The application of multicommutated flow techniques to the determination of iron

Carmen Pons, Rafael Forteza, António O.S.S. Rangel, Víctor Cerdà

New flow techniques such as multicommutated flow-injection analysis (MCFIA), multi-syringe FIA (MSFIA) and multi-pumping flow systems (MPFSs) have been developed. The low reagent consumption achieved by these techniques should be highlighted, as they can be regarded as environmentally friendly alternatives to conventional FIA. We present several applications of these novel flow techniques to the determination of iron.

Carmen Pons, Rafael Forteza, Víctor Cerdà*
Department of Chemistry, University of the Balearic Islands, Carretera de Valldemossa Km.7.5, E-07122 Palma de Mallorca, Spain

António O.S.S. Rangel
Escola Superior de Biotecnologia, Universidade Católica Portuguesa, Rua Dr. António Bernardino de Almeida, 4200-072 Porto, Portugal

*Corresponding author.
Tel.: +34 971173261;
Fax: +34 971173426;
E-mail: victor.cerda@uib.es

Keywords: MCFIA; MPFS; MSFIA; Multicommutated flow-injection analysis; Multi-pumping flow system; Multi-syringe flow-injection analysis

Introduction

The emergence of flow techniques in the early 1950s played a major role in routine analysis, since they provided precise, accurate and rapid measurements with minimal sample handling. Furthermore, sample volume and reagent consumption were decreased with regard to batch methods.

In past years, new flow techniques, such as multicommutated flow-injection analysis (MCFIA) [1,2], multi-syringe flow-injection analysis (MSFIA) [3,4] and multi-pumping flow-injection systems (MPFSs) [5,6] have arisen as possible alternatives to classical flow techniques (i.e. segmented flow analysis (SFA) [7], flow-injection analysis (FIA) [8] and sequential injection analysis (SIA) [9]). However, FIA is still the most widely used technique. Moreover, the number of applications reported on FIA during its first years is much higher than those on SIA, MCFIA, MSFIA and MPFS. This fact can be attributed to the easy implementation of FIA, since this technique does not require a computer to control the system [10].

Minimization of reagent consumption (green chemistry) and the monitoring of environmental parameters are among the currents trends in analytical chemistry. In this sense, multicommutated techniques (MCFIA, MSFIA and MPFS) are especially suitable for these purposes, since reagents are propelled to the system only when necessary and they allow development of fully automated systems with a high injection throughput. Multicommutated techniques have been successfully applied to the determination of metals [11–14], pesticides [15,16], pharmaceutical preparations [17,18] and nutrients [19–22] in different sorts of samples (i.e. food [12], soils [13], environmental samples [11,19–22]).

Nutrients are a key parameter in the evaluation of water quality. Iron is an essential micronutrient for organisms, as it is involved in many biological processes. However, the speciation analysis of iron is also of great interest in the study of the aqueous environmental chemistry of trace elements [23,24].

There are several references in the literature to the determination of iron exploiting multicommutated techniques [13,25–28]. Nevertheless, these works have not been applied to the determination of low levels of iron. Taking into consideration the low concentrations of iron in some media, different strategies, such as solid-phase extraction (SPE), have been proposed in order to achieve lower limits of detection (LODs). We present in this article some multicommutated systems that we developed for the determination, speciation analysis and SPE of iron [29–32]. Moreover, we discuss in detail the properties of these systems and their advantages over the conventional flow techniques.

Multicommutated systems for the determination of iron

Fig. 1 shows different multicommutated flow systems that we developed to carry out the spectrophotometric determination, SPE and speciation analysis of iron [29–32]. In these assemblies, ammonium thiocyanate was used as chromogenic reagent for Fe(III). The determination of total iron was achieved by the on-line oxidation of iron(II) to iron(III) with a hydrogen-peroxide stream. A diode-array PC-plug-in spectrometer with a PC 2000 A/D card (Ocean Optics, Dunedin, FL, USA) was used as detector.

Multicommutated flow-injection system

The replacement of six-port rotary valves used in FIA assemblies by three-way solenoid commutation valves in MCFIA introduces flexibility and saves reagents, since they are injected into the system only when necessary. Moreover, the injected sample volume can be selected by controlling the commutation timing via software. [1,2].

