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Talanta 66 (2005) 210–217

Talanta

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The use of anion-exchange disks in an optrode coupled to a multi-syringe flow-injection system for the determination and speciation analysis of iron in natural water samples

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Received 29 June 2004; received in revised form 22 October 2004; accepted 16 November 2004
Available online 24 December 2004

Abstract

A combination of multi-syringe flow-injection analysis (MSFIA) technique with an optical fibre reflectance sensor for the determination of iron in water samples has been developed in this work. Anion-exchange solid phase extraction (SPE) disks have been used as solid phase. Ammonium thiocyanate has been chosen as chromogenic reagent for Fe(III). The complex $Fe[SCN]_6^{3-}$ is retained onto the SPE disk and spectrophotometrically detected at 480 nm. The complex is eluted with 0.25 mol l^{-1} hydrochloric acid in 75% ethanol. Total iron can be determined by oxidising Fe(II) to Fe(III) with hydrogen peroxide.

A mass calibration was run within the range of 0.4–37.5 ng. The detection limit ($3s_b/S$) was 0.4 ng. The repeatability (RSD), calculated from 9 replicates using 0.5 ml injections of a 25 $\mu g\, l^{-1}$ concentration, was 3.6%. The repeatability between five anion-exchange disks was 5.4%. An injection throughput of 7 injections per hour for a sampling volume of 1 ml has been achieved.

The applicability of the proposed methodology in natural water samples has been proved.

The properties of anion-exchange and chelating SPE disks have been studied and compared.

Keywords: Optical fibre reflectance sensor; Multisyringe flow injection analysis (MSFIA); Anion exchange disk; Chelating disk; Iron; Speciation analysis

1. Introduction

Solid-phase extraction (SPE) technique can be regarded as a suitable strategy to achieve trace enrichment (concentration), matrix simplification and medium exchange [1]. This technique usually involves the elution of the retained species in order to carry out the detection so that the pre-concentration capabilities gained are partially lost [2]. This shortcoming can be avoided by the use of flow-through optical fibre chemical sensors or optrodes which are usually based on the detection of a change in the optical properties of an immobilised reagent interfaced to an instrument via optical fibres. These sensors have been widely developed since their great flexibility, possibility for miniaturization, low cost and rugged construction allows to perform the analysis in situ [3,4].

Recently, a novel optical fibre reflectance sensor coupled to multi-syringe flow-injection analysis (MSFIA) has been developed by the authors for the determination and speciation analysis of trace levels of iron [5]. This system combines the advantages of MSFIA technique [6,7] such as a high sample throughput, robustness, reagent saving and versatility with those given by optrodes such as high sensitivity and reliability. Iron was pre-concentrated onto a chelating SPE disk placed into a sandwich-shape cell. The advantages of chelating disks over the conventional resin have been previously discussed by the authors [8] In this sense these disks offer higher throughput, better repeatability and lower backpressure. According to Poole [1], SPE disks were developed with the aim to provide higher sample processing rates and re-

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doi:10.1016/j.talanta.2004.11.009

