Available online at www.sciencedirect.com
SCIENCE DIRECT®
Talanta 65 (2005) 1203–1208
Talanta
www.elsevier.com/locate/talanta

Development of a solid surface fluorescence-based sensing system for aluminium monitoring in drinking water

J.F. García Reyes, P. Ortega Barrales, A. Molina Díaz*

Department of Physical and Analytical Chemistry, Faculty of Experimental Sciences, University of Jaén, Paraje Las Lagunillas, E-23071 Jaén, Spain

Received 2 April 2004; received in revised form 20 August 2004; accepted 25 August 2004
Available online 29 September 2004

Abstract

A novel, single and robust solid surface fluorescence-based sensing device assembled in a continuous flow system has been developed for the determination of trace amounts of aluminium in water samples. The proposed method is based on the transient immobilization of the target species on an appropriate active solid sensing zone (C_{18} silica gel). The target species was the fluorogenic chelate, formed as a result of the on-line complexation of Al(III) with chromotropic acid (CA) at pH 4.1. The fluorescence of the complex is continuously monitored at an emission wavelength of 390 nm upon excitation at 361 nm. The instrumental, chemical and flow-injection variables affecting the fluorescence signal were carefully investigated and optimized. After selecting the most suitable conditions, the sensing system was calibrated in the range 10–500 $\mu g\,l^{-1}$, obtaining a detection limit of 2.6 $\mu g\,l^{-1}$, and a R.S.D. of 2.2%, with a sampling frequency of 24 h^{-1}. In addition, the selectivity of the proposed methodology was evaluated by performing interference studies with different cations and anions which could affect the analytical response. Finally, the proposed method, which meets the EU regulations regarding the aluminium content in drinking waters, was satisfactorily applied to different water samples, with recoveries between 97 and 105%. The simplicity, low cost and easy operation are the main advantages of the present procedure.

Keywords: Flow-injection; Fluorescence; Drinking water; Optosensor; Chromotropic acid

1. Introduction

During the last years, increasing efforts have been devoted to the analysis of trace metal ions especially due to the potential toxicological effects on human health [1]. The interest concerning the biological effects of aluminium has considerably increased due to the knowledge about potential toxic effect of aluminium [2,3].

Aluminium is one of the most abundant elements in the earth's crust, being thus, ubiquitous in the environment. In aquatic ecosystems, elevated levels of aluminium are known to cause toxicity in fish, algae, bacteria, plants and other aquatic species. In human, aluminium was thought to be relatively harmless, but recent research tends to support that exposure to aluminium can be related with a number of human pathology including dementia, Parkinson and Alzheimer diseases. In addition, Al(III) has the potential to produce toxicity that has been most commonly seen in patients who have reduced or absent renal function because the kidney is the primary organ of Al elimination [4].

On the other hand, despite aluminium is present at low levels ($\mu g\,l^{-1}$) in natural waters, significant amounts are added to water supplies as a flocculating agent, increasing in many cases its final concentration. The addition of aluminium based coagulants has the potential to leave a trace amount of aluminium in the treatment of drinking water. In order to optimise the coagulation process in drinking water plants using aluminium based coagulants, and to control aluminium level in finished water, monitoring of Al content

* Corresponding author. Tel.: +34 953012147; fax: +34 953012141.
E-mail address: amolina@ujaen.es (A.M. Díaz).

0039-9140/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.08.045

during the treatment of raw water is also urgently required [5,6].

Graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled plasma mass spectrometry (ICP-MS) have been, by far, the most commonly employed analytical techniques for aluminium determination. However, the use of these techniques involves higher purchase and maintenance costs.

As an alternative approach to classic atomic spectroscopy techniques, molecular fluorescence spectroscopy offers attractive analytical advantages in terms of sensitivity, selectivity, speed, simplicity and cost-effectiveness [7]. Fluorimetric methods are generally very sensitive and some of them have been successfully developed for the fluorimetric determination of aluminium based on the formation of metal complexes. The main fluorogenic reagents which has been described for the determination of aluminium are: hydroxyflavones (quercetin [8], morin [9–12], purpurin [13]), lumogallion [14], oxines (8-hydroxyquinoline-5-sulfonic acid [15–17], 8-hydroxyquinoline [18]), salycilhydrazones [19–21] (i.e., salicylaldehyde picolinoylhydrazone), etc. Although these methods, in general, are sensitive enough, they usually lack of selectivity, and moreover, some of the chelating agents has to be synthesized (they are not commercially available).

