

FERROSPECTRAL SORBED ON DEAE SEPHADEX A-25 FOR THE SOLID PHASE SPECTROPHOTOMETRIC DETERMINATION OF IRON AND COBALT BY BATCH AND CONTINUOUS FLOW MODES

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ABSTRACT

In this work, Ferrospectral;3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine (FST) sorbed on DEAE Sephadex A-25 is used as solid phase for spectrophotometric determination of iron and cobalt by batch and continuous flow modes. In batch simultaneous determination, the second derivative at 536.0 and 601.4 nm were used for iron and cobalt determination, respectively. In this modality, the detection limits (3 σ criterion), for iron and cobalt were 1.3, 9.1, $\mu\text{g L}^{-1}$ and the determination ranges were: 4.3 to 220 and 30.3 to 800 $\mu\text{g L}^{-1}$. The method by FIA mode was carried out by stopped flow and then the analytical signal was evaluated by second derivative at 560.9 and 482.3 nm for iron and cobalt determination; respectively. In FIA modality, the detection limits for iron and cobalt were 6.4, 31 $\mu\text{g L}^{-1}$, and the determination ranges 21 to 200 and 106 to 1000 $\mu\text{g L}^{-1}$ iron and cobalt, respectively. In both modalities the repeatability for iron and cobalt were < 4 % and the recovery was near to 100%. These methods were applied successfully in drinking water and soil samples.

Keywords: Solid phase spectrometry, Fe (II), Co (II), 3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine-DEAE Sephadex A-25, Batch and continuous determination.

INTRODUCTION

At this time, there are various methodologies for the metals determination in different matrices such as food samples^{1,2} environment^{3,4}, biological^{5,6,7}, among others. However, very few methods has been reported for simultaneous determination of iron and cobalt by spectrophotometry, since the absorption bands of both analytes are highly overlapped

Most of the methodologies are carried out with highly sophisticated instrument that requires a thorough sample preparation, previous to measuring the analytical signal.

This situation has been described in numerous papers in which various metals are determined by inductively coupled plasma (ICP) with mass spectroscopy detector (MS) or optical emission detector (OES)^{1,5,8} or by flame atomic absorption spectroscopy (FAAS) with graphite furnace (GF-AAS)^{9,10}, besides using different electrochemical techniques^{11,12}, but the difficulty of these techniques are its high costs.

In order to decrease the limits of detection have been developed and implemented different methodologies, in which the first stage include an extraction of analytes using external energy¹³, a sorbent material⁹, or the presence of some reagent to react chemically with the analyte⁸.

Many methods use the formation of colored complexes to become more selective and sensitive. A spectrophotometric method for the determination of iron, cobalt and nickel using 1-(2-pyridylazo)-2-naphthol (PAN) has been proposed¹⁴. The iron, cobalt and nickel determination using 2,2'-dipyridylketone-2-pyridylhydrazone and isoquinoline-3-aldehyde-2-pyridylhydrazone has been proposed¹⁵.

Other methods based in the formation of complexes for determination of iron and cobalt also has been described^{16,17}. However these methods have low sensitivity to resolve actual problems, because in many cases, it is necessary to achieve very low detection limits, especially in those analytes that have a high toxicity.

In many cases, the use of sensors increases the sensitivity and selectivity in the method^{18,19,20}. This paper proposes the development of a sensor formed by an anion-exchange resin, which is paired with 3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine, Ferrospectral (FST), a chelating agent, which bind Fe (II) and Co (II) in presence of hydroxylamine at pH 4.75.

In order to optimize the time of analysis and strengthen the proposed method intends to work in the use of continuous systems, which reduces time and cost analysis. The literature shows that there are methods for the determination of iron by this route²¹, but does not include the determination of cobalt and other metals, in this way suggests the development of an analytical

method, accurate, sensitive and selective for the determination of Fe (II) and Co (II) by forming complexes with a resin-FST sensor and its evaluation by second order derivative spectrophotometry, comparing strategies working both in static (batch system) or continuous system (flow injection analysis, FIA) and analyzing the study variables using a multivariate design, giving an understanding of both the chemical and statistical significance of chemical and spectral variables of the method. Beside in this work a Tygon cell is introduced, what allows to diminish considerably the cost of the method in relation to the use of flow cell.

This method is applied to soil samples, but the developed method also allows the determination of analytes in any aqueous sample, or to be treated so that the analytes are in aqueous medium.