An MCFIA set-up is shown in Fig. 1(a) [29]. This system allows the determination and the speciation analysis of iron in a wide range of concentrations. It comprises a peristaltic pump (Ismatec, Type Reglo Digital, Switzerland) and six three-way solenoid commutation valves (N-Research, Caldwell, N.J., USA).

The determination of the lowest iron concentrations benefits from the retention of the analyte onto a chelating resin (iminodiacetic groups), which has been placed in a poly(methyl methacrylate) micro-column (Fig. 2(a)). For this purpose, commutation valve V4 should be in Off position.

Analytical signals obtained exploiting MCFIA and SPE are shown in Fig. 3(a). By contrast, valve V4 should be in the On position when the determinations of high levels of Fe(III) and/or Fe(II) or cleaning procedures are required.

Time-consuming steps, such as the replacement of the injection coil or the periodical unloading of the liquid-driver, are not required in MCFIA. For this reason, this technique is especially suitable for SPE. However, the use of a peristaltic pump represents the main disadvantage of this system, since the flexible tubing of the peristaltic pump needs to be replaced periodically. MSFIA avoids this shortcoming.

Multi-syringe flow-injection analysis

MSFIA combines the multi-channel operation and high injection throughput of FIA with the robustness and the versatility of SIA. Thus, the basic element of MSFIA is a multi-syringe burette (Crison Instruments, Alella, Barcelona, Spain) that allows the simultaneous movement of four syringes (analogous to those used in SIA assemblies), which are connected *en bloc* to the same stepper motor. Furthermore, three-way isolation valves