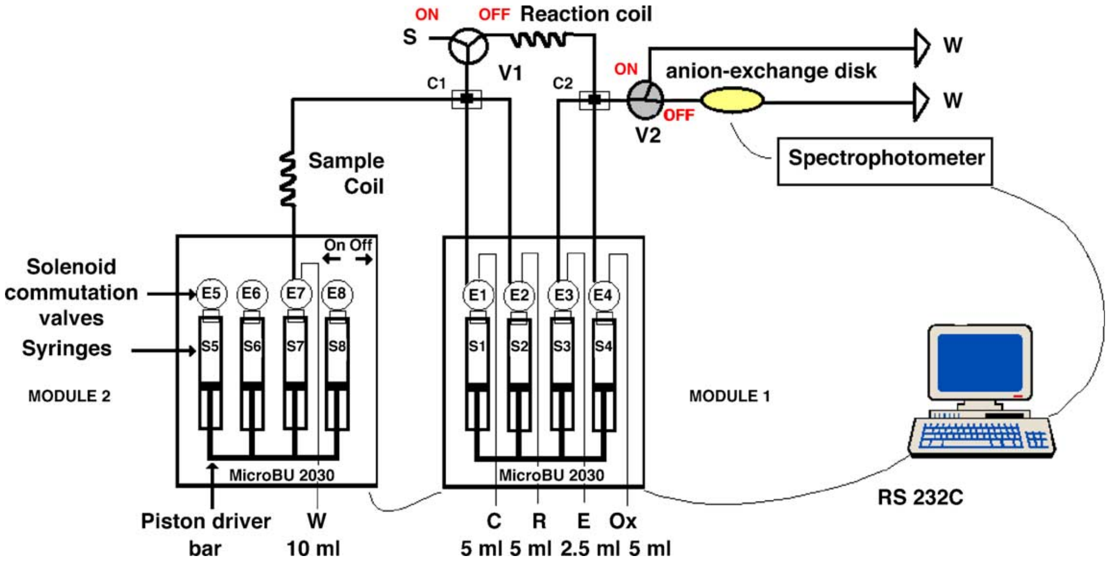

Fig. 1. Experimental set-up proposed for the determination of iron. C: Carrier; E: Eluent; R: Chromogenic reagent; Ox: Oxidizing agent; W: Waste; V1 and V2: commutation valves; C1 and C2: cross junctions; Sample coil: 8 m long × 1.5 mm i.d. Tubing connecting C1–V1: 9 cm long × 0.8 mm i.d; reaction coil: 7 cm long × 0.8 mm i.d; C2–V2: 4 cm long × 0.8 mm i.d; V2-anion-exchange disk: 15 cm long × 0.8 mm i.d.

duce plugging due to suspended particles and matrix components. Only a few references were found, in the literature, on the use of optrodes applied to the determination iron [9,10]. However, these references deal with an approach which is very different from ours.

In this paper, an optrode coupled to MSFIA using anion-exchange disks as solid phase for the determination and speciation analysis of iron in natural water samples is described. In this system, Fe(III) merges with a thiocyanate stream in order to form the complex $\mathrm{Fe[SCN]_6}^{3-}$ which is retained onto the anion-exchange disk and spectrophotometrically detected at 480 nm. This approach is very similar to the aforementioned one [5]. Thus, the main differences between both systems are consequence of the SPE disk used. One of the aims of this work has been to study and compare the properties of these two systems.

2. Experimental

2.1. Reagents

All chemicals were of analytical reagent grade. Millipore-purified water was used throughout. Stock standard solution of 100 mg $\mathrm{l^{-1}}$ iron(III) was prepared by dissolving 0.863 g of ammonium iron(III) sulphate dodecahydrate in water and 10 ml of concentrated hydrochloric acid were added before making to volume to 1000 ml. A stock standard solution of 100 mg $\mathrm{l^{-1}}$ iron(II) was freshly prepared by dissolving 0.702 g of ammonium iron(II) sulphate hexahydrate in water and 0.1 mol of sulphuric acid were added before diluting to 1000 ml. Working standards were prepared by diluting the stock solutions with a suitable buffer (final concentration: 0.1 mol $\mathrm{l^{-1}}$). A 0.75 mol $\mathrm{l^{-1}}$ ammonium thiocyanate was employed as a chromogenic reagent for Fe(III) determination. A 0.25 mol $\mathrm{l^{-1}}$ HCl solution in 75% ethanol was used as eluent stream. A 0.25 mol $\mathrm{l^{-1}}$ hydrogen peroxide solution was chosen as an oxidising agent to convert $\mathrm{Fe^{2+}}$ into $\mathrm{Fe^{3+}}$.

The anion-exchange disks were from 3M Empore (Ref. 2252).