EXPERIMENTAL

Instruments and Apparatus

A Shimadzu (Shimadzu Co, Kyoto, Japan) spectrophotometer with 1 and 10 mm glass cells were used for measurement of the absorbance and derivative absorption spectra in solid phase and aqueous solution, respectively. For all the tested solutions, the spectra were recorded over a range of 350 to 800 nm versus the corresponding reagent blanks by using slit width values and sampling intervals of 2.0 and 0.2 nm, respectively. A scan speed of 480 nm min⁻¹ was also used. The derivative spectra were obtained using a software Shimadzu kit version 3.7 (P/N 206-60570-04).

All solid samples were weighed to within ± 0.01 mg by using a Sartorius R 200D analytical balance. An Orion Digital Research Ion-Analyzer 701 with glass and saturated calomel electrodes was used for pH determinations. A magnetic stirrer HI 190 M Hanna instrument for the preconcentration step was also used.

A High performance microwave digestion unit, model MLS-1200 mega was used for digestion of soils samples.

The optimizations of variables by experimental full factorial design were carried out by means of software Statgraphics Plus software version 5.1.

Chemicals and Reagents

All reagents were of analytical grade and the solutions were prepared with high-purity water from a NANO pure Barnstead ultrapure water system device.

Commercial standard solutions of 1000 mg L⁻¹ Fe (II) and Co (II) were purchased from Merck® (Darmstadt, Germany). The FST was also purchased from Merck® (Darmstadt, Germany). The pH 4.75 was adjusted with a CH₃COOH 0.1 mol L⁻¹/CH₃COONa 0.1 mol L⁻¹ buffer solution (HAc/Na⁺Ac⁻, pH

4.75). DEAE Sephadex A-25 anionic exchanger was purchased from Aldrich® (St. Louis, USA).

In the validation of the method a High Purity Control Standards (QCS-19)® was used. The content of this standard in 100 mg L⁻¹ is: Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Se, Ti, V, Zn, Ni and trace of HF in 4% HNO₃ v/v.

Procedure to form the sensor FST- DEAE Sephadex A-25

In a glass baker of 400 mL 100 mL of FST 5x10⁻³ mol L⁻¹ and 2 g of DEAE Sephadex A-25 were added. The mixture was stirring for 1h and then filtered. The solid phase was isolated and dried at 100 °C for 2 h.

Procedure for Preconcentration and Determination in batch of Metal Ions

The preparation of the samples were carried out in a final volume of 100 mL aqueous solution and were added between 10 and 140 µL of Fe (II) and 50 and 500 µL of Co (II), both metallic ions concentration were of 100 mg L⁻¹. Then were added 10 mL of HAc/Na⁺Ac⁻ (pH 4.75) buffer solution and 1 mL of hydroxylamine 10%. In each solution 80 mg of FST- DEAE Sephadex A-25 was added and stirred for 30 minutes. Parallel, in the same conditions a reagent blank without the analytes was prepared. The solid phase and reagents blank were packed in quartz cells of 1 mm optical path and the absorption spectra vs. reagents blank were carried out on wavelengths range between 350 to 800 nm. The second order derivative was obtained using a smoothing factor of 40,000 and a scale factor of 10,000.

Manifold and procedure

The FIA manifold is shown in Figure 1. With an injection valve IV3, HCl 2 mol L⁻¹ was first inserted in the carrier in order to obtain the base line. Sample (IV1) and ligand (IV2) were injected simultaneously in a carrier solution prepared daily containing buffer and hydroxylamine (1/1 v/v) at a flow rate of 1.0 mL min⁻¹. The iron of the sample was reduced in the mixing coil R (60 cm x 0.5 mm i.d.) and both analytes also reacted with the ligand in R. The complexes were transported to the detector and the signal was monitored at 550 nm. A Tygon tube of 2 cm x1.5 mm i.d. that contains DEAE Sephadex A-25 resin was used as flow through sensor which retains complexes of Fe (II) and Co (II). When the signal reached the maximum height the flow was stopped. The absorption spectrum was scanned between 400 and 800 nm and obtained the second derivative spectrum, using a smoothing factor of 40,000 and a scale factor of 10,000. Subsequently the pump was switched and the eluent (HCl 2 mol L⁻¹) was injected (IV3) to eliminate the complexes of the resin and then other sample can be injected.

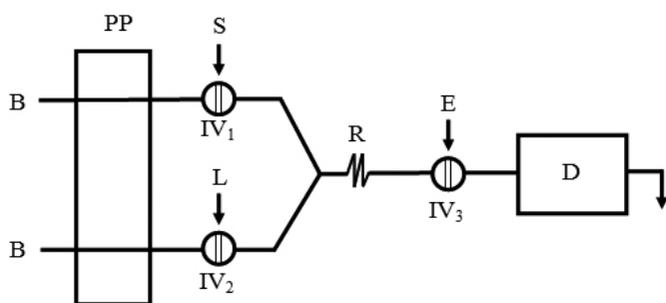


Figure 1. Manifold for Co (II) and Fe (II) determination. B, Buffer; PP, peristaltic pump, S, sample; L, ligand; IV, injection valve, R, reactor coil; E, eluent; D, detector.