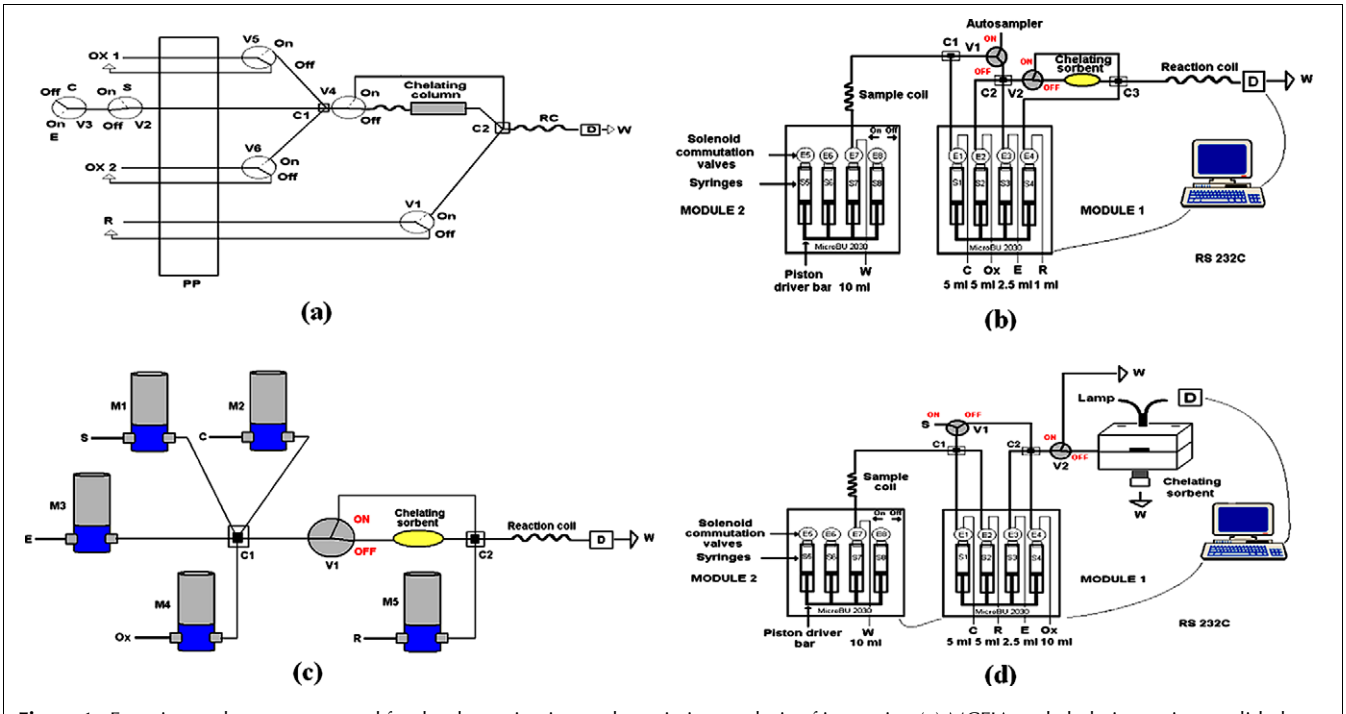

Figure 1. Experimental set-up proposed for the determination and speciation analysis of iron using (a) MCFIA and chelating resin as solid phase, (b) MSFIA and chelating disks as solid phase, (c) MPFS and chelating disks as solid phase, and (d) MSFIA and an optical fiber reflectance sensor. S: Sample; C: Carrier; E: Eluent; R: Chromogenic reagent; Ox: Oxidizing agent; W: Waste; D: Detector; PP: Peristaltic pump; V1-V6: commutation valves; M1-M5: micro-pumps; C1-C3: cross junctions.

