH = 7) was used to avoid zone acidity sample change[15,26]. The effect of the sample volume was investigated from 20 μL to 400 μL (changing the length of the sample loop in the commutator) with injection of buffer solution at pH 3 (see Figure 6). As it can be noted in this figure, the potentiometric response increases as the sample volume increased from 20 μL to 300 μL and remains constant for sample volumes greater than 300 μL. Thus, the sample volume of 300μL was selected for further experiments.

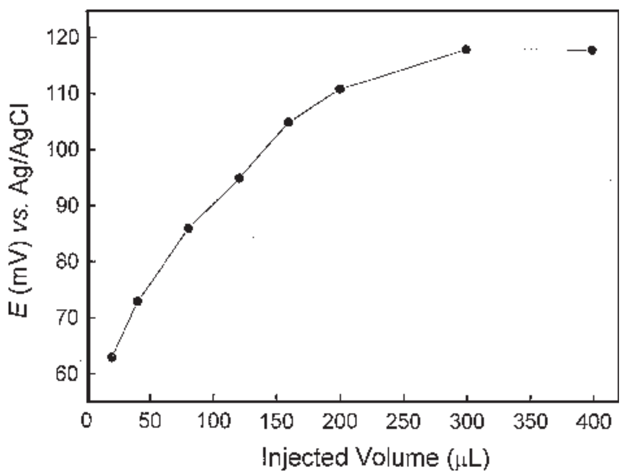

Figure 6. Injection sample volume dependence on the operational potential (at 25ºC) of the Fe_2O_3-based graphite-epoxy tubular electrode (30% Fe_2O_3).

The effect of the flow rate was evaluated for successive injections of buffer solution at pH 3. The highest sensitivity was obtained at a flow rate of 3.2 mL min^{-1}; a significant decrease of the potentiometric response occurred at flow rates higher than 3.2 mL min^{-1} (Figure 7). However, at flow rates lower than 3.2 ml min^{-1} the tubular electrode presented slight memory effects and a long washing time, decreasing the analytical frequency. The dynamic response of the tubular electrode was studied by injecting buffer solution at pH 3. A time response close to 30 s was observed for this electrode.

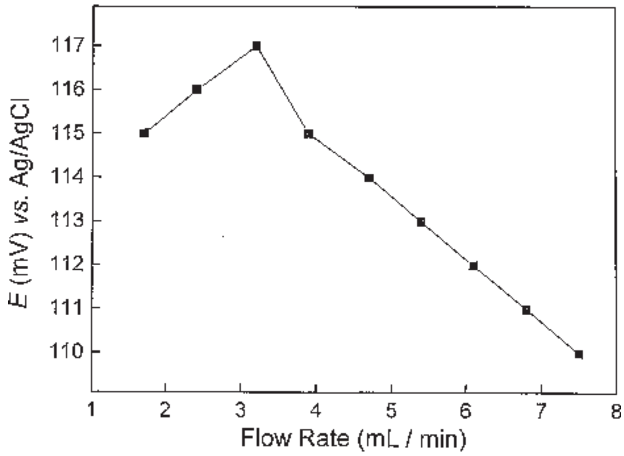

Figure 7. Flow rate dependence of the operational potential (at 25ºC) of the Fe_2O_3-based graphite-epoxy tubular electrode (30% Fe_2O_3) for an injection volume of 300 mL of buffer solution at pH 3.

The effect of several species such as Li^+, Na^+, Mg^{2+}, Ca^{2+}, NH_4^+, SO_4^{2-}, NO_3^-, CH_3COO^- and HCO_3^- at 1.0 x 10^{-3} mol L^{-1} in the solution samples (pH = 7) on the potentiometric response of the tubular electrode was evaluated in triplicate. The presence of all of the cations investigated did not cause any interference in this pH. On the other hand, the presence of acetate and hydrogen carbonate anions had a slight influence in the potentiometric response of the tubular electrode due to their influence in the buffer equilibrium. When the pH of the solution samples was higher than 9, the presence of NH_4^+ had a significant influence on the electrode response, since the ammonium ion is converted to ammonia at such pH.

The flow injection system showed a linear response of *E vs.* pH in the range 2 to 12 (*E*/mV = 178.2 - 26.5 pH; r = 0.9995) (Figure 4). The precision of the $Fe_2O_3^-$ based graphite-epoxy tubular electrode was tested by 13 repeated runs in a buffer solution of pH 6 (see Figure 8), and a relative standard deviation (r.s.d) of 2% was observed. An analytical frequency of 90 h^{-1} was obtained and the useful lifetime of the electrode was at least six months (more than 2000 determinations) without any problems of instability or loss of sensitivity. The electrode was periodically activated with a simple polish of its surface using 600 emery paper. For this a piece of this paper was rolled in a way to enter into the channel where the composite electrode was deposited and through which the solution flows (see Figure 1).

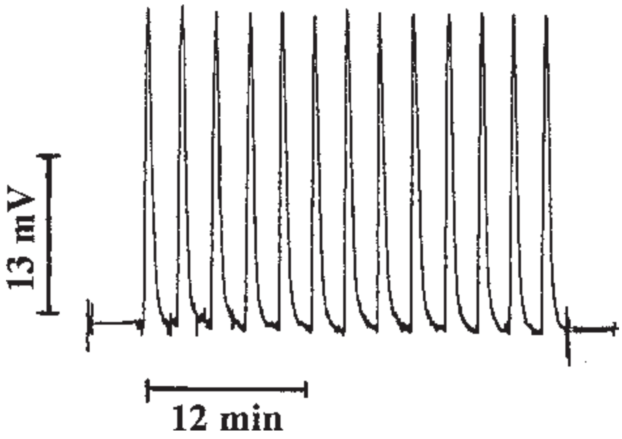

Figure 8. Recorder output of the pH sensitive Fe_2O_3-based graphite-epoxy tubular electrode corresponding to successive injections of buffer solution at pH 6.