Finally, 1 mol $\mathrm{l^{-1}}$ formic acid-formate buffer of pH 2.5 was prepared for pH adjustment of standard solutions and samples [11].

2.2. Instrumentation

The multisyringe flow-injection analysis (MSFIA) system used for the determination and speciation analysis of iron at trace levels of concentration can be seen in Fig. 1.

The system is constituted basically by two multisyringe burettes with programmable rate[1] (MicroBU2030, Crison, Alella, Barcelona). Each syringe (S) has a three-way isolation solenoid valve (N-Research, Caldway, NJ, USA) on its head (E). The multisyringe burette may control up to four additional commutation solenoid valves (N-Research, Caldway, NJ, USA). In our case, two additional solenoid valves have been used.

The optical part of the system consists of a deuterium-halogen light source (Top Sensor Systems, Netherlands) [12] connected to a power supply of ±12 V. A bifurcated optical fibre bundle (Ocean Optics, Dunedin, FL, USA) (Ref. QBIF400-UV-VIS) of 400 μm total diameter, made of two individual strands with one remote end randomly bifurcated, was attached to a flow cell. One of the arms of the optical

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[1] May be requested at http://www.sciware-sl.com/; sciwaresl@yahoo.es.

fibre was connected to the detector and the other attached to the light.

Measurements were carried out at 480 nm using a diode-array PC-plug-in spectrometer with a PC 2000 A/D card (Ocean Optics, Dunedin, FL, USA). Manifold was constructed with 0.8 and 1.5 mm i.d. poly(tetrafluoroethylene) (PTFE) tubes.

For instrumental control, data acquisition and processing the software package AutoAnalysis (see Footnote 1) written in Delphi and Visual C++ was used [13].

2.3. Flow cell

The optical fibre/flow cell used consisted of two opaque square blocks made of poly(ether ether ketone) (PEEK) (Fig. 2). The same flow cell was used in a previous work [5] and it is based on the sandwich-shape cell described by Miró et al. [14]. A thin window made of acrylic-polymer was placed in order to protect the optical fibre from aggressive reagents. A PTFE spacer with a thickness of 0.5 mm was placed between the two blocks since it determines the flow path and the effective retention zone. A polyethylene frit with an average pore diameter of 10 μm is attached under the solid-phase extraction disk in order to hold it and avoid its distortion.

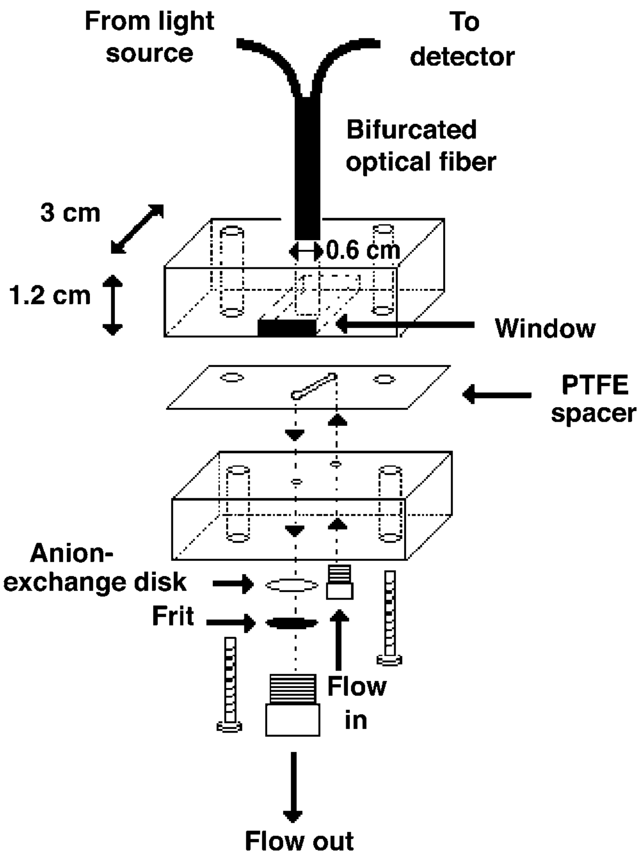

Fig. 2. Design of the flow-cell employed.