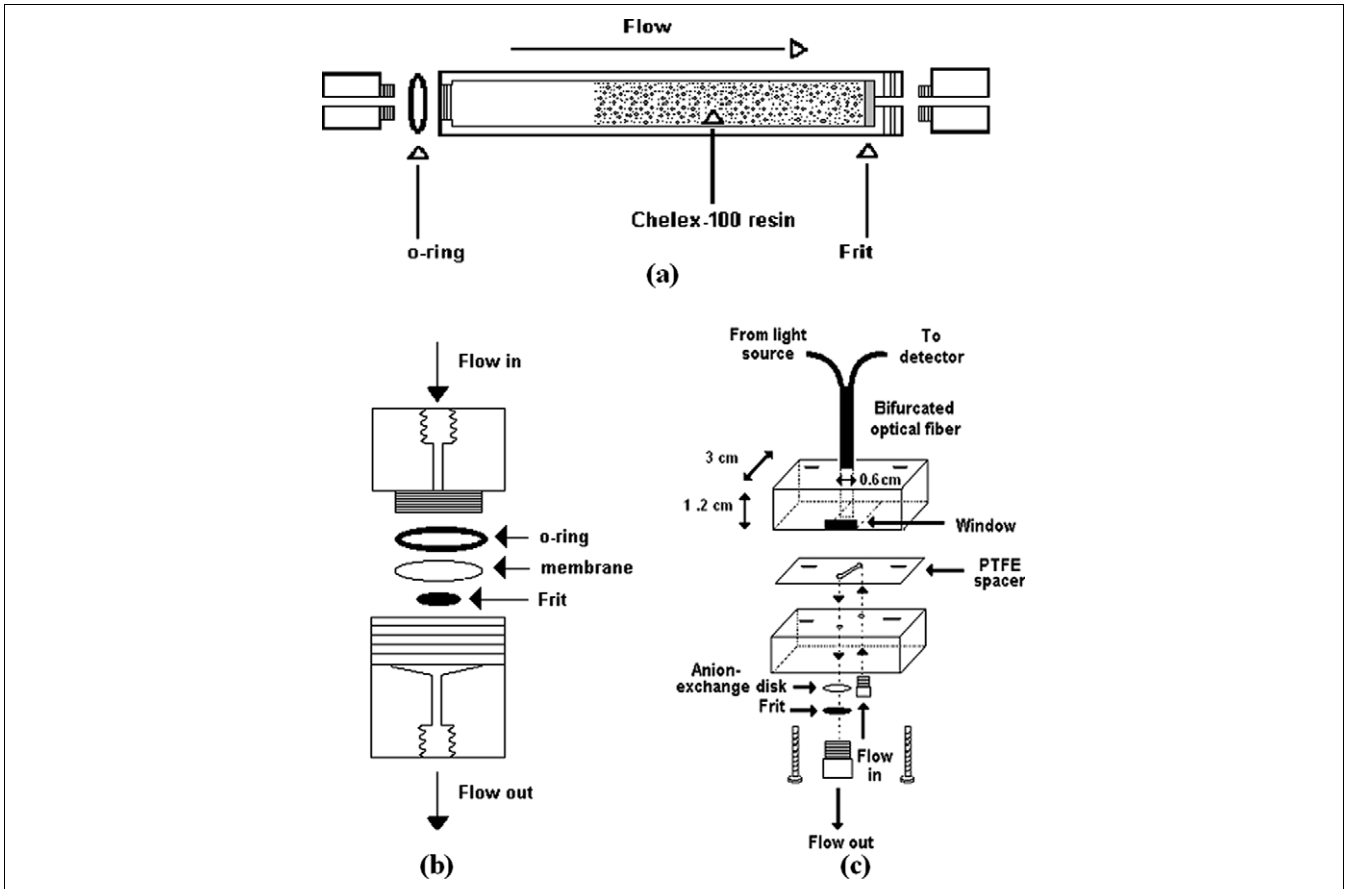

Figure 2. Poly(methyl methacrylate) devices for the solid-phases: (a) Resin. Spectrophotometric detection takes place after the elution of the retained species; (b) SPE disk. Spectrophotometric detection takes place after the elution of the retained species; (c) SPE disk. Detection is based on reflectance measurements and takes place at the SPE disk surface.

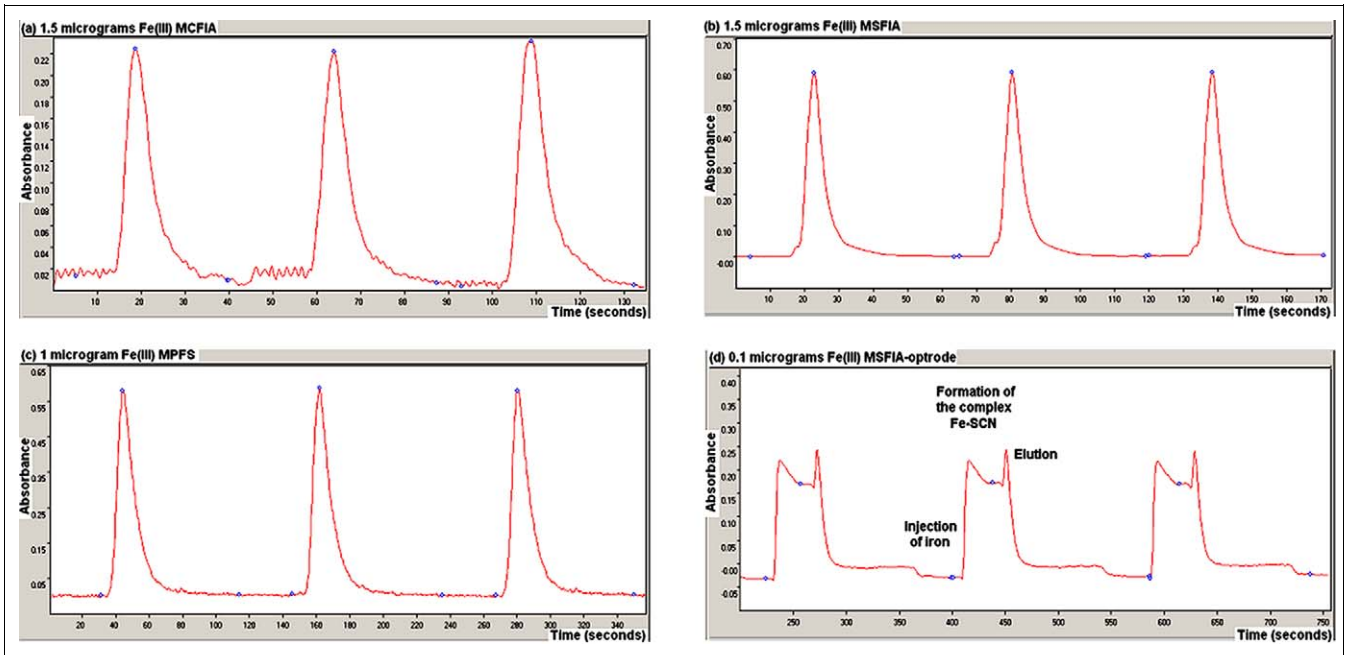

Figure 3. Analytical signals obtained: (a) with an MCFIA system (1.5 μg of Fe(III) were preconcentrated); (b) with a MSFIA system (1.5 μg of Fe(III) were preconcentrated); (c) with a MPFS system (1.0 μg of Fe(III) were preconcentrated); (d) with an optrode coupled to a MSFIA system (0.1 μg of Fe(III) were preconcentrated).

have been placed on the head of each syringe with the aim of increasing the versatility of the technique and reducing reagent consumption [3,4].

