ELSEVIER

Analytica Chimica Acta 343 (1997) 191–197

ANALYTICA CHIMICA ACTA

Flow injection-assisted optical sensor for determination of iron(II) and iron(III) in natural water

A.C. Lopes da Conceição[a,*], M.T. Tena[b], M.M. Correia dos Santos[a], M.L. Simões Gonçalves[a], M.D. Luque de Castro[b]

[a]*Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisbon Codex, Portugal*
[b]*Department of Analytical Chemistry, Faculty of Sciences, University of Córdoba, E-14004 Córdoba, Spain*

Received 15 July 1996; received in revised form 29 November 1996; accepted 1 December 1996

Abstract

An approach for speciation of iron (as Fe(II) and Fe(III)) based on integration of retention of the Fe(III)–SCN complex with detection using a conventional spectrophotometer is proposed here. The device (namely, a flow-cell packed with an exchange resin) has been coupled to a flow-injection manifold with inner-coupled injection valves which enables discrimination between Fe(III) and Fe(II) taking advantage of a redox minicolumn housed in the loop of one of the valves. The method thus proposed has good selectivity with a determination limit of 80 $\mu g l^{-1}$ and affords a determination range of 80–500 $\mu g l^{-1}$ for Fe(II) plus Fe(III). Application to synthetic and real samples containing both the oxidation states of iron lead to average recoveries of 103% and 101% for Fe(II) and total iron (Fe(II)+Fe(III)), respectively, thus showing the usefulness of the overall approach.

Keywords: Flow injection; Sensors; Iron; Waters

1. Introduction

Under anoxic conditions, reduced chemical species such as Fe(II), Mn(II) and S(II) are produced in natural water, following in principle the thermodynamic redox sequence, although most of the redox reactions involved take place at significant rates only if microbially mediated.

The occurrence of anoxic conditions causes cycling of elements such as iron at the oxic–anoxic interface, e.g., Fe(II) formed during anoxia, can be oxidized and precipitated afterwards when the reduced species comes into contact with oxygen. Interstitial waters of sediments in estuaries have generally an upper layer in oxic conditions and a lower one in anoxia and can have low values of pH due to industrial effluents [1].

Discrimination between Fe(II) and Fe(III) in natural waters is relevant since iron is one of the few elements that is an active participant in aquatic redox processes; namely, in oxidation of organic matter, in soils, sediments, surface waters (at pH<6) and at oxic–anoxic boundaries. In fact the iron cycle includes the reductive dissolution of iron(III) (hydr)oxides by organic ligands partly photocatalyzed in surface waters and the oxidation of Fe(II) by oxygen catalyzed by surfaces. Microorganisms and plants produce a large number of biogenic ligands effective in the dissolution of Fe(III) and other (hydr)oxides such as oxalic,

*Corresponding author. Fax: +351 1 352 4372.

PII S0003-2670(96)00595-8

maleic, acetic, succinic, tartaric, ketogluconic and *p*-hydroxybenzoic acids in total concentration of about 10^{-5}–10^{-4} M. The reductive dissolution of iron(III) (hydr)oxides is also important for iron uptake by higher plants [1]. Within this context the determination of total iron(II) and iron(III) in natural waters will allow the determination of each chemical species formed by these two different oxidation states, from computer simulations, once the concentration of the ligands and the stability constants of the complexes are known.

Flow injection (FI) has proved to be a powerful tool for the development of speciation methods [2,3] thanks to its unquestionable versatility and the possibility of on-line coupling with other complementary techniques which are mandatory for the treatment of complex samples [4]. Several approaches have been followed for the simultaneous determination of Fe(II) and Fe(III) by FI. An amperometric detection with a glassy carbon electrode had been used to discriminate between both valence states and the method was then used in the analysis of rocks [5]. An electrochemical detector in series with a flame atomic absorption spectrophotometer was also used in the simultaneous speciation of iron(II) and iron(III) [6]. The potentialities of FI spectrophotometry followed by atomic absorption spectrometry was also analysed in the determination of Fe(II) and total Fe [7]. Most applications deal, however, with a single spectrophotometric detection. Methods based on 1,10-phenanthroline as the spectrophotometric reagent allow the determination of Fe(II) and total iron after reduction of Fe(III) [8–10]. Alternatively, iron(III) may be determined directly using a chelating agent with a strong affinity for Fe(III) like hydroxamic acids [11]. In most situations described the determination limit is close to 0.5 mg l^{-1}, although lower detection limits can be achieved using a chemiluminescence detection [12,13].