2.4. Procedure

In the system five syringes (S1, S2, S3, S4 and S7) with their corresponding three-way commutation valves (E1, E2, E3, E4 and E7) were used. The position “off” (solenoid disabled) of the valves connects syringes to a right channel and “on” (solenoid enabled) to a left one.

Two multisyringe modules were necessary to carry out the methodology proposed for the determination of iron. One module included syringe S7 (with its commutation valve E7) which was responsible for sample loading and dispensing. The other syringes (S1, S2, S3 and S4) with their commutation valves (E1, E2, E3 and E4) contained the carrier (Millipore water), the chromogenic agent (i.e. ammonium thiocyanate), the eluent (i.e. hydrochloric acid in ethanol) and the oxidant (i.e. hydrogen peroxide), respectively. Furthermore, two additional three-way solenoid commutation valves (V1 and V2) were coupled to the system to carry out the injection of the required sample volume and to allow the deviation of the flow when cleaning procedures are required, respectively.

The oxidation of Fe(II) to Fe(III) prior to analysis allows the determination of total iron concentrations. For this purpose, the oxidant stream contained by syringe S4 is delivered to the system and enables the conversion of Fe(II) into Fe(III). Table 1 shows the procedure used for the determination of trace levels of Fe(III). Analogously, for the determination of total iron following the latter strategy, syringe S4 should deliver the oxidant stream to the system during the injection of the sample and ammonium thiocyanate.

2.5. Sample conditioning

Using the technique proposed, a certified water sample (Natural Water Research Institute, Canada) from Lake Ontario [TMDA-54.3] has been analysed and a seawater sample has been spiked. A portion of formic acid-formate (1 mol l^{-1}, pH 2.5) was added to a known volume of sample to give a final concentration of 0.1 mol l^{-1} formic acid-formate.

3. Results and discussion

Iron(III) merges with an ammonium thiocyanate stream in order to form the complex $Fe[SCN]_6^{3-}$ which is retained onto an anionic-exchange disk. This complex is detected by means of diffuse reflectance measurements at 480 nm. The complex is eluted by using 0.25 mol l^{-1} hydrochloric acid in 75% ethanol so that the sorbent is regenerated and ready for another injection. The optical fibre reflectance sensor response can be seen in Fig. 3.

3.1. Optimisation of chemical parameters

Optimisation of chemical parameters was carried out by the univariate method.

Table 1
Analytical procedure for determination of iron(III)

Steps	Volume (ml)		Flow rate (ml min^{-1})		Position of solenoid valves						
	Mod 1	Mod 2	Mod 1	Mod 2	E1	E2	E3	E4	E7	V1	V2
1. Sample tube washing	–	4 d	–	10	Off	Off	Off	Off	On	Off	On
2. Filling the sample coil with sample	–	4 p	–	5	Off	Off	Off	Off	On	On	Off
3. Pre-conditioning of the anion-exchange disk	2 d	–	2	–	Off	Off	On	Off	Off	Off	Off
4. Injection of carrier	0.5 d	–	1	–	On	Off	Off	Off	Off	Off	Off
5. Sample loading and injection of NH_4SCN in order to form the complex Fe–SCN. Acquisition of the spectra	0.1 d	–	1	–	Off	On	Off	Off	Off	Off	Off
	1.0 d	1 d	0.5	0.5	Off	On	Off	Off	On	Off	Off
	0.1 d	–	1	–	Off	On	Off	Off	Off	Off	Off
6. Injection of carrier between loading and elution	0.5 d	–	1	–	On	Off	Off	Off	Off	Off	Off
7. Adjustment of the piston bar position	3.5 p	–	5	–	Off	Off	Off	Off	Off	Off	Off
8. Elution	5 d	–	2	–	Off	Off	On	Off	Off	Off	Off
9. Stop measurement											
10. Adjustment of the piston bar position	5 p	–	5	–	Off	Off	Off	Off	Off	Off	Off
11. Repeat 3 times from Step 4											

The indicated values for volume and flow-rate are referred to syringe 1 (module 1) and to syringe 7 (module 2). Flow directions: p (pick up) and d (dispense).