Procedure for digestion of soils samples

In the samples preparation of soil for determination of Fe (II) and Co (II) two soils were used, sampled in the Central Zone of Chile. An aliquot of approximately 200 mg of sample of each soil was accurately weighted and transferred to digestion funnel. Aliquots of 4 mL concentrated HNO₃ (Merck, Darmstadt, Germany), 4 mL concentrated HF (Merck, Darmstadt, Germany) and 4 mL H₂O₂ 30% (Merck, Darmstadt, Germany) were added. For microwave digestion procedure the program used was: 5 min to 250 W, 5 min to 400 W, 10 min to 500 W and 1min to ventilation. Finally, the samples were carried out to dryness and reconstituted with 10 mL of water²².

RESULTS AND DISCUSSION

The Co (II) and Fe (II) metallic ions react with FST giving color complexes, these complexes are formed with -N: group. On the other hand, FST contains sulfonic groups, which can be retained in anionic exchange, DEAE Sephadex A-25, which could be used as solid phase and/or sensor. In first time FST was previously retained on the resin to obtain a solid phase. In an aqueous phase, containing independently Fe (II) and Co (II) in presence of hydroxylamine and buffer pH 4.75, was added FST-resin and stirred the solid phase. The spectra of metallic complexes retained on the sensor scanned vs. FST-DEAE Sephadex A25 is shown in Figure 2, as can be seen each metallic ion presents a well defined bands, this means that Fe (II) and Co (II) are retained in the solid phase, this fact can be attributed to formation of complexes with the -N:. These results are indicative of the possibility to develop an analytical method in batch mode. Further, it was assessed the reversibility of the system, to the solid phases contained each metallic cation. It was added HCl 1.0 mol L⁻¹ as eluting agent and only the cations were rapidly and quantitatively liberated. This fact allows using this solid phase as sensor in FIA or in continuous systems.

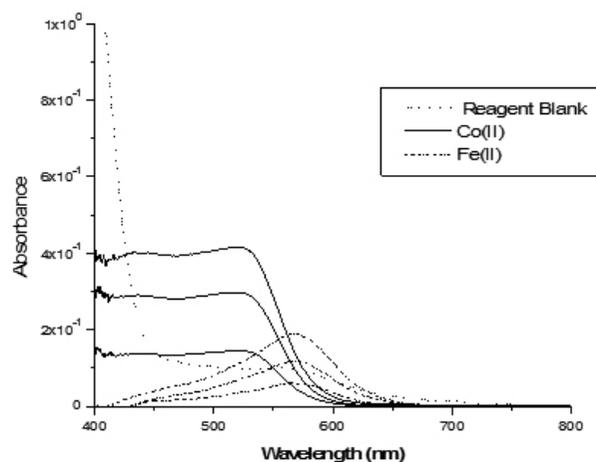


Figure 2. Zero order spectra of the complexes retained on FST-DEAE Sephadex A-25, against reagent blank. Concentration: Co (II) between 1.7x10⁻⁶ and 5.1x10⁻⁶ mol L⁻¹, Fe(II) between 1.8x10⁻⁷ and 5.4x10⁻⁷ mol L⁻¹.

Adsorption isotherm

For the determination of the sorption capacity of the solid phase FST-DEAE Sephadex A- 25, the amount of sorbed Co (II) and Fe (II) were studied independently as a function of each concentration (Figure 3). The model proposed by Langmuir was analyzed. The linearization of Langmuir isotherm can be obtained by plotting Ce/q as a function of Ce.

The slope of the plot yields the maximum capacity (qm) whereas its linear coefficient represents the Langmuir constant (K). The correlation coefficients of the linear equation obtained in this study were 0.999. An analysis of the sorption behavior for Langmuir model reveals that equation give up a good fit. Thus, the adsorption isotherms of Co (II) and Fe (II) are according to the Langmuir equation (Figure 3b) and the graphical treatments of the data give as results 0.076 mg and 0.049 mg of Co (II) and Fe (II) per gram of FST DEAE Sephadex A-25 as maximum saturation capacity and equilibrium binding constants were; K 5.1x10⁴ and 5.5 x10⁴ mol⁻¹ L, for Co (II) and Fe (II), respectively. The Langmuir treatment demonstrated that the surface is nearly fully covered with monomolecular layer of Co (II) and Fe (II) at high concentrations. In high concentrations adsorption does not increase linearly. The main sorption sites of the FST-DEAE Sephadex A-25 were the -N: groups forming a solid phase chelates.