Fig. 1(b) shows an MSFIA system that comprises two multi-syringe modules and two additional commutation valves (V1 and V2) [30], which are responsible, respectively, for injecting the required sample volume and for delivering the sample slug and/or reagents to the solid-phase when pre-concentration should take place. Chelating disks have been used as solid phase. The chelating SPE disk has been placed in a poly(methyl methacrylate) device (Fig. 2(b)). The use of SPE disks offers several advantages over the conventional resin, such as higher injection throughput and lower back-pressure. Analytical signals obtained by using MSFIA and SPE can be seen in Fig. 3(b).

In SPE, high sample volumes are required so that steps such as sample coil washing and filling can decrease the injection throughput. Nevertheless, the incorporation of an additional multi-syringe burette increases the possibilities within the system. Therefore, the decrease in the injection throughput of the proposed system is not noticeable since the sample is placed in a different module from the reagents.

Multi-pumping flow system

Multi-pumping flow systems (MPFSs) are based on using solenoid micro-pumps for propelling liquids. These low-cost, robust and reliable devices are responsible for both sample-reagent introduction and manifold commutation. Minimal reagent consumption is achieved, since each micro-pump is operated individually in inserting the solutions. In comparison with other flow techniques, the pulsed flow of the micro-pumps is better and faster at homogenizing the reaction zone [5,6].

A multi-pumping flow system (MPFS) set-up can be seen in Fig. 1(c) [31]. To develop this system, five solenoid micro-pumps (Bio-Chem Valve Inc., Boonton, New Jersey, USA) and a solenoid valve (V1) (Takasago Electric Inc, Nagoya, Japan) were required. This set-up allows the determination, SPE and speciation analysis of iron in a wide range of concentrations. The chelating SPE was placed in the poly(methyl methacrylate) shown in Fig. 2(b). This technique is highly versatile, robust and simple.

Analogously to MCFIA, MPFS is suitable for SPE. Nevertheless, the injection throughput is lower than with MSFIA since the maximum flow-rate attainable is decreased through the back-pressure from the chelating disk. We also recommend periodic re-calibration of the solenoid micro-pumps. Results obtained for SPE of Fe(III) (Fig. 3(c)) are very similar to those obtained using MCFIA and MSFIA.

Optical-fiber reflectance sensor coupled to MSFIA

In the systems shown in Fig. 1(a,b,c), spectrophotometric detection takes place after elution of the retained species. The preconcentration capabilities gained are partially lost as a consequence of the dispersion effect.

Lower LODs can be obtained by using optical-fiber chemical sensors (optrodes), which are usually based on detecting a change in absorbance or reflectance of an

Table 1. Analytical parameters and optimised experimental variables

Parameter	**MCFIA (Fig. 1(a)) [8]**	**MSFIA (Fig. 1(b)) [9]**	**MPFS (Fig. 1(c)) [10]**	**MSFIA (Fig. 1(d)) [11]**
Detection technique	Spectrophotometry	Spectrophotometry	Spectrophotometry	Solid-phase reflectometry
Sorbent	Chelex 100 resin	Chelex 100 discs	Chelex 100 discs	Chelex 100 discs
[NH_4SCN] (mol l^{-1})	0.5	1.25	1.5	0.75
Eluent	2 mol l^{-1} HNO_3	2 mol l^{-1} HCl	2 mol l^{-1} HCl	2 mol l^{-1} HCl
[H_2O_2] (mol l^{-1}) in procedures with SPE	0.025	0.025	0.05	0.25
[H_2O_2] (mol l^{-1}) in procedures without SPE	1.2 mol l^{-1} in 2 mol $l^{-1}HNO_3$	0.025	0.05	–
Pre-concentration flow-rate (ml min^{-1})	1.5	5	1	1
Elution flow-rate (ml min^{-1})	2.5	2.5	1	1
Maximum sampling volume tested (ml)	10	30	20	6
Detection limit (ng) with SPE	84	19	10	1.2
Detection limit (μg l^{-1}) with SPE (referred to the max. sampling flow-rate tested)	8.3	0.6	0.5	0.2
Working range (ng) with SPE	84–5000	19–3000	10–1750	1.2–250
Working range (mg l^{-1}) without SPE Fe(III)	1–30	0.1–20	0.05–10	–
Working range (mg l^{-1}) without SPE Total Fe	2–40	0.2–35	0.2–15	–
Repeatability (%) with SPE/n	2.5/9	2/11	1.6/10	2/9
Repeatability (changing the sorbent) (%) /n	5/5	2.2/5	5.4/5	3.6/5
Injection throughput/sample volume (ml) (injections h^{-1}) with SPE	9/5	10/5	6/5	5/5
Injection throughput (injections h^{-1}) without SPE	60	68	120	–