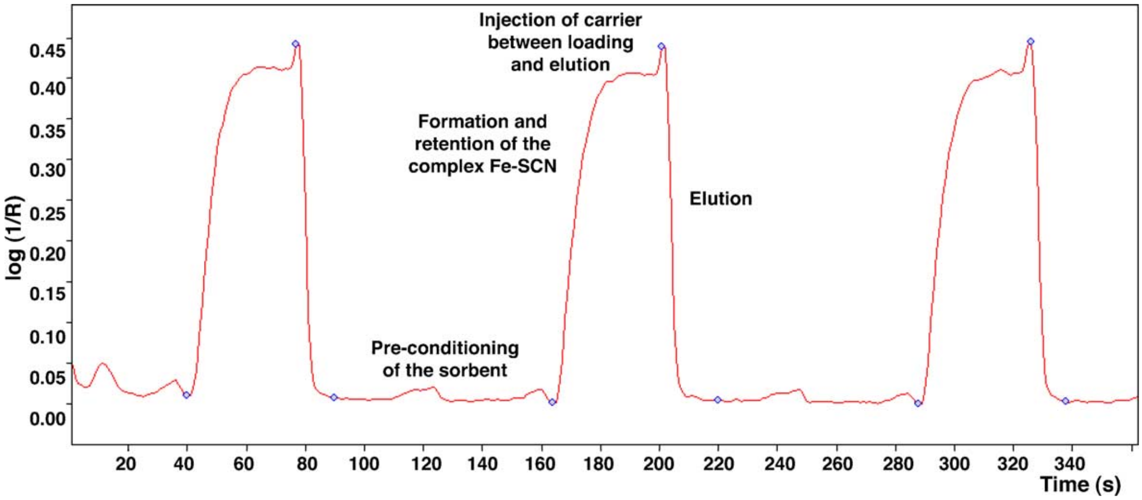

Fig. 3. Recordings obtained for the determination of iron (12.5 ng of Fe(III) were injected).

A solution of hydrochloric acid in ethanol was used as eluent stream. The concentrations of the two reagents were studied by pre-concentrating 0.5 ml of a 0.125 mg l^{-1} Fe(III) solution (Fig. 4). The influence of ethanol concentration was evaluated keeping the hydrochloric concentration at 0.5 mol l^{-1}. A concentration of 75% was chosen for subsequent experiments as it gave the highest analytical signal together with a good repeatability. The hydrochloric acid concentration was studied with the ethanol concentration set to 75%. The sensitivity increased with increasing reagent concentration up to 0.125 mol l^{-1}, above which it remained constant. A concentration of 0.25 mol l^{-1} was adopted for further experiments.

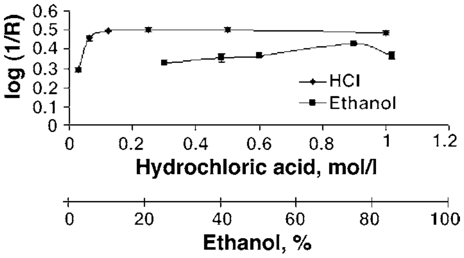

Fig. 4. Effect of the concentration of eluent on the analytical signal (62.5 ng of Fe(III) were injected).