The use of chromotropic acid (CA) (4,5-dihydroxynaphthalene-2,7-disulfonic acid) as a fluorogenic reagent for aluminium determination has been explored recently [22,23]. In fact, CA exhibits high selectivity towards Al(III) [22]. Therefore, it can be used to establish robust and sensitive methods to determine aluminium.

An increase in selectivity in fluorescence spectroscopy can be achieved by performing the measurement in a solid support, ideally active only to the target species. In this sense, the implementation of solid phase spectroscopy (SPS) and unsegmented flow analysis systems has been widely used in recent years, in order to develop continuous-flow methods originating the so called flow-through optosensors [24–31].

In this paper, the feasibility of using a flow-through optosensor for the sensitive and selective determination of trace Al(III) in drinking waters is reported. The aim of this work was the development of this methodology and its implementation to the monitoring of Al(III) in drinking water samples, using a simple flow-injection system combined with solid surface fluorescence detection. This work provides a straightforward and cost-effective methodology for routine analysis of aluminium.

2. Experimental

2.1. Apparatus and instruments

A Cary-Eclipse Luminescence Spectrometer (Varian, Mulgrave (Australia)) was used to perform all the relative fluorescence intensity measurements. The spectrofluorimeter was equipped with a Hellma flow cell 176.052-QS (25 μl of inner volume and a light path length of 1.5 mm) (Jamaica, NY, USA). The spectrofluorimeter was connected to a computer with a Cary Eclipse (Varian) software package for data collection and treatment. The flow cell was filled with C_{18} silica gel microbeads with the aid of a syringe. The flow-through cell was blocked at the outlet with glass wool, to avoid displacements of the C_{18} gel beads. The flow-injection assembly is outlined in Fig. 1. It was built using a four-channel Gilson Minipuls-3 peristaltic pump (Villiers le Bel, France), two low pressure six-port teflon rotary valves Rheodyne type 5020 (Rohnert Park, CA, USA), both used as injection valves. Methanol-resistant pump tubes type Solvflex (Elkay Products, Shrewsbury, MA, USA), 0.8 mm i.d. teflon tubing (Omnifit, Cambridge, UK), teflon mixing Y-pieces (Omnifit, Cambridge, UK) and a 3-m reaction coil were also used.

2.2. Reagents and solutions

All chemicals were analytical-reagent grade and doubly distilled water was used throughout. Aluminium stock solutions (1000 μg ml^{-1} Al(III)) were prepared with $Al(NO_3)_3{\cdot}9H_2O$ in 1% HNO_3 (Fluka). Chromotropic acid (CA) (4,5-dihydroxynaphthalene-2,7-disulfonic acid, disodium salt dihydrate) was purchased from Aldrich. A 1000 μg ml^{-1} stock solution of CA (2.5 mM) was prepared by dissolution of the appropriate amount in methanol (Panreac). This solution remained stable for at least one month when stored under refrigeration at 4 °C. Formic acid/sodium formate buffer solutions (0.4 M; pH 4.1) were prepared using formic acid and sodium formate from Panreac.

Dimethyloctadecylsilyl bonded amorphous silica gel beads (C_{18}) (Waters, Inc., Milford, MA, USA) with average particle sizes of 55–105 μm, was used as the active sensing support. Strongly basic anion exchanger resin Dowex 1X2-200 (100–200 mesh) 2% cross linkage (Sigma–Aldrich), dextran type gel without exchangeable groups (Sephadex G-15 (Aldrich)) and anion exchanger on dextran (Sephadex QAE A-25 and DEAE A-25 (Aldrich)) were also evaluated.