immobilized reagent interfaced to an instrument via optical fibers [33,34]. Fig. 1(d) shows a combination of MSFIA with an optical-fiber reflectance sensor. This system comprises two multi-syringe modules, two additional solenoid commutation valves and a sandwich-shape flow cell [32] (Fig. 2(c)) that contains the chelating SPE disk.

First, iron(III) is retained onto a chelating SPE. Afterwards, an ammonium thiocyanate stream is delivered to the system in order to form the complex Fe-SCN, which is detected by means of diffuse reflectance measurements. Iron is then eluted with hydrochloric acid so that the chelating SPE is regenerated and ready for another injection. The optrode response can be seen in Fig. 3(d).

Comparison of the multicommutated systems

The analytical parameters and optimized experimental variables of the systems depicted in Fig. 1 are summarized in Table 1. According to the LODs obtained, the four systems developed are suitable for the determination of iron in several natural water systems (e.g., the concentrations of total dissolved iron in polluted urban clouds [35] and average river water [36] are 224 μg/l and 40 μg/l, respectively).

The methodologies presented in this article have been validated by replicate analysis of certified water materials and spiked seawater samples.

However, the determination and the speciation analysis of iron in seawater are of interest since iron may be the limiting nutrient for phytoplankton growth in certain ocean regions. In this sense, it has been suggested that oceanic iron fertilization could be feasible for removing green-house carbon dioxide from the atmosphere [37].

The LOD achieved by the system shown in Fig. 1 (d) (i.e. 0.2 μg/l) allows the determination and the speciation analysis of iron in near-shore waters. Thus, the concentrations of total filterable iron in coastal water samples from the northeastern Mediterranean are in the range 22.3–0.21 μg/l [38].

Conclusions

Low reagent consumption is achieved by multicommutated flow techniques, which can be regarded as an environmentally friendly alternative to FIA. However, these systems can also be adapted to monitoring of environmental parameters.

The methodologies developed have proved applicable in several natural water systems. The low LOD achieved by the combination of MSFIA with an optical-fiber chemical sensor allows the determination of iron in near-shore waters. In this sense, the determination and the speciation analysis of iron in seawater is essential to understand biogeochemical cycling in the ocean and the effect of iron on phytoplankton growth.

Acknowledgement

The authors are grateful to the MCyT (Ministerio de Ciencia y Tecnología) for supporting project CTQ2004-01201 and to CRUP (Conselho de Reitores das Universidades Portuguesas) through Acção Integrada Luso-Espanhola n° E-146/04. Carmen Pons thanks MCyT for awarding a Ph.D. grant.