The influence of the concentration of ammonium thiocyanate was evaluated within the range of 0.1–1.25 mol l^{-1} and it was observed that the peak height absorbance increased with increasing ammonium thiocyanate concentration up to 0.75 mol l^{-1}, above which it remained constant. A concentration of 0.75 mol l^{-1} was selected for subsequent experiments as it provided both reproducibility and a high peak signal. For this optimisation, 1.5 ml of a 0.025 mg l^{-1} Fe(III) standard were pre-concentrated.

Hydrogen peroxide was chosen as the oxidising agent for the determination of total iron. A 0.25 mol l^{-1} H_2O_2 concentration ensured total oxidation of Fe(II) into Fe(III). In order to test the effect of the oxidising agent, 30 ng of iron(II) were dispensed into the system.

3.2. Optimisation of physical parameters

Reactor length and pre-concentration and elution flow-rates were the physical parameters optimised following the univariate method. For this purpose, 1.5 ml of a 0.025 mg l^{-1} Fe(III) standard were pre-concentrated.

The effect of the length of the reaction coil was evaluated from 7 to 150 cm using coiled reactors. The peak height decreased with increase of length due to the fast kinetics of the colour forming reaction. A 7 cm length reactor coil was chosen since it gave the best peak height together with a good repeatability.

Pre-concentration flow-rate was studied within the range of 0.5–2.5 ml min^{-1} (Fig. 5). The highest peak signals were obtained within the range of 1–1.5 ml min^{-1}. A pre-concentration flow-rate of 1 ml min^{-1} was chosen since it provided both repeatability and a high peak signal. Moreover, higher flow-rates decrease the lifetime of the SPE disk.

Analogously, elution flow rates were varied within the range of 0.5–2 ml min^{-1} under the same experimental conditions using a pre-concentration flow-rate of 1 ml min^{-1} (Fig. 5). The highest signals were obtained with the lowest flow-rates assayed. A flow rate of 1 ml min^{-1} which provided a good signal and repeatability was chosen as a compromise between the sensitivity of the methodology and the sampling frequency.

3.3. Lifetime of the anion-exchange disk

In order to investigate the effect of successive injections on the life of the anion-exchange disk, 0.5 ml of a 0.125 mg l^{-1} Fe(III) standard were consecutively injected. It is possible to use the same anion-exchange disk up to 30 injections. At these injections, the retention efficiency has decreased 5%. Different eluents were investigated with the aim to prolong the anion-exchange disk lifetime but the results did not improve.

3.4. Optrode response

Analogous to light absorption, diffuse reflectance is dependent on the composition of the system. Several models have been proposed for the analysis of diffuse reflectance. Thus, in opaque and thick layers, the Kubelka–Munk function ($F(R)$) relates the analyte concentration (C) to the reflected light intensity as it follows [15]

$$F(R) = \frac{(1-R)^2}{2R} = \varepsilon CS$$

where R represents the ratio of the reflected radiation intensity in the presence of analyte (sample signal minus blank signal) to that without analyte, ε the molar absorptivity and S is related to scattering.

In the proposed system, the plot $F(R)$ versus mass of iron was found to be a non-linear function (a combination of a straight line and a hyperbola) (Fig. 6). On the other hand, the plot log $(1/R)$ (apparent absorbance) versus concentration of iron (Fig. 6b) was adopted as the calibration graph since it was linear in a wider range (up to 37.5 ng). In this sense, reflectance measurements can be treated as if absorbance had been measured in some instances as it is stated in the literature [16].

3.5. Analytical parameters

The feasibility of a mass calibration was proved by injecting different sampling volumes ranged from 0.5 to 5 ml of the same amount of analyte (35 ng) and, moreover, no relationship between the sampling volume and the relative standard deviation was obtained. In this sense, the advantages of performing a mass calibration (i.e. only one standard is required to perform the regression line and either concentrated or diluted samples can be analysed by only varying the aspirated sample volume) have been reported previously [17,18]. An example of mass calibration curve is given in Fig. 6b.