Our experience with FI prompted us to develop methods which show again the potential of FI speciation. Among the ways through which FI can help speciation, namely, by manipulating the propulsion unit, the injection valve, the transport systems and/or the detector-data treatment [3], we have focused on the valve and the detector. An inner-coupled injection-valve approach, previously reported by our team for nitrate/nitrite speciation [14] has been used to accomplish discrimination between the two most common forms of iron (Fe(III) and Fe(II)) in a single injection operation. A unique regenerable redox column (molybdophosphate heteropolyacid – Folin–Ciocalteu's reagent – supported on an exchange resin [15]) housed in the loop of the secondary injection valve was used to obtain the iron(II) ion suitable to undergo the derivatization reaction. An integrated retention/detection approach was incorporated in the manifold with the aim to improve sensitivity by in situ concentration [16]. A precedent of this retention/detection system was previously reported for aluminium speciation but one injection for each species to be determined was required in that case.

In this work a flow-cell packed with an exchange resin has been coupled to a flow-injection manifold with inner-coupled injection valves which enables discrimination between Fe(II) and Fe(III) taking advantage of a redox minicolumn housed in the loop of one of the valves. The integration of retention of the iron(III)–thiocyanate complex with detection using a conventional spectrophotometer is proposed. The iron(III)–thiocyanate method for iron determination had been previously used by us in the determination of iron(III) by FI in water and wine samples [17].

Optimization of chemical and FI variables and determination of the linear range of response, determination limit and precision of the method have been studied. The method has been applied to an estuary sample.

2. Experimental

2.1. Reagents and apparatus

The water used in the experiments, to rinse and to prepare the solutions was distilled and deionized (from a Milli Q, Millipore water purification system).

A stock solution of iron(III) (1.000 g l^{-1}) was prepared by dissolving ammonium iron(III) sulphate dodecahydrate from Merck (extra pure) in water and 10 ml of 1 M nitric acid were added before diluting to 1 l.

A solution of iron(II) was freshly prepared just before running the experiments by dissolving the ammonium iron(II) sulphate hexahydrate from Merck