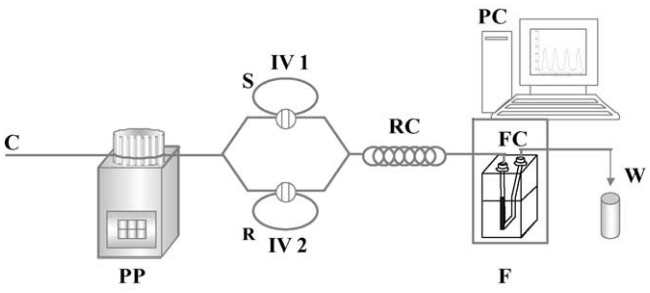

Fig. 1. Flow-injection manifold. Abbreviations: C, carrier stream; PP, peristaltic pump; IV1, sample injection valve (S, sample); IV 2, reagent injection valve (R, reagent); RC, reaction coil; FC, flow cell; F, spectrofluorimeter; PC, computer; W, waste.

2.3. Manifold configuration and analytical procedure

The manifold used is shown in Fig. 1. The carrier stream (0.04 M formic acid/formate buffer pH 4.1) was divided in two channels (with a Teflon T-mixing piece) where the sample and the reagent (CA 10 mg l^{-1}) were injected simultaneously by means of two parallel six-port rotary injection valves. Then, the two streams merged in a unique channel where the Al(III)-CA chelate was formed in a 3-m reaction coil, just before reaching the active sensing phase (with C_{18} gel-beads used as solid support), in which the chelate was transiently retained/concentrated, being its fluorescence signal continuously monitored at 390 nm upon excitation at 361 nm. The carrier solution acts in this case as carrier/regenerating solution, rendering the solid-phase ready for the next sample injection. A typical fiagram is shown in Fig. 2.

3. Results and discussion

3.1. Preliminary studies

3.1.1. Spectral features

Taking into account that the emission fluorescence spectrum of the fluorogenic reagent and that of the chelate were partially overlapped, the intrinsic fluorescence of the reagent was evaluated in order to select an optimum pair of excitation/emission wavelength in which the signal produced by the reagent (blank) were as lower as possible. At pH 4.1, the maximum excitation/emission wavelengths for chromotropic acid were 347/374 nm. However, nearly selective excitation of the chelate rather than the ligand could be accomplished at wavelengths longer than 360 nm. After a carefully study, 361/390 nm was chosen to measure the chelate because it offered a compromise value between chelate sensitivity and low signal of the blank (ligand).

3.1.2. Instrumental variables

The instrumental parameters of the spectrofluorimeter were also set to provide the higher ratio chelate signal/blank.

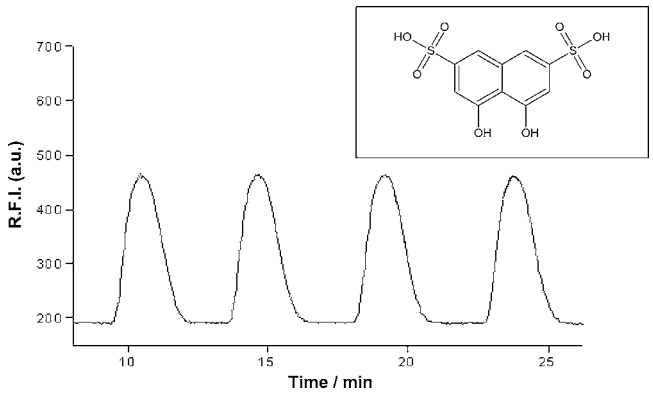

Fig. 2. Recorded signals in the determination of 125 μg l^{-1} of Al(III). Inset: structure of chromotropic acid.

Therefore, instrumental parameters and conditions of measurement were carefully investigated in order to achieve the best possible chelate/ligand signal ratio. The instrument excitation and emission slit widths were studied in the range from 1 to 20 nm. Excitation and emission slits were adjusted at 2.5 and 10 nm, respectively. A study of the photomultiplier tube (PMT) voltage was also carried out in the range from 600 to 1000 V. The final PMT voltage used was 825 V.

3.1.3. Selection of the solid active support

Different types of commercially available active solid phases were studied for the proposed method: anion exchangers on dextran (Sephadex QAE A-25 and Sephadex DEAE A-25), a dextran type without exchangeable groups (Sephadex G-15), a strong anion exchanger Dowex 1X2-200 (100–200 mesh) and a non polar sorbent (C_{18}-bonded phase silica gel) were evaluated.

C_{18}-bonded phase silica gel was chosen as sensing phase because it provided the better sensitivity and moreover, it involved an easier regeneration step, avoiding the use of an additional regenerative solution to render the sensing phase ready for the next injection. Thus, the sampling throughput, the life time of the solid support and also the simplicity of the sensing system were increased.

