



Anal. Bioanal. Chem. Res., Vol. 9, No. 3, 243-250, July 2022.

Simultaneous Determination of Traces of Cobalt and Iron Ions after Pre-concentration by Surface-active Ionic Liquid-assisted Cloud Point Microextraction

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(Received 24 October 2021 Accepted 19 December 2021)

The present study deals with the simultaneous determination of Co(II) and Fe(II) ions using derivative spectroscopy after pre-concentration by surface-active ionic liquid-assisted cloud point extraction. Wider linear range, less detection limit and more reproducibility along with the improved extraction efficiency highlight the advantages of the proposed method compared to the conventional CPE method. On the other hand, in comparison to the hydrophilic ionic liquids, a more effective and efficient extraction medium is provided due to the formation of homogeneously dispersed micro-droplets of surface-active ionic liquid (SAIL) micelles. Some important variables affecting the extraction efficiency such as sample pH, the concentration of SAIL 1-hexadecyl-3-methylimidazolium chloride (C₁₆MeImCl), the volume of Triton X-114, the concentration of the chelating agent, the concentration of NaCl, centrifugation conditions, equilibrium temperature and time were optimized. Under the selected optimized conditions, the resulting calibration graph obtained by derivative spectroscopy was linear in the range of 0.15 to 2.0 mg l⁻¹ for cobalt and 0.05 to 0.75 mg l⁻¹ for iron at zero-crossing wavelengths of 598 and 567 nm, respectively. The detection limits achieved were 0.07 mg l⁻¹ for cobalt and 0.01 mg l⁻¹ for iron ions. The relative standard deviation in all cases was less than 4%. The proposed method was successfully applied to the simultaneous determination of cobalt and iron ions in various real samples.

Keywords: Surface active ionic liquid, Pre-concentration, Cloud point extraction, Derivative spectroscopy

INTRODUCTION

Spectrophotometric methods are one of the most widespread analytical techniques that have been used in various fields of scientific investigations. Compared to the other advanced analytical techniques, these methods are more economical and offer simpler operations [1,2]. However, they don't have enough selectivity to apply to the simultaneous determination of analytes in multi-component systems without using any separation step. This dilemma could be solved by applying derivative spectrophotometry, by using this technique simultaneous determination of analytes in multi-component samples would not be impossible. In addition, using this technique enables us to

eliminate background interferences and resolve the problem of overlapping absorption bands without the need for prior separation or using a masking agent. In derivative spectrophotometry, measurement of the height of a derivative peak of the analyte is performed at those wavelengths at which the absorbance of the other component is equal to zero. Thus, the measured amplitude is proportional only to the concentration of the assayed compounds. This approach of quantitative determination is called the 'zero-crossing technique' [3,4]. On the other hand, it should be mentioned that the low concentration of analyte ions in real samples makes it difficult to do spectrophotometric measurements without any pre-concentration step. Thus, in order to circumvent the low sensitivity of spectrophotometric methods, several sample preparation techniques have been developed to pre-

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concentrate the analyte ions.

Among the numerous pre-concentration methods, cloud point extraction (CPE) has received attention due to its rapidity, cheapness, and safety [5-7]. In spite of the mentioned advantages, some modification procedures have been proposed to improve the analytical specifications of the determination step. Ionic liquids (ILs) are characterized by their attractive physicochemical properties [8,9], considering these features, they have been used as a green solvent in various fields of chemistry [10-12]. Some kinds of ILs are easily water-soluble and on the other hand, some of them have hydrophobic properties, which are commonly used in microextraction methods as a green extracting solvent. In addition, there is another important type of ILs that shows aggregation behavior and surface activity in aqueous solutions, these surface-active ionic liquids (SAILs) have been introduced as a suitable alternative to the conventional surfactants [13]. Unfortunately, considering their water solubility, despite their attractive features, it is impossible to use this kind of ILs as an extracting solvent. In fact, though the formation of SAIL's micelles provides a homogeneous and efficient extraction media the separation of the SAIL phase from the aqueous phase at the final stage of the extraction process would be impossible. This drawback can be overcome by mixing the SAILs with the other proper surfactants such as Triton-X114. By this means, the extracting SAIL phase could be separated simply by temperature controlling like that is done in the CPE method. Using the mentioned route it would be possible to utilize the unique properties of ionic liquids besides the advantages of CPE. In this work, the surface-active ionic liquid C₁₆MeImCl was used to improve the analytical features of the CPE procedure applied to the pre-concentration and simultaneous determination of cobalt and iron ions by visible spectroscopy. Due to the important biological roles of iron in carrying oxygen, enzymatic reactions, metabolism of cells, and biosynthesis, this ion is one of the most necessary ingredients for the life system. The Deficiency of iron can cause anemia, diabetes, liver and kidney damages, and cardiovascular diseases, while its accumulation may cause hemochromatosis [14,15]. Cobalt is an important constituent of cyanocobalamin and has a key role in the function of hormones, neurotransmitters, and other biologically important compounds such as bile acids

and DNA. On the other hand, excessive cobalt uptake may lead to diseases such as asthma, vasodilation, flushing, and cardiomyopathy [16-18]. Due to the nutritional and toxicological importance of cobalt and iron ions, their rapid, sensitive and selective determination in different environmental samples is essential.

EXPERIMENTAL

Chemicals

C₁₆MeImCl was obtained from Acros Organics, Geel, Belgium. Ammonium pyrrolidine dithiocarbamate (APDC) (Merck, Darmstadt, Germany) was used as the complexing agent. The nonionic surfactant Triton X-114, ammonium iron(II) sulfate and cobalt(II) nitrate were purchased from Sigma, St. Louis, MO, USA. Britton–Robinson buffer was used for pH adjustment. The stock solution of this buffer was prepared from a mixture containing equal concentrations (0.04 M) of boric, phosphoric and acetic acid and adding appropriate amounts of 0.2 M sodium hydroxide solution to achieve the desired pH.