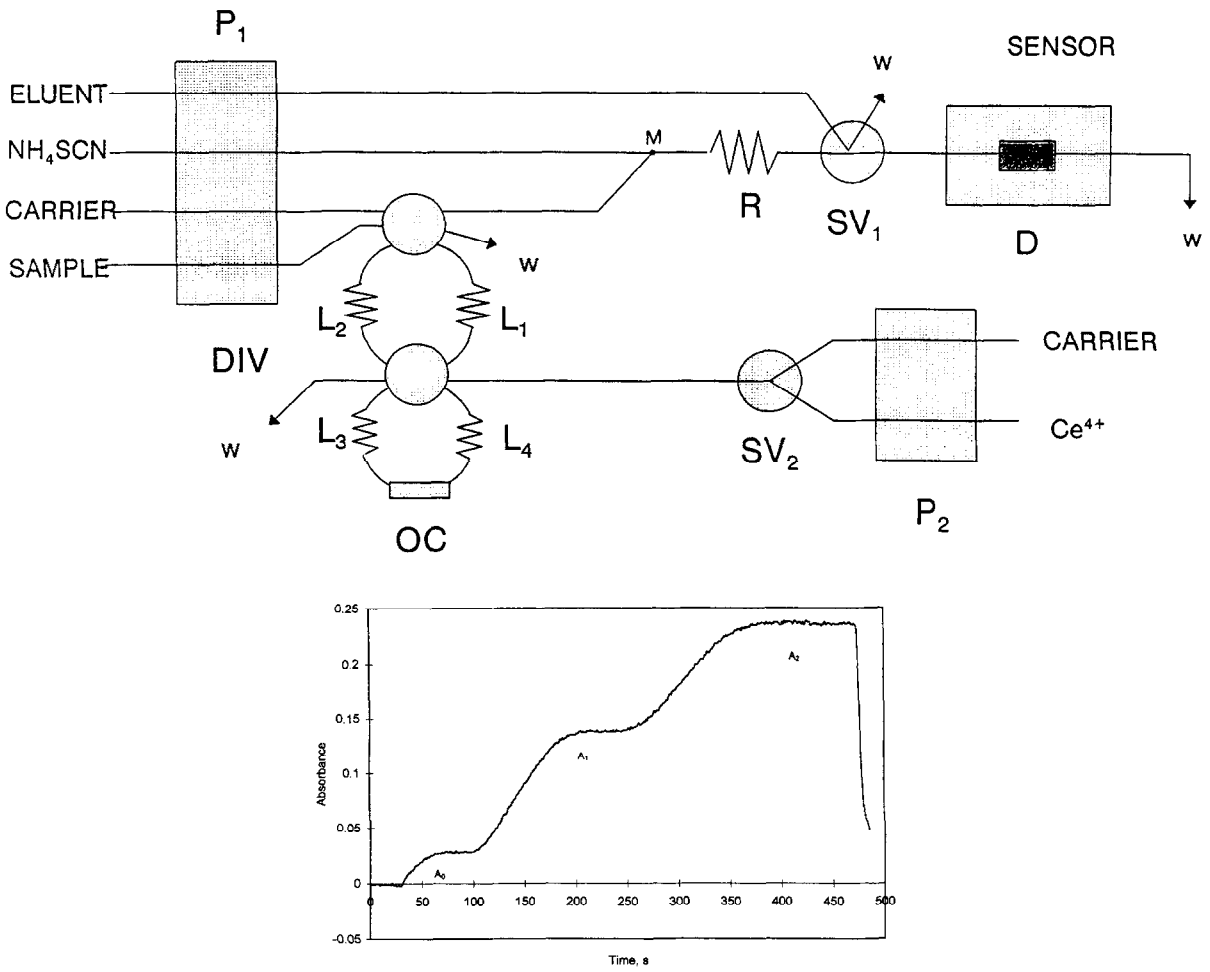

Fig. 1. (A) FI manifold. D: Detector, DIV: Double injection valve, L_1–L_4: Loops, OC: Oxidation column, P_1, P_2: Pumps, R: Reaction coil, SV_1, SV_2: Switching valves, M: Three-way adapter, W: Waste. (B) Absorbance values at λ=481.0 nm as a function of time corresponding to a 0.30 ppm of iron(III) solution – A_0: Blank signal, A_1: Sample signal corresponding to volume L_1, A_2: Sample signal corresponding to volume L_1+L_2.

(extra pure) in water at pH=2 by the addition of nitric acid.

The Folin–Ciocalteu's reagent as well as all the other p.a. chemicals were from Merck.

The ion exchangers were Dowex-1 strongly basic anion exchanger (mesh size (50–100) and cross-linkage 4%) and DEAE Sephadex anion exchanger (dry bead size 40–120 μm) both from Sigma.

The manifold (Fig. 1(A)) consisted of two four-channel Gilson Minipuls-peristaltic pumps, four Rheodyne 5020 PTFE rotary valves, an Omnifit 1003 three-way adapter and a Perkin-Elmer lambda-2 spectrophotometer equipped with a Hellma 178.52 QS flow-cell and connected to a PC with Pecss Software Package for UV/VIS/NIR spectroscopy.

Conditioning of the ion exchanger and flow-cell. The procedure previously described [17] was as follows: the Dowex-1 resin was cleaned with water and conditioned by triplicate treatment with 4 M hydrochloric acid, 2 M sodium hydroxide and water, which converted the resin to the chloride form. In order to retain the resin in the flow-cell the outlet of the cell was packed with glass wool. The cell itself was packed with resin up to 8 mm from the bottom, so that the

light beam could pass through the upper part of the packed resin.

Conditioning of the ion exchanger and oxidation column. The oxidation column consisted of a 1.5 cm length PTFE tube (0.2–0.3 cm i.d.) packed with DEAE Sephadex. The outlet of the tubing was packed with glass wool to retain the resin in the tube. The resin then was saturated with Folin–Ciocalteu's reagent 1% in water.

2.2. Procedure

The sample (2 ml) containing 80–500 ng ml^{-1} of total iron at pH=2 is inserted into the carrier stream (0.01 M nitric acid) at a flow-rate of 1.30 ml min^{-1} and split in two fractions (L_1 and L_2): one fraction in L_1 is immediately mixed at point M (Fig. 1(A)) with the reagent solution (0.25 M ammonium thiocyanate/ 0.01 m nitric acid) at a flow-rate of 1.30 ml min^{-1}. The iron(III)–thiocyanate complex formed in the mixing coil R is retained on the Dowex-1 anion exchanger located in the flow-cell. An increase in absorbance (A_1 in Fig. 1(B)) at 480 nm (the wavelength of maximum absorption of the iron–thiocyanate complex) and corresponding to Fe(III) is observed due to the retention of the complex. The other fraction (from L_2) goes first through an oxidation column (DEAE Sephadex saturated with Folin–Ciocalteu's reagent, OC in Fig. 1) where iron(II) is oxidized to iron(III) by Ce(IV). Only then this fraction is mixed at point M with the reagent solution and the formation of the iron(III)–thiocyanate complex takes place (in the mixing coil R) which gives rise to an additional increase in absorbance, corresponding the total increase in absorbance to the total iron (A_2 in Fig. 1(B)). The thiocyanate complex is quickly eluted both by formation of the iron–fluoride complex and by ionic displacement from the resin due to the high fluoride concentration in the eluent.