The solid phase was preconditioned daily by circulating pure methanol for two minutes (just before the first sample injection), rendering the solid support ready for a large number of sample injections.

3.2. Chemical variables

3.2.1. Nature and concentration of the carrier and pH of the sample

Taking into account that the carrier pH would be close to the optimum pH value for the reaction between Al(III) and CA, the effect of the carrier was studied in the range from 3.0 to 4.3, keeping in mind both the acid–basic equilibrium of the chelating agent and the partial formation of $Al(OH)_3$ (various parallel reactions can underlie the complexation process depending on the pH of the medium [22]). Results obtained are included in Fig. 3a.

From the results obtained, the optimum pH of the carrier was 4.1. Therefore, different buffer systems were evaluated: citric acid/citrate, acetic acid/sodium acetate and formic acid/sodium formate. The buffer which showed better results was formic acid/sodium formate, which yielded higher analytical signal at the same concentration level. The effect of the buffer concentration was studied in the range from 0.02 to 0.2 M. A 0.04 M value was selected for further experiments because it provided enough buffer efficiency and better analytical signal than higher concentrations.

To ensure the robustness of the method, both sample and reagent solutions were buffered at the same conditions of the carrier, taking into account that small changes in the pH

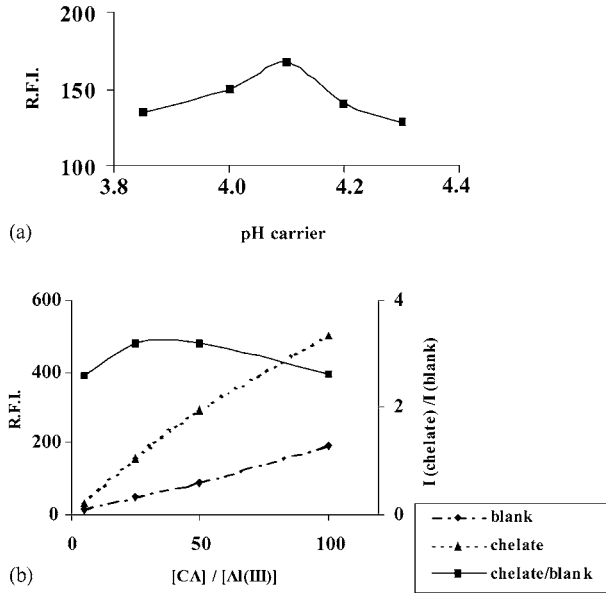

Fig. 3. Study of chemical variables: (a) carrier pH; conditions: [Al(III)] = 100 μg l^{-1}; [CA] = 24.98 μM and (b) reagent concentration; [Al(III)] = 100 μg l^{-1}; ([CA]/[Al(III)] expressed as w/w ratio).

medium could undergo significant differences in the fluorescence signal.

3.2.2. Concentration of the fluorogenic reagent

The concentration of the fluorogenic reagent was also carefully considered. The concentration was studied in the range 2.5–50 μM (1–20 mg l^{-1}) of chromotropic acid. Both the blank and the analytical signal increased with the concentration of the reagent. The results obtained in this study are summarized in Fig. 3b. It can be seen that the blank values increased as CA concentration increased and the increase in the fluorescence signal of the Al–CA complex caused by the excess of ligand was parallel to that for the blank. As a compromise between, analytical signal and blank values, the CA concentration was established at 24.98 μM (10 mg l^{-1}).

3.3. Flow injection variables

The flow-injection variables studied were the reaction coil length, the injected sample volume, the injected reagent volume and the effect of the flow rate.

3.3.1. Optimisation of the reaction coil length

The experiment was performed under the optimized chemical variables. The influence of the reaction coil length was evaluated using a 100 μg l^{-1} Al(III) standard solution. The effect of the reaction coil length was studied from 0.5 to 5 m. The results obtained are included in Fig. 4a. In order to obtain as high sensitivity as possible, a reaction coil length of 3 m was selected for further experiments.