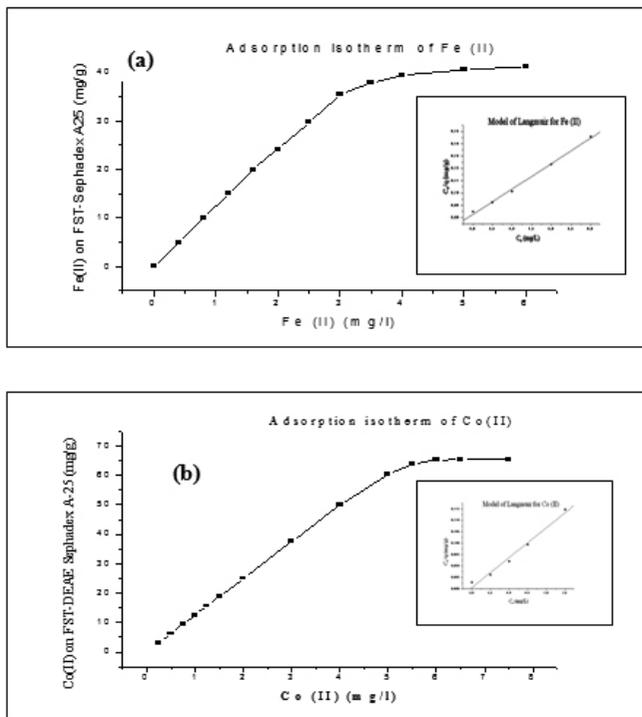


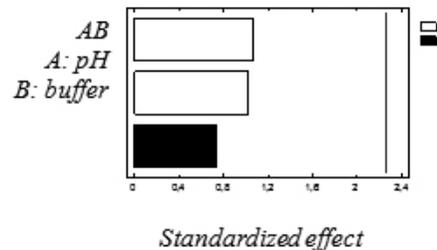
Figure 3. Adsorption isotherms of FST-DEAE Sephadex A-25 for Co(II) and Fe (II). 80 mg of FST-DEAE Sephadex A-25, 2 mL hydroxylamine, 10 mL of buffer HAc 0.1 mol L⁻¹/NaAc 0.1 mol L⁻¹. (a) Co (II) at $\lambda = 500$ nm and (b) Fe (II) at $\lambda = 561.5$ nm.

Experimental factorial designs.

The traditional way of studying the influence of several variables on a response is the univariable (one variable at a time) method. However, this classical method involves a large number of independent experiments and some important conclusions on the interaction among variables may be missed²³. An efficient way to overcome these drawbacks is to use the experimental factorial design methodology, which is a collection of statistical and mathematical techniques useful for studying, improving and optimizing the development of analytical method²⁴. The factorial design with two-level (2^k) is the largely popular, where k is the number of variables, because it is possible to obtain information about the significance of each variables and their interactions. Two-level factorial designs have many advantages in analytical procedures and the total number of experiments in factorial design is much lower compared to the univariable approach. In order to determine the behavior of the response variable on the region of interest a mathematical model must be used²⁴.

In this work for the simultaneous determination in batch of Fe (II) and Co (II), the optimization of chemical and preconcentration variables were realized independently for each metallic ion. For the chemical variable an experimental full factorial design 2² was used with one central point and in triplicate (15 experiments), where it was optimized, pH and buffer concentration in the intervals 6-4 and 0.5-0.05 mol L⁻¹, respectively. For the optimization of preconcentration the same design was used with two central points and in quadruplicate. The variable optimized were mass of solid phase and stirring time used as limit values 120-80 mg and 30-10 min, respectively. The Figure 4 shows the Pareto graphics for the chemical optimization of the determination of Fe (II) and Co (II) and Figure 5 presents the graphics that correspond to optimization of preconcentration step.

Standardized Pareto Chart for Fe (II)



Standardized Pareto Chart for Co (II)

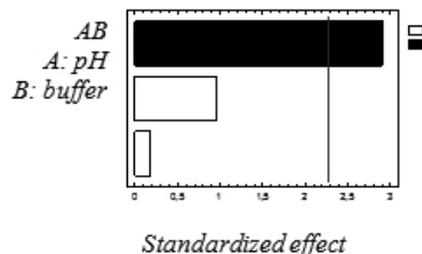
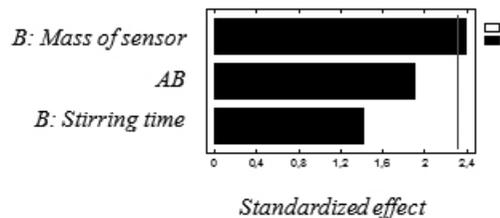


Figure 4. Pareto graphics for Fe (II) and Co (II) for optimization step of chemical variables.