References

[1] B.F. Reis, M.F. Giné, E.A.G. Zagatto, J.L.F.C. Lima, R.A. Lapa, Anal. Chim. Acta 293 (1994) 129.
[2] M. Catalá Icardo, J.V. García Mateo, J. Martínez Calatayud, Trends Anal. Chem. 21 (2002) 366.
[3] V. Cerdà, J.M. Estela, R. Forteza, A. Cladera, E. Becerra, P. Altimira, P. Sitjar, Talanta 50 (1999) 695.
[4] B. Horstkotte, O. Elsholz, V. Cerdà, J. Flow Injection Anal. 22 (2005) 99.
[5] R.A.S. Lapa, J.L.F.C. Lima, B.F. Reis, J.L.M. Santos, E.A.G. Zagatto, Anal. Chim. Acta 466 (2002) 125.
[6] J.L.F.C. Lima, J.L.M. Santos, A.C.B. Dias, M.F.T. Ribeiro, E.A.G. Zagatto, Talanta 64 (2004) 1091.
[7] L.J. Skeggs, Am. J. Clin. Path. 28 (1957) 311.
[8] J. Ruzicka, E.H. Hansen, Anal. Chim. Acta 78 (1975) 145.
[9] J. Ruzicka, G.D. Marshall, Anal. Chim. Acta 237 (1990) 329.
[10] V. Cerdà, J.M. Estela, Int. J. Environ. Anal. Chem. 85 (2005) 231.
[11] G. de Armas, M. Miró, A. Cladera, J.M. Estela, V. Cerdà, Anal. Chim. Acta 455 (2002) 149.
[12] E. Ródenas-Torralba, Á. Morales-Rubio, M. de la Guardia, Food Chem. 91 (2005) 181.
[13] D.M.C. Gomes, M.A. Segundo, J.L.F.C. Lima, A.O.S.S. Rangel, Talanta 66 (2005) 703.
[14] L.O. Leal, R. Forteza, V. Cerdà, Talanta 69 (2006) 500.
[15] G. de Armas, M. Miró, J.M. Estela, V. Cerdà, Anal. Chim. Acta 467 (2002) 13.
[16] J.F. Ventura-Gayete, S. Armenta, S. Garrigues, Á. Morales-Rubio, M. de la Guardia, Talanta 68 (2006) 1700.
[17] A.C.B. Dias, J.L.M. Santos, J.L.F.C. Lima, E.A.G. Zagatto, Anal. Chim. Acta 499 (2003) 107.
[18] K.L. Marques, J.L.M. Santos, J.L.F.C. Lima, J. Pharm. Biomed. Anal. 39 (2005) 886.
[19] F.R.P. Rocha, B.F. Reis, Anal. Chim. Acta 409 (2000) 227.
[20] J. Klimundova, R. Forteza, V. Cerdà, Int. J. Environ. Anal. Chem. 83 (2003) 233.
[21] I.P.A. Morais, M. Miró, M. Manera, J.M. Estela, V. Cerdà, M.R.S. Souto, A.O.S.S. Rangel, Anal. Chim. Acta 506 (2004) 17.
[22] M.I.G.S. Almeida, M.A. Segundo, J.L.F.C. Lima, A.O.S.S. Rangel, Talanta 64 (2004) 1283.
[23] S.J. Ussher, E.P. Achterberg, P.J. Worsfold, Environ. Chem. 1 (2004) 67.
[24] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, sixth ed., John Wiley and Sons, Chichester, West Sussex, UK, 1999 p. 775.
[25] B.F. Reis, M. Knochen, G. Pignalosa, N. Cabrera, J. Giglio, Talanta 64 (2004) 1220.
[26] M.A. Feres, B.F. Reis, Talanta 68 (2005) 422.
[27] F.R.P. Rocha, P.B. Martelli, B.F. Reis, Talanta 55 (2001) 861.
[28] F. Albertús, A. Cladera, V. Cerda, Analyst (Cambridge, UK) 125 (2000) 2364.

[29] C. Pons, M. Miró, E. Becerra, J.M. Estela, V. Cerdà, Talanta 62 (2004) 887.
[30] C. Pons, R. Forteza, V. Cerdà, Anal. Chim. Acta 524 (2004) 79.
[31] C. Pons, R. Forteza, V. Cerdà, Anal. Chim. Acta 550 (2005) 33.
[32] C. Pons, R. Forteza, V. Cerdà, Anal. Chim. Acta 528 (2005) 197.
[33] A.J. Guthrie, R. Narayanaswamy, D.A. Russell, Analyst (Cambridge, UK) 113 (1988) 457.
[34] M. Miró, W. Frenzel, J.M. Estela, V. Cerdà, Analyst (Cambridge, UK) 126 (2001) 1740.
[35] J.W. Munger, J.M. Waldman, D.J. Jacob, M.R. Hoffmann, J. Geophys. Res. 88 (1983) 5109.
[36] S.R. Taylor, S.M. McLennan, The Continental Crust: Its Composition and Evolution, Blackwell, Oxford, UK, 1985.
[37] J.H. Martin, S.B. Fitzwater, Nature (London) 331 (1988) 341.
[38] M. Öztürk, N. Bizsel, E. Steinnes, Marine Chem. 81 (2003) 19.