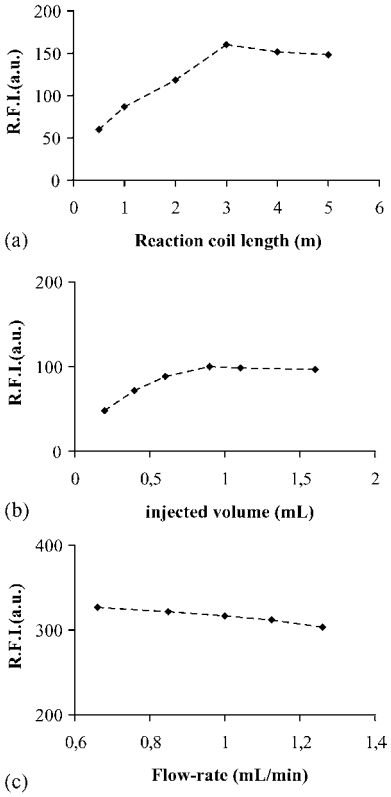

Fig. 4. Flow-injection variables: (a) reaction coil length; (b) injected sample volume; (c) flow rate.

3.3.2. Injected sample volume

An interesting feature of the optosensing concept is its potential to regulate/increase the sensitivity required simply by varying the injected sample volume, because the higher the sample injected, the higher the mass of the target species injected and retained on the sensing phase and therefore, the higher the analytical signal [32].

In this case, the effect of the sample volume was studied for Al(III) in the range from 200 to 2000 μl, using the same volume of reagent in the other injected loop. The results are shown in Fig. 4b. From the results obtained, it can be concluded that injected volumes higher than 900 μl does not provide an increase in analytical signal. Therefore, 900 μl was selected as sample volume. Then, the effect of the injected volume of reagent was also studied. Keeping constant the sample volume, no increase in the analytical signal was observed at values above 1100 μl. This value was chosen for further experiments.

3.3.3. Flow rate

The effect of the flow rate was investigated from 0.66 to 1.4 ml min^{-1}. The higher the flow rate was, the lower the analytical signal and also the elution time progressively diminished whereas the sampling frequency increased. Results obtained are included in Fig. 4c. It should be noted that the slight signal decreasing at higher flow rates, involves a fast retention/desorption kinetic process of the chelate on the ac-

tive solid support. On the other hand, flow rates higher than 1.26 ml min^{-1} could not be used owing to overpressure problems in the flow system. Therefore, a 1.26 ml min^{-1} flow rate was chosen as a compromise between sensitivity and total signal time.

3.4. Analytical performance

3.4.1. Calibration graph and analytical features

The analytical parameters of the proposed method were evaluated after the system was optimized. Calibration graphs were obtained according to the procedure described above, with different Al(III) standard solutions. Results obtained were summarized in Table 1. Sampling throughput and R.S.D. were also evaluated.

The analytical figures of merit obtained with the proposed optosensor compare very well against other recently reported fluorimetric optosensors [10,11], both using morin as the fluorogenic agent. Furthermore, this automatic procedure represents a simple and cost-effective methodology which can be easily implemented in a laboratory for routine analysis of Al(III). In addition, the proposed method fulfils the EU regulations regarding the aluminium content in drinking water (200 $\mu g\,l^{-1}$).

3.4.2. Interference study

Chromotropic acid is a very selective (but not specific) fluorogenic agent for aluminium, so, in order to explore the selectivity against other ions and test the usefulness of the proposed continuous-flow method, a study of the effect of different ions on the fluorescence signal of the system was undertaken. Different ions were added at concentration levels higher than those usually present in the samples scope of the proposed method (drinking water). Foreign species (mainly metal ions) which are likely to be present in real samples were added to solutions containing 200 $\mu g\,l^{-1}$ of Al(III), and their influence on the analytical signal was investigated. Tolerance level was defined as the amount of foreign species that produced an error not exceeding ±5% in the determination of each analyte. Results obtained are summarised in Table 2. The results were excellent because the tolerance levels found were higher than the expected levels of these ions in real samples, except for Fe(III), in which the tolerance level is in the same order of concentration usually found in real samples. This interference can be easily circumvented by adding a solution of ascorbic acid in the sample (40 $\mu g\,ml^{-1}$) of ascorbic increasing thus, the tolerance level up to the same obtained for Fe(II).