It was found that the concentration of HAc/Na⁺Ac⁻ buffer is only significant in the determination of Co (II), this fact can be attributed to that solid phase could retain to Ac⁻ ion of buffer. On the range studied, the pH is not significant for both analytes. Taking into account the graphics area, that the buffer volume is constant and the simultaneous determination of iron and cobalt will be carried out, was selected a concentration 0.1 mol L⁻¹ (pH = 4.75), in order to increase the buffer capacity.

Standardized Pareto Chart for Fe (II)



Standardized Pareto Chart for Co (II)

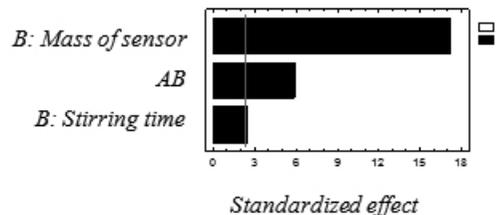


Figure 5. Pareto graphics for Fe (II) and Co (II) for optimization step of preconcentration variables.

In the preconcentration optimization was found that mass of sensor FST-resin is significant for Fe (II) and Co (II) determination because the preconcentration is favoured when the amount of solid phase decrease. On the other hand, the amount of solid phase and stirring time interaction is slightly significant for Co (II), because the formation of the complexes are rapid, for this reason it is possible to establish that kinetic effect are not present. According to these results, the optimal stirring time is 30 min, and the optimal amount of sensor is 80 mg for both analytes.

Selection of spectral variables

Derivative order and analytical wavelength

In this work the digital derivative spectrophotometry technique is used, which is based on mathematic computational model proposed by Savitzky and Golay²⁵. To optimize the derivative order, the first to the fourth derivative spectra of the respective complexes retained in solid phase were recorded. In Figure 6 are shown the first and second derivative, higher derivative orders were discarded because the sensibilities decrease and the noise is also increased. Derivative spectrophotometry^{26,27} is widely used and effective in systems where there are overlapping signals. Comparing these spectra derivative, the first derivative presents higher sensitivities that the second, but the first derivatives only present a zone characteristic for the Co (II) determination. The second derivatives for the Co (II) determination present zero crossing at 493 and 556 nm; further in the range of 650 and 800 nm, it does not present analytical signal. On the other hand, second derivatives for the Fe (II) determination also present zero crossing at 536.0 and 601.4 nm, being possible this simultaneous determination. In this context, second derivative spectra were selected for the determination of Co (II) and Fe (II) in a sample by means of the zero crossing method at analytical wavelength of 601.4 and 556.0 nm. These wavelengths were selected in order to favor the sensitivity of the method.

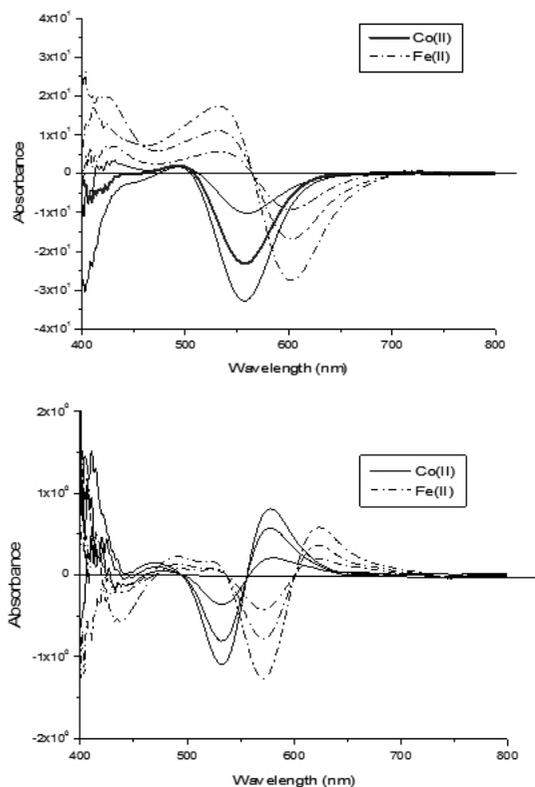


Figure 6. First and second derivative of the complexes retained on FTS-DEAE Sephadex A25, against reagent blank. (a) First derivative and (b) Second derivative. Concentration: Co (II) between 1.7×10^{-6} and 5.1×10^{-6} mol L⁻¹, Fe (II) between 1.8×10^{-7} and 5.4×10^{-7} mol L⁻¹.

Selection of the smoothing and scale factor.