3. Results and discussion

3.1. Optimization of the FIA system

3.1.1. Retention/detection unit

According to the results obtained in a previous study [17], where several types of flow-cell were tested, a Hellma 178.52 QS flow-cell was used. Concerning the level of the resin in the flow-cell, a critical value corresponding to the height at which the light beam passes through the resin, a resin bed with 8 mm height was found the optimum.

The influence of the resin particle size and the degree of cross-linking was also checked and a resin with a mesh size of 50–100 and a cross-linkage of 4% did provide the maximum plateau height and minimum baseline absorbance.

3.1.2. Chemical variables

The chemical variables of the FI system are summarized in Table 1.

The pH of the solutions is an important variable since for pH<2 complex formation between Fe(III) and F^- is not complete [18] and for pH>2 $Fe(III)(OH)_3$ precipitation may occur. So the pH of all solutions except for the conditioning solution was kept at 2 by the addition of nitric acid. In the case of Ce(IV) solution, a more acidic medium was used (0.50 M in H_2SO_4) in order to avoid the precipitation of Ce(IV) hydroxide.

The variation of absorbance with the thiocyanate concentration was analysed experimentally, in batch conditions. It was noticed that the analytical signal increases with that concentration up to a certain value. This corresponds to the predominance of the complex $[Fe(III)(SCN)_4]^-$ in solution, as can be seen in Fig. 2, where the distribution of the various Fe(III)–thiocyanate complexes (calculated using for the formation

Table 1
Chemical variables in the FI system

	HNO_3 (M)	NH_4SCN (M)	NaF (M)	Ce(IV) (M)	H_2SO_4 (M)
Carrier	1×10^{-2}				
Reagent solution	1×10^{-2}	0.25			
Eluent solution	1×10^{-2}	0.25	0.125		
Conditioning solution				1.78×10^{-4}	0.50

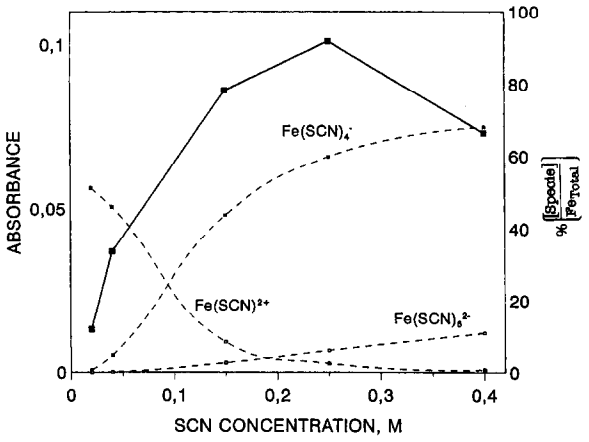

Fig. 2. Absorbance values at λ=481.0 nm (■) and distribution of various Fe(III)–thiocyanate complexes (- - -) as a function of thiocyanate concentration.

constants the values in [18]) as well as absorbance values are plotted as a function of the thiocyanate concentration.

So a thiocyanate concentration of 0.25 M was used in the reagent and eluent solutions. The presence of thiocyanate in the eluent solution was important in order to have a constant baseline throughout the FI recordings.

An acidic solution of SCN^- plus fluoride ion was chosen as the eluent. Using the values presented in Table 1 the iron–thiocyanate complex was completely eluted in a few seconds, probably by both formation of the iron–fluoride complex and ionic displacement from the resin.

The Folin–Ciocalteu's reagent must be regenerated following the oxidation of Fe(II) to Fe(III). This is accomplished by the use of a cerium(IV) solution. The value presented in Table 1 for the Ce(IV) concentration corresponds to the minimum value needed to regenerate the Folin–Ciocalteu's reagent, as was experimentally determined following the variation of absorbance of an iron(II) sample after oxidation as a function of the Ce(IV) concentration in the conditioning solution.