Conclusions

The proposed Fe_2O_3-based graphite-epoxy tubular electrode responds to H^+/OH^- ion activity over a wide pH range (2 - 12) with a slope of -26.5 mV/decade (at 25°C). The best potentiometric response (E/mV = 178.2 - 26.5 pH; r = 0.9995) was obtained with an electrode composition in mass of 30% Fe_2O_3, 20% graphite and 50% epoxy resin, injection sample volume of 300 µL and flow rate of 3.2 mL min^{-1}. Due to its low fabrication cost, high analytical frequency (90 h^{-1}), long lifetime (greater than six months or 2000 determinations) and good stability the proposed electrode is a suitable alternative as a pH sensor in flow injection potentiometry.

Acknowledgments

The financial support from PADCT/CNPq and FAPESP, and also the scholarships granted by CNPq to M. F. S. T. and N. M. C. are gratefully acknowledged.

References

1. Fatibello-Filho, O.; Borges, M. T. M. R. *Anal. Chim. Acta* **1998**, *366*, 81.
2. Holobar, A.; Benes, R.; Weigl, B. H.; Oleary, P.; Raspor, P.; Wolfbeis, O. S. *Anal. Method. Instrum* **1995**, *2*, 92.
3. Bellerby, R. G. J.; Turner, D. R.; Millward, G. E.; Worsfold, P. J. *Anal. Chim. Acta* **1995**, *309*, 259.
4. Vives, S. S.; Hernadez, M. J. M.; Herrera, J. L. M.; Ramos, G. R. *Anal. Chim. Acta* **1992**, *268*, 29.
5. Sprenger, U.; Bachmann, K. *Anal. Chim. Acta* **1991**, *243*, 191.
6. Dakashev, A. D., Fresenius J. *Anal. Chem.* **1997**, *357*, 392.
7. Horvai, G.; Pungor, E. *Anal. Chim. Acta* **1991**, *243*, 55.
8. Su, X. L.; Nie, L. H.; Yao, S. Z., Fresenius, J. *Anal. Chem.* **1998**, *360*, 272.
9. Dimitrakopoulos, L. T.; Dimitrakopoulos, T.; Alexander, P. W.; Logic, D.; Hibbert, D. B. *Anal. Commun.* **1998**, *35*, 395.
10. Chen, Z.; Alexander, P. W. *Anal. Chim. Acta* **1996**, *332*, 187.
11. Capelato, M. D.; dos Santos, A. M.; Fatibello-Filho, O.; Gama, R. *Anal. Lett.* **1996**, *29*, 711.
12. Hauser, P. C.; Cardwell, T. J.; Cattrall, R. W.; Tan, S. S.; Hamilton, I. C. *Anal. Chim. Acta* **1989**, *221*, 139.
13. Egorov, V. V.; Sin'kevich, Y. V. *Talanta* **1999**, *38*, 23.
14. Cardwell, T. J.; Cattrall, R. W.; Oconnell, G. R.; Petty, J. D.; Scollary, G. R. *Electroanalysis* **1992**, *4*, 805.
15. Martelli, P. B.; Reis, B. F.; Zagatto, E. A. G.; Lima, J. L. F. C.; Lapa, R. A. *Quím. Nova* **1998**, *21*, 133.
16. Woias, P.; Koch, S.; Muller, E.; Barrow, D.; Cefai, J.; Curtis, G.; Hughes, H. *Sens. Actuators B* **1993**, *15*, 68.
17. Chen, J. N.; Niu, N. M.; Ding, X. F. *Sens. Mater.* **1997**, *9*, 163.
18. Alegret, S.; Alonso, J.; Bratroli, J.; Paulis, M.; Lima, J. L. F. C.; Machado, A. A. S. C. *Anal. Chim. Acta* **1984**, *164*, 147.
19. Alegret, S.; Florido, A.; Lima, J. L. F. C.; Machado, A. A. S. C. *Talanta* **1989**, *36*, 825.
20. Ferreira, I. M. P. L. V.; Lima, J. L. F. C. *J. Flow Injection Anal.* **1993**, *10*, 17.
21. Fatibello-Filho, O.; Teixeira, M. F. S.; Aniceto, C.; Pereira, A. V.; Costa Neto, C. O. *Lab. Robot. Autom.* **1999**, *11*, 163.
22. Perrin, D. D.; Dempsey, B. *Buffers for pH and Metal Ion Control*, Chapman and Hall, London, 1974.
23. Arata, K. *Adv. Catalysis* **1990**, *37*, 177.
24. Parks, G. A.; de Bruyn, P. L. *J. Phys. Chem.* **1962**, *66*, 967.
25. Yates, D. E.; Levine, S.; Healy, T. W. *J. Chem. Soc. Faraday Trans. 1* **1974**, *70*, 1807.
26. Hongbo, H.; Hansen, E. H.; Ruzicka, J. *Anal. Chim. Acta* **1985**, *169*, 209.

Received: June 16, 1999

FAPESP helped in meeting the publication costs of this article.