For a $\Delta\lambda$ value of 450 nm the smoothing factor, corresponding to the number of points using in the derivation were the following: 5,000, 10,000, 20,000

and 40,000. When the smoothing factor increases, the heights of derivative signal decreased, but the noise decreased more significantly, obtaining superior signal/noise ratios. A value of 40,000 was selected, because in these conditions the signal/noise ratio was favored and the sensibilities were underrated in order to decrease the error of the results. The derivative spectra, when this smoothing factor was used, distortion effects are not present. A value of 10,000 was selected as scale factor only to favor the lecture of the analytical signal, but not affect the sensitivity because the analytical signal and the standard deviation of the blank increase in the same proportion.

Analytical Features

The analytical features, for the batch determination of Co (II) at 556.0 nm and Fe (II) 601.4 nm were determined by second order derivative spectrophotometry using a smoothing factor of 40,000 and an amplification factor of 10,000 in 100 mL as total volume solution.

The equation for the Co (II) and Fe (II) determination obtained by the least squares method are shown in Table 2. The detection limits (3σ criterion), quantification limits (10σ criterion), and determination ranges for Co (II) and Fe (II) are also shown in Table 1. The accuracy and the repeatability of the method were obtained using 10 samples containing 3.9×10^{-7} mol L⁻¹ and 2.3×10^{-7} mol L⁻¹ of Co (II) and Fe (II), respectively. The recoveries and as relative standard deviations, are also included in Table 1. Mixtures of Fe (II) and Co (II) of different concentrations were carried out by the proposed method and the results are shown in Table 2.

FIA determination

Optimization of the FIA system

The FIA system was optimized by examining the influence of chemical and FIA variables by means of an experimental full factorial design. The chemical variables (2^2 design) with two different levels of each variable were studied. For FST concentrations (7.5×10^{-4} - 7.5×10^{-3} mol L⁻¹) and HCl concentrations (2 - 3 mol L⁻¹) were assessed. A FST of 7.5×10^{-3} mol L⁻¹ and HCl 2 mol L⁻¹ were found to be providing the optimal results. The buffer concentration was scarcely influential. In the optimized of hydrodynamic flow variables (2^4 design) were selected different values based on preliminary results in order preventing the effects of sensor contraction. The variables studied included the injected volumes (V), mixing reactor length (R), V1 (82-200 μ L) V2 (83-300 μ L) V3 (82-200 μ L) and R (46-76 cm) were study and it were found to be optimal 200, 300, 100 and 76 cm, respectively.

In these conditions the signals of Fe (II) and Co (II) at concentration between 50 to 200 ng mL⁻¹ were obtained. The diagrams obtained are shown in Figure 7.

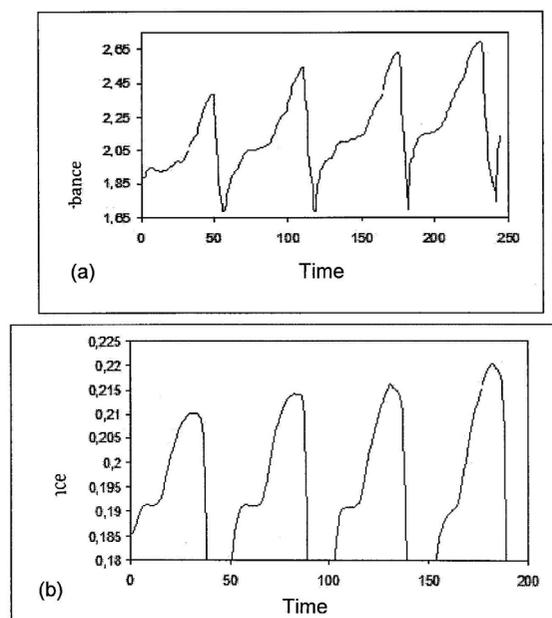


Figure 7. Diagrams of (a) Fe (II) to different concentrations (50 ng mL⁻¹, 100 ng mL⁻¹, 150 ng mL⁻¹, 200 ng mL⁻¹) (b) spectrum of Co (II) to different concentrations (50 ng mL⁻¹, 100 ng mL⁻¹, 150 ng mL⁻¹, 200 ng mL⁻¹).

The batch method above described for the simultaneous determination of Fe (II) and Co (II), was also implemented by FIA system. According to the procedure described in experimental, different solutions of analytes were injected into manifold. When the FIA signal reached the maximum absorbance, the flow was stopped and the signals acquire a constant value because the reaction was completed. In first time, it was injected each analyte individually and when the stability conditions were obtained the spectra were scanned and it was found that the bands are overlapped, so that second derivative was obtained (Figure 8).