Table 1
Analytical parameters

Parameter	
Linear dynamic range ($\mu g\,l^{-1}$)	10–500
Calibration graph	
Intercept	10.9
Slope (l μg^{-1})	1.38
Correlation coefficient	0.9992
Detection limit ($\mu g\,l^{-1}$)[a]	2.6
Quantification limit ($\mu g\,l^{-1}$)[b]	8.6
R.S.D.% (n = 10)	2.18 (200)[c]
Sampling frequency (h^{-1})	24

[a] 3 σ criterion (n = 10).
[b] 10 σ criterion (n = 10).
[c] Concentration level, $\mu g\,l^{-1}$.

Table 2
Tolerated ratios of some potentially interfering species for 100 $\mu g\,l^{-1}$ of Al(III)

Species	Tolerated ratio ([species]/[Al(III)], $\mu g\,l^{-1}$)
Cl^-, Na^+, K^+, CO_3^{2-}, HCO_3^-, SO_4^{2-}, NH_4^+, NO_3^-	5000 [a]
Ca^{2+}, PO_4^{3-}	1000
Mg^{2+}	200
Ni^{2+}, Fe^{2+}, Co^{2+}	100
Hg^{2+}, Cd^{2+}	50
Zn^{2+}, Sn^{2+}	20
Cr^{3+}, Pb^{2+}	10
Fe^{3+}	5 (100)[b]

[a] Maximum ratio tested.
[b] In the presence of ascorbic acid (40 $\mu g\,ml^{-1}$).

3.4.3. Analytical applications

In order to study the usefulness of the proposed method, it was applied to the determination of aluminium in different types of drinking water samples: commercial bottled mineral water samples and tap water. The Al(III) concentration found in all mineral water samples was below the detection limit of the proposed method (these results were obtained using ICP-MS). The Al(III) concentration found in tap water was 27.1 ± 0.8 $\mu g\,l^{-1}$ (n = 3). This result compared well with that obtained with ICP-MS: 30 ± 1 $\mu g\,l^{-1}$ (n = 3). To evaluate the accuracy of the method, recovery studies were also undertaken at three different concentration levels. Results obtained are summarized in Table 3. Mean recovery values ranged from 97 to 105%. From the results obtained,

Table 3
Recovery study in water samples

Sample	Al(III)	
	Added ($\mu g\,l^{-1}$)	Recovery ± R.S.D. (%)[a]
Water 1	50	103 ± 2
	100	101 ± 2
	200	99 ± 2
Water 2	50	103 ± 1
	100	99.3 ± 0.8
	200	97 ± 1
Water 3	50	98 ± 2
	100	100.2 ± 0.8
	200	97 ± 1
Tap water	50	105 ± 2
	100	103 ± 2
	200	101 ± 1

[a] n = 3.

it can be concluded that the accuracy of this continuous-flow methodology was demonstrated, representing a feasible and cost-effective methodology for analysing Al(III) in drinking water samples.

4. Conclusions

The potential of solid-phase optosensing concept as an appropriate tool for rapid monitoring of aluminium content in drinking water has been demonstrated: the proposed fluorimetric sensing device meets the requirements regarding the maximum levels established by the EU regulation for aluminium in drinking water (200 $\mu g\, l^{-1}$, a quality parameter of water for human consumption).

Compared with other previously reported optosensors for this metallic ion [10,11], the proposed automatic method shows a series of attractive advantages, as can be said: simplicity, as the carrier solution also elutes the retained species, time and cost-effectiveness, as well as the use of a common reagent. Moreover, its analytical performance compared well against these recently published fluorescence-based optosensors, both using morin as the reagent. This is the first automatic procedure described for aluminium which uses CA as fluorogenic reagent.

Acknowledgments

The authors acknowledge funding support from MCYT (project no. BQU 2002-02872), partially co financed by FEDER. J.F.G.R. also acknowledges an FPU program scholarship from MEC.