The calibration graph for iron(III) ranged from 0.4 to 37.5 ng (apparent absorbance = 0.0098 ± 0.0007 ng iron + 0.069 ± 0.014; r^2 = 0.9971; n = 6). The confidence limits of the intercept and the slope were calculated at the 95%

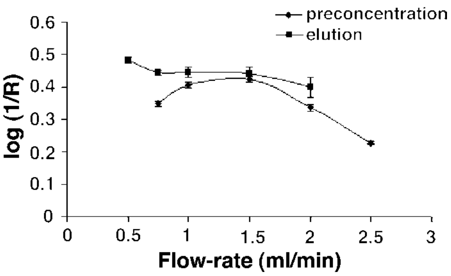

Fig. 5. Effect of the pre-concentration and elution flow-rates (37.5 ng of Fe(III) were injected).

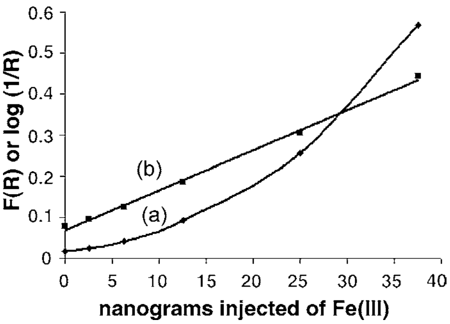

Fig. 6. (a) Study of the applicability of the Kubelka–Munk function; (b) calibration curve obtained under the optimum conditions using standards of Fe(III).

Table 2
Comparison with other systems

Parameter	MSFIA (present work)	MSFIA [5]	MSFIA [8]	FIA [19]	FIA [20]	FIA [21]	FIA [22]
Detection technique	Solid-phase reflectometry	Solid-phase reflectometry	Spec	CL	ICP-MS	Bead injection	Spec/Cat
Sorbent	Anion-exchange discs	Chelex 100 discs	Chelex 100 discs	Amberlite XAD-4-HEED	PTFE Knotted reactor	Chelex 100 resin	8-HQ immobilised onto vinyl polymer gel
Reagent	0.75 mol l^{-1}	0.75 mol l^{-1}	1.25 mol l^{-1}	0.9 m mol l^{-1} BSF +1% (v/v) H_2O_2	0.12% (w/w) APDC	0.5% (w/v) o-phen/1% (w/v) ascorbic acid	0.046 mol l^{-1} DPD+5% (v/v) H_2O_2
Eluent	0.5 mol l^{-1} HCl in 75% Ethanol	2 mol l^{-1} HCl	2 mol l^{-1} HCl	0.075 mol l^{-1} HCl	1 mol l^{-1} HNO_3	–	0.144 mol l^{-1} HCl
Pre-concentration flow-rate (ml min^{-1})	1	1	5	2.8	5	3	2.5
Elution flow-rate (ml min^{-1})	1	1	2.5	1	1.1	–	0.32
Detection limit (ng)	0.4	1.2	19	0.096	0.2	450, 300	3.5×10^{-3}
Working range (ng)	0.4–37.5	1.2–250	19–3000	0.256–61.6	0.5–300	450–1980, 300–3300	0.14–35
Repeatability (%)	3.6	2	2	<4	2.9	–	2.5
Repeatability (changing the sorbent) (%)/*n*	5.4/5	3.6/5	2.2	NR	NR	4	NR
Life-time of the sorbent (injections)	30	50	90	NR	NR	–	NR
Injection throughput/sample volume (ml) (injections h^{-1})	6/5	5/5	10/5	8/5.6	21/2.5	14/9, 9/15	12/2.5

Spec: spectrometry; Cat: catalytic; CL: chemiluminiscence; ICP–MS: inductively coupled plasma–mass spectrometry; PTFE: polytetrafluoroethylene; NR: not reported.

confidence level. The same calibration graph can be used for the determination of total iron. The detection limit (DL), calculated as $3s_b/S$, where s_b is the standard deviation for 10 measurements of the blank and S is the slope of the calibration graph, is 0.4 ng. The repeatability (R.S.D.) calculated from 9 replicates using 0.5 ml injections of a 0.025 mg l^{-1} Fe(III) solution was 3.6%. The repeatability between five anion-exchange disks was 5.4%. An injection throughput of 7 injections per hour for a sampling volume of 1 ml has been achieved.