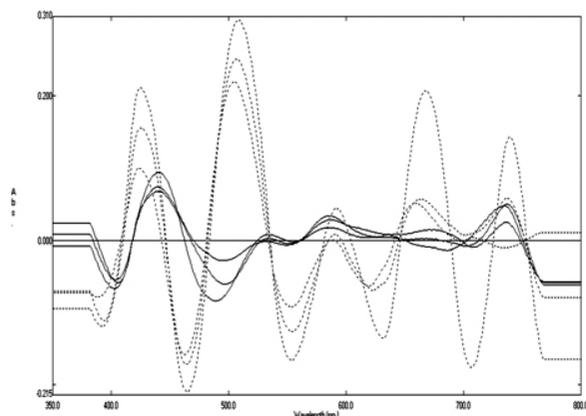


Figure 8. Second derivative spectra recorded of zero order spectra of samples recorded after stopped flow process. (—) Iron; 20, 30 and 40 ng mL⁻¹. (....) Cobalt; 400, 500 and 600 ng mL⁻¹.

According to Figure 8, the second derivative of each complex shows characteristic points for the determination of both analytes. Iron was determined at 560.9 nm and cobalt at 482.3 nm corresponding to the zero crossing point of derivative spectra of cobalt and iron, respectively. In this condition, the second derivatives are similar with those obtained in batch.

Features of proposed FIA method

Under the optimized working conditions, a series of standards solution of Fe (II) between 40 to 200 ng mL⁻¹ and of Co (II) 120 to 1000 ng mL⁻¹ were injected independently into the manifold. The linear relations between peak height in DU and the concentration of the metallic ions and the analytical features are shown in Table 1. Mixtures of Fe (II) and Co (II) of different concentrations were injected and then under stopped flow conditions spectra and their derivatives were obtained. The results are summarized in Table 2.

Table 1 Analytical features for batch and FIA determination.

Analytical parameters	Batch determination		FIA determination	
	Iron	Cobalt	Iron	Cobalt
Detection limit (µg L ⁻¹)	1.3	9.1	6.4	31
Determination limit (µg L ⁻¹)	4.3	30.4	21	106
Determination range (µg L ⁻¹)	4.3- 220	30.3-800	21 – 200	106 - 1000
Repeatability (RSD, %)	3	2	3	4
Regression lines	DU = 2.9x10 ⁻² C + 0.05	DU = 2.9x10 ⁻³ C + 0.005	DU = 2.8x10 ⁻³ C - 0.05	DU = 2.9x10 ⁻⁴ C + 0.03
Correlation coefficient	0.994	0.998	0.994	0.997

Where DU, in derivative units, and C correspond to analyte concentration in ng mL⁻¹.

Table 2 Analytical features for batch and FIA determination.

Fe(II)/Co(II) ratio	Recovery* (%±SD)			
	Batch determination		FIA determination	
	Iron	Cobalt	Iron	Cobalt
60 /50	103.7 ± 3	100.0 ± 1	103.2 ± 2	D
80/50	104.6 ± 4	102.6 ± 3	103.5 ± 3	D
110/50	100.5 ± 4	103.6 ± 3	104.6 ± 4	D
50/150	101.4 ± 1.4	103.5 ± 2	103.2 ± 4	102.6 ± 3
50/200	99.8 ± 0.2	104.1 ± 1	104.6 ± 3	99.8 ± 3
50/300	96.6 ± 3.4	99.0 ± 1	104.6 ± 3	101.2 ± 3

Study of interferences

The method provides high selectivity, because the alkali and alkaline earth metals, Cr (III), Pb (II), Se (IV), Mo (VI), Sb (III), As (III), Cd (II), Hg (II) and Mn (II) do not interfere tested to a maximum of 6 mg L⁻¹. The presence Cu (II) 0.1 mg L⁻¹, Ni (II) 1 mg L⁻¹ and Zn and Cd (II) 6 mg L⁻¹ alter the signal spectrum. This interference is due to the cations present in the sample competing for the active centers on solid phase.

In order to eliminate the copper interference in the analytical measurements studies were carried out in order to mask the presence of this interference. This was carried out using sodium citrate dihydrate as masking agent, obtaining an optimum amount of 2.5 g of citrate solution that does not affect the shape or the height of the spectral signals of a mixture of Fe (II)-FST and Co (II)-FST retained in solid phase. It is necessary to highlight that the experimental conditions were kept constant according to experimental procedure. However, it was necessary to control the pH because the citrate increases its value. Under these conditions increased the tolerance limit of Cu (II) to 2 mg L⁻¹.