References

[1] R.C. Massey, D. Taylor, Aluminium in Food and the Environment, RSC, Cambridge, 1990.
[2] P. Zatta, P. Zambenedetti, R. Milacic, Analusis 26 (2000).
[3] R.A. Yokel, Coord. Chem. Rev. 228 (2002) 97.
[4] R.J.P. Williams, Coord. Chem. Rev. 228 (2002) 93.
[5] C. Brach-Papa, B. Coulomb, C. Branger, A. Margaillan, F. Theraulaz, P. Van Loot, J.L. Boudenne, Anal. Bioanal. Chem. 378 (2004) 1652.
[6] C.W.K. Chow, S.D. Thomas, D.E. Davey, D.E. Mulcahy, M. Drikas, Anal. Chim. Acta 499 (2003) 173.
[7] R.A. Agbaria, P.B. Oldham, M. McCarroll, L.B. McGrown, I.M. Warner, Anal. Chem. 74 (2002) 3952.
[8] H. Lian, Y. Kang, S. Bi, Y. Arkin, D. Shao, D. Li, Y. Chen, L. Dai, N. Gan, L. Tian, Talanta 62 (2004) 43.
[9] S.M.Z. Al-Kindy, F.O. Suliman, S.B. Salama, Microchem. J. 74 (2003) 173.
[10] M.J. Ruedas-Rama, A. Ruiz-Medina, A. Molina-Díaz, Talanta 62 (2004) 879.
[11] S.M.Z. Al-Kindy, R. Badia, M.E. Diaz-García, Anal. Lett. 35 (2002) 1763.
[12] L.A. Saari, W.R. Seitz, Anal. Chem. 55 (1983) 667–670.
[13] M. Ahmad, R. Narayanaswamy, Sens. Actuators, B 81 (2002) 259–266.
[14] J.A. Resing, C.I. Measures, Anal. Chem. 66 (1994) 4105.
[15] C. Brach-Papa, B. Coulomb, J.-L. Boudenne, V. Cerdá, F. Theraulaz, Anal. Chim. Acta 457 (2002) 311.
[16] G. De Armas, M. Miró, A. Cladera, J.M. Estela, V. Cerdá, Anal. Chim. Acta 455 (2002) 149.
[17] Z. Zhang, W.R. Seitz, Anal. Chim. Acta 171 (1985) 251–258.
[18] A. Alonso, M.J. Almendral, M.J. Porras, Y. Curto, C. García de María, Anal. Chim. Acta 447 (2001) 211.
[19] G. Albendín, M.P. Manuel-Vez, C. Moreno, M. García-Vargas, Talanta 60 (2003) 425.
[20] C. Jiang, B. Tang, R. Wang, J. Yen, Talanta 44 (1994) 197.
[21] F. Sánchez-Rojas, E. Cristofol-Alcaráz, J.M. Cano Pavón, Analyst 119 (1994) 1221.
[22] E. Destandau, V. Alain, E. Bardez, Anal. Bioanal. Chem. 378 (2004) 402.
[23] C.-I. Park, K.-W. Cha, Talanta 51 (2000) 769.
[24] A. Sanz-Medel, Anal. Chim. Acta 283 (2003) 367.
[25] A. Molina-Díaz, M.L. Fernández de Córdova, A. Ruiz-Medina, J. Pharm. Biomed. Anal. 28 (2002) 399.
[26] J.F. García-Reyes, E.J. Llorent-Matínez, P. Ortega Barrales, A. Molina-Díaz, Anal. Bioanal. Chem. 378 (2004) 429.
[27] J.F. García-Reyes, P. Ortega-Barrales, A. Molina Díaz, Anal. Chim. Acta 493 (2003) 35.
[28] J.F. Fernandez-Sanchez, A. Segura-Carretero, J.M. Costa-Fernandez, N. Bordel, R. Pereiro, C. Cruces-Blanco, A. Sanz-Medel, A. Fernandez-Gutierrez, Anal. Bioanal. Chem. 377 (2003) 614.
[29] J.M. Traviesa-Alvarez, J.M. Costa-Fernández, R. Pereiro, A. Sanz Medel, Talanta 62 (2004) 827.
[30] L.F. Capitán-Vallvey, M.C. Valencia, E. Arana Nicolas, Anal. Chim. Acta 503 (2004) 179.
[31] R.J. Cassela, L.S.G. Teixeira, S. Garrigues, A.C.S. Costa, R.E. Santelli, M. De la Guardia, Analyst 125 (2000) 835.
[32] P. Ortega Barrales, M.L. Fernández de Córdova, A. Molina Díaz, Anal. Chem. 70 (1998) 271.