3.6. *Interference studies*

The effect of potential interferent anions on the determination of iron such as chloride, nitrate, sulphate and carbonate has been investigated at the 5% interference level. These anions were studied taking into consideration their high concentration in the samples assayed. To carry out this study, 1 ml of a 25 μg l^{-1} of a Fe(III) standard was injected. A concentration of 100 mg l^{-1} of nitrate, sulphate and carbonate was tried and they did not decrease significantly the analytical signal. As far as chloride is concerned, no significant differences were found for an interferent/analyte ratio higher than 20000.

3.7. *Applications to real samples*

The accuracy of the proposed method was tested by the analysis of a certified water sample [TMDA-54.3] (National Water Research Institute, Canada). Three replicates of the sample using a sampling volume of 0.5 ml were analyzed. The certified and the obtained values were 399 ± 23 μg l^{-1} ($k = 2$) and 367 ± 21 μg l^{-1}, respectively. The Student t-test for mean comparison did not reveal any statistically significant difference at the 0.05 significance level. The t-calculated value for the sample (1.86) was inferior to the critical one (viz. 4.30) for two degrees of freedom.

A seawater sample has been spiked with Fe(II) (25 μg l^{-1}) and Fe(III) (25 μg l^{-1}). The recovery of Fe(III) and total iron added to the sample was 92% for Fe(III) and the one for total iron was 95%.

Thus, the results obtained show that the proposed methodology can be applied to the determination of iron in water samples.

3.8. *Comparison of anion-exchange disks with chelating disks*

A similar system for the determination of trace levels of iron using chelating SPE disks has been proposed by the authors [5]. The comparison of the properties of anion-exchange and chelating disks as solid phases was carried out (Table 2). Thus, the use of anion-exchange disks over of chelating disks offers several advantages such as a better detection limit, sensitivity and injection throughput. The main shortcoming of the system developed is the short lifetime of the anion-exchange SPE. However, 30 injections could be enough to carry out the analysis of the standards and some samples and moreover, the replacement of the SPE disks is very easy and that the repeatability between anion-exchange disks is good.

Several flow methods have been reported in the literature for the pre-concentration and determination of iron. As can be seen in Table 2, the lowest detection limit is obtained exploiting the catalytic effect of iron on the oxidation of *N*,*N*-dimethyl-*p*-phenylenediamine dihydrochloride (DPD) by hydrogen peroxide [22]. However, this method does not carry out the speciation analysis of iron. The detection limit achieved in this work is better than the given by bead injection [21]. Moreover, the detection limit obtained in this work can be comparable with the obtained using chemiluminiscence (CL) [19] or inductively coupled mass spectrometry (ICP–MS) [20].

4. Conclusions

The developed optrode has been proved to be suitable for the determination and speciation analysis of trace levels of iron in water samples. This sensor has been coupled to MS-FIA technique and takes benefit from the advantages of this flow technique such as robustness and versatility. Moreover, the well-known shortcoming of FIA assemblies (i.e. recalibration of the flexible tubing in peristaltic pumps) is avoided. On the other hand, optosensing systems allow the monitoring in environmental samples.

The high repeatability, sensitivity and low detection limit obtained in this work should be pointed out.

Acknowledgements

The authors are grateful to the MCyT (Ministerio de Ciencia y Tecnología) for supporting the projects PPQ2001-0347 and PPQ2001-0474. Carmen Pons thanks to MCyT for the allowance of a Ph.D. grant.

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