3.1.3. FI variables

Since the formation of the Fe(III)–thiocyanate complexes is very fast, the length of the reaction coil R, where complex formation occurs, (see Fig. 1(A)), has no influence on the measured signal. A 2 cm coil was used in order to shorten the residence time.

A value of 1.30 ml min^{-1} was adopted for the flow-rate as a compromise between sampling frequency and reproducibility: the retention of the complex on the resin is instantaneous, so the flow-rate does not affect the peak height; nevertheless, values higher than 1.30 ml min^{-1} should not be used, since the baseline becomes more irreproducible when the residence time decreases.

The sample volume influences the analytical signal changing the plateau height as well as the residence time and the blank signal: increasing sample volumes L_1 and L_2 (Fig. 1(A)) result in proportionally increasing peak heights, residence times and blank signals. L_1=L_2=1 ml was considered to be the optimum sample volume.

3.2. Features of the method

The optimum conditions just discussed for the variables influencing the FI system were used in establishing suitable calibration curves. These were obtained by plotting absorbance values A_1 and A_2 (after subtracting the blank signal A_0, in Fig. 1(B)) as a function of the iron(III) concentration. The features of calibration graphs are summarized in Table 2.

The method presents a determination limit of 80 μg l^{-1}, a linear range of 80–500 μg l^{-1} and a precision of ±5 μg l^{-1}.

At the low pH used iron(II) oxidation is a slow process. However, the oxidation of iron(II) is faster in

Table 2
Features of the calibration graphs

Measured parameter	Linear range (μg ml^{-1})	Intercept	Slope	r^2	RSD [a] (%)
A_1	0.08–0.5	-5×10^{-3}	0.39	0.995	3.4
A_2	0.08–0.5	-4×10^{-3}	0.80	0.999	1.7

[a] Concentration.

Table 3
Concentration range of selected major ions in natural waters [20]

Ion	Average values	
	Fresh water ($M\times10^3$)	Sea water ($M\times10^3$)
Cl^-	0.22	550
SO_4^{2-}	0.12	28
F^-	0.0053	0.07
Na^+	0.27	470
Mg^{2+}	0.34	54

the presence of thiocyanate that stabilizes iron(III) in the form of $[Fe(III)(SCN)_4]^-$ complex. A standard solution of iron(II) (free of iron(III)) is being used in order to evaluate any unwanted oxidation in the FI manifold whose signal has to be subtracted.

3.3. Application to synthetic and real samples

The proposed approach is to be used in the determination of iron (III) and iron(II) in natural water samples, therefore, possible interferences from the major components of natural waters were checked by varying their concentration in the range usually found in fresh water and sea water (Table 3). Interferences may be due to either changes in ionic strength or complexation of the major anions and cations with iron and thiocyanate, respectively. The cations Ca^{2+} and K^+ were not included since they do not form complexes with thiocyanate. The same applies for sodium but its variation accounts (together with the Cl^- variation) for the values of ionic strengths found in estuaries and seas.

In all the above situations no interferences were found, i.e., the measured signal remained constant within the limits of the precision of the method.

Other cations that form stable complexes with thiocyanate may interfere. However, no interference was found in the presence of copper in the concentration range 6.3×10^{-8}–6.3×10^{-6} M. Possible interferences from other cations, such as Co(II), Hg(II), Bi(III), are very unlikely since they are found in most natural waters at even lower concentrations.

Due to the high concentration of thiocyanate present in the medium, interference by other anions that exist in the natural sample at lower concentrations is not probable. Iodide and nitrite ions are possible interferences of the analytical method because they can reduce iron(III) to iron(II) [19] but they have not been detected in our oxic natural water samples.

The kinetics of retention of the $[Fe(III)(SCN)_4]^-$ complex in the resin decreases with increased ionic strength (I) of the samples which corresponds to a less sharp rise of absorbance. This was noticed particularly for estuarine samples with chloride and sodium concentrations close to 0.5 M. So a longer retention time was necessary until the absorbance plateau was reached.