Validation and application

The methods were validated using a High Purity Quality Control Standards QCS-19[®]. An aliquot 0.1 mL of this sample was measured and diluted to a 100 mL solution. The recoveries of Co (II) and Fe (II) were between 97 and 103%. The RSD was < 2%. The proposed methods were applied directly to drinking water; these samples were obtained of the Laboratory of Analytical Chemistry of Faculty of Science, University of Chile. When the batch method was applied 35±0.02 ng mL⁻¹ for iron were found and cobalt was only detected. Similar results for iron determination by FIA mode were found, but cobalt does not was detected for this proposed method. The proposed methods were also applied in two soils sampled in the Central Zone of Chile. For the soil 1 was found 0.37±0.01 and 0.06±0.02 mg g⁻¹ for iron and cobalt, respectively. For the soil 2 was found 0.38±0.05 and 0.073±0.01 mg g⁻¹ for iron and cobalt, respectively.

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REFERENCES

- Nardi, E.P., F. S. Evangelista, L. Tormen, T. D. Saint Pierre, A. J. Curtius, S. S. de Souza and F. Barbosa Jr. *Food Chem.* **112**: 727–732. (2009)
- Murakami M. and N. Ae. *J. Hazard. Mater.* **162**: 1185 – 1192. (2009).
- Soylak, M. and R. Sungur. *J. Hazard. Mater.* **146**: 142 – 147. (2007).
- Ghaedi, M., K. Niknam, A. Shokrollahi, E. Niknam, H. R. Rajabi and M. Soyak. *J. Hazard. Mater.* **155**: 121 – 127. (2008).

5. Suleiman, J. S., B. Hu, C. Huang and N. Zhang. *J. Hazard. Mater.* **157**: 410–417. (2008)
6. Kazi, T. G., M. K. Jamali, M. B. Arain, H. I. Afridi, N. Jalbani, R. A. Sarfraz and R. Ansari. *J. Hazard. Mater.* **161**: 1391–1398. (2009).
7. Aguerssif, N., M. Benamor, M. Kachbi and M. T. Draa. *J. Trace. Elem. Med. Bio.* **22**: 175–182. (2008).
8. Bezerra, M. A., S. M. do Nascimento-Maêda, E. P. Oliveira, M. F. Batista de Carvalho and R. E. Santelli. *Spectrochimica Acta Part B: Atom. Spectrosc.* **62**: 985–991. (2007).
9. Ghaedi, M., F. Ahmadi and A. Shokrollahi. *J. Hazard. Mater.* **142**: 272–278. (2007).
10. Tuzen, M. and M. Soylak. *J. Hazard. Mater.* **162**: 724–729. (2009).
11. Laglera, L. M., G. Battaglia and C.M.G. van den Berg. *Anal. Chim. Acta.* **599**: 58–66. (2007).
12. Segura, R., M.I. Toral and V. Arancibia. *Talanta* **75**: 973–977. (2008).
13. Rezić, I. *Ultrason.Sonochem.* **16**: 63–69. (2009).
14. Zarei, K., M. Atabati and Z. Malekshabani. *Anal. Chim. Acta.* **556**: 247–254. (2006)
15. DiTusa, M. R. and A. A. Schilt. *Microchem. J.* **32**: 44–49. (1985)
16. Toral, M. I., P. Richter, L. Silva and A. Salinas. *Microchem. J.* **48**: 221–228. (1993)
17. Richter, P., M.I.Toral and P. Hernández. *Anal. Lett.* **26**: 1013–1025. (1996).
18. Santos, W.J.R., P. R. Lima, A.A. Tanaka, S. M.C.N. Tanaka and L.T. Kubota. *Food Chem.* **113**: 1206–1211. (2009).
19. Gąsiorowska, M., J. A. Soroka, M. J. Sawicka and E. K. Wróblewska. *Talanta* **78**: 49–51. (2009).
20. Sharma, R.K. and P. Pant. *J. Hazard. Mater.* **163**: 295–301. (2009).
21. Teixeira, L.S.G. and F. R.P. Rocha. *Talanta* **71**: 1507–1511. (2007).
22. Ascar, L., I. Ahumada and P. Richter. *Chemosphere.* **70**: 1211–1217. (2008)
23. Massumi A., N. M. Najafi and H. Barzegari. *Microchem. J.* **72**: 93–101. (2002).
24. Myers, R.H. and D.C. Montgomery. *Response Surface Methodology: Process and Product Optimization Using Designed Experiments.* Wiley. (2002).
25. Savitzky, A. and M.J.E. Golay. *Anal. Chem.* **36**: 1627–1639. (1964).
26. M. I. Toral, J. Rivas, M. Saldías, C. Soto, S. Orellana. *J. Chil Chem. Soc.* **53** (2) 1543–1547. (2008)
27. C. Soto, D. Contreras, M. I. Toral, L. Basaez and J. Freer. *J. Chil Chem. Soc.* **54** (2009).