The recovery of iron(III) and iron(II) added to synthetic and natural samples for oxic zones with an iron content below the detection limit of the method

Table 4
Recovery of Fe(II) and Fe(III) added to synthetic and natural samples within an error of ≤5%

Sample	Origin	I	Fe(II) added ($\mu g\ ml^{-1}$)	Fe(II) recovery (%)	Fe(III) added ($\mu g\ ml^{-1}$)	Fe(III) recovery (%)	Total recovery (%)
1	Synthetic	0.01 [a]	0.10	103			
2	Synthetic	0.01	0.20	92			
3	Synthetic	0.01	0.20	99			
4	Synthetic	0.01	0.30	102			
5	Synthetic	0.01	0.40	108			
6	Synthetic	0.01	0.10	116	0.30	103	106
7	Synthetic	0.01	0.25	109	0.25	99	104
8	Synthetic	0.056 [b]	0.30	95	0.10	119	101
9	Tejo estuary	0.70	0.15		0.20		97
10	Tejo estuary	0.70	0.20		0.15		97

[a] HNO_3 0.01 M.
[b] NaCl 5.6×10^{-2} M+HNO_3.

is being presented in Table 4. As can be seen, the recovery of Fe(II) added to samples averaged to 103%, while that of total iron averaged to 101%, so the method presents good accuracy.

4. Conclusions

The method proposed enables discrimination between Fe(III) and Fe(II) taking advantage of a redox minicolumn housed in the loop of one of the valves: from two absorbance measurements corresponding to a single injection, the Fe(III) and total iron content are determined, the Fe(II) concentration being given by difference.

The method has good selectivity owing to the use of the anionic resin and the high concentration of thiocyanate and fluoride in the medium which prevents the retention of most anions. Good sensitivity is achieved by in situ concentration of $[Fe(III)(SCN)_4]^-$ complex in the retention/detection approach used, the determination limit being $80\,\mu g\,l^{-1}$ and the linear range of response $80–500\,\mu g\,l^{-1}$.

Applications to synthetic and natural water samples with low pH show the usefulness of the overall approach: the recovery of iron(II) added to samples averaged 103% while that of total iron (iron(II)+iron(III)) averaged 101%.

Acknowledgements

The authors thank CRUP (Portugal) and MEC (Spain) for the award of a grant to facilitate collaboration between the two laboratories.

References

[1] W. Stumm, L. Sigg and B. Sulzberger, Chemistry of the Solid–Water Interface, Wiley, New York, 1992.
[2] M.D. Luque de Castro, Talanta, 33 (1986) 45.
[3] M.D. Luque de Castro, D.W. Bryce and A. Izquierdo, Talanta, 42 (1995) 1215.
[4] M. Valcárcel and M.D. Luque de Castro, Non-Chromatographic Continuous Separation Techniques, Royal Society of Chemistry, London, 1991.
[5] J.W. Dieker and W.E. Van der Linden, Anal. Chim. Acta, 114 (1980) 267.
[6] E.B. Milosavljevic, L. Solujic, J.H. Nelson and J.L. Hendrix, Fresenius' Z. Anal. Chem., 330 (1988) 614.
[7] J.L. Burguera and M. Burguera, Anal. Chim. Acta, 161 (1984) 375.
[8] B.P. Bubnis, M.R. Straka and G.E. Pacey, Talanta, 30 (1983) 841.
[9] A.T. Faizullah and A. Townshend, Anal. Chim. Acta, 167 (1985) 225.
[10] J. Alonso, J. Bartrolí, M. Del Valle and R. Barber, Anal. Chim. Acta, 219 (1989) 345.
[11] A.T. Senior and J.D. Glennon, Anal. Chim. Acta, 196 (1987) 333.
[12] E.G. Sarantonis and A. Townshend, Anal. Chim. Acta, 184 (1986) 311.
[13] E.A. Virginia, J.S. Kenneth and C.H. Kenneth, Anal. Chem., 63 (1991) 893.
[14] J.S. Cosano, J.L. Calle, J.L. Pinillos, P. Linares and M.D. Luque de Castro, Tecn. Lab., 147 (1988) 32.
[15] P. Cañizares, M.T. Tena and M.D. Luque de Castro, Anal. Chim. Acta, 323 (1996) 55.
[16] M. Valcárcel and M.D. Luque de Castro, Flow-Through (Bio)Chemical Sensors, Elsevier, Amsterdam, 1994.
[17] F. Làzaro, M.D. Luque de Castro and M. Valcarcel, Anal. Chim. Acta, 219 (1989) 231.
[18] A.E. Martell and R.M. Smith, Critical Stability Constants, vol. 4, Plenum, New York, 1976.
[19] F. Snell and C.T. Snell, Colorimetric Methods of Analysis, 3rd edn., Vol. II, Van Nostrand, New York, 1954.
[20] W. Stumm and J.J. Morgan, Aquatic Chemistry, 3rd edn., Wiley, New York, 1996.