Apparatus

The absorption and derivative spectra were recorded on a SPECORD 250 UV-Vis. spectrophotometer (Analytikjena Co). A Metrohm pH-meter (Model 827), equipped with a combined glass calomel electrode, was employed for pH adjustments. A Julabo thermostatic water bath (Seelbach, Germany) model GMBH D-77960 was used for temperature control. Phase separation was achieved *via* a Hettich Universal centrifuge Model 320R (Tuttlingen, Germany).

Procedure

10 ml of the standard solution of cobalt (0.15 to 2.0 mg l⁻¹) or Fe (0.05 to 0.75 mg l⁻¹) or their mixture was pipetted into a 15 ml conical test tube. Then, 0.3 ml of 0.01 M C₁₆MeImCl solution, 0.9 ml Triton-X114 (1.0%), and 0.055 ml of 2 × 10⁻² M APDC solution were added to the tube. The pH of the solution was adjusted to the optimized value (5.2) by adding 1 ml of Britton-Robinson buffer solution. After that, 0.75 ml of 1.0% (w/v) NaCl solution was added and the test tube was kept at 45 °C in the water bath for 10 min. The mixture was then centrifuged for 10 min at 3000 rpm; the upper aqueous phase was separated

using a syringe and the residue was diluted by adding 0.5 ml of ethanol. For simultaneous determination of analytes, the first-order derivative absorption spectrum of the obtained solution was recorded in the wavelength range of 400 to 800 nm. Then, by measuring the absorbance values at 598 and 567 nm for cobalt and iron, respectively, the concentration of each ion was determined by implementing the corresponding calibration curve.

Real Sample Analysis

To test the applicability of the proposed method, two samples of water (tap and rainwater), two synthetic solutions containing iron and cobalt mixture, and a sample of the Permendur 49 alloy (Merck, Darmstadt, Germany; composition: 49% cobalt, 49% iron and 2% vanadium) were used. To analyze the alloy sample, after the dissolution of the appropriate amounts of it, the resulting solution was diluted to 1.0 liter with deionized distilled water. Water samples were collected in clean polyethylene bottles and analyzed as soon as possible.

RESULTS AND DISCUSSION

Absorption Spectra

As Fig. 1a shows, the absorption spectra of Co(II)-APDC and Fe(II)-APDC complexes are overlapped in the visible region with absorption maxima at 657 nm and 601 nm, respectively. The absorption spectrum of the mixture of cobalt and iron complexes is shown in Fig. 1a too. In the binary mixture, due to the overlap of the absorption bands, it is impossible to determine the concentration of these ions simultaneously. Therefore, first-order derivative spectroscopy was proposed for the simultaneous determination of cobalt and iron in binary mixtures. The first-order derivative spectrum of both complexes and their mixture are shown in Fig. 1b. For quantitative extraction of cobalt and iron ions by the mixed-micellar system, some parameters affecting the extraction efficiency such as sample pH, the concentration of SAIL, volume of Triton X-114, the volume of APDC solution, amount of salt (NaCl), centrifugation conditions, equilibration temperature and time were optimized.

Extracting Phase Composition

At first, the variations in the analytical signal as a

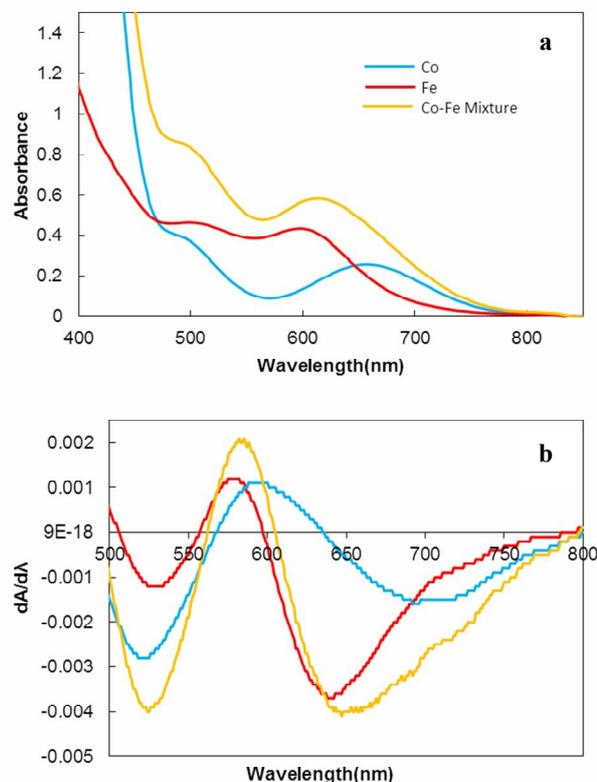


Fig. 1. (a) Absorption spectra of Co-APDC, Fe-APDC and their mixture. (b) First-order derivative spectra of Co-APDC, Fe-APDC and their mixture.

function of the amount of Triton X-114 were investigated (Fig. 2a). The results showed that when the volume of surfactant solution (1.0% v/v) varies in the range 0.3-1.5 ml, the maximum absorbance for both complexes is observed at 0.9 ml. Then, to investigate the effect of SAIL concentration on the analytical signal, different amounts of C₁₆MeImCl were added to the extraction mixture. According to our results (Fig. 2b), the maximum absorbance for both complexes was observed in the presence of 0.3 mM C₁₆MeImCl.

pH Study

In the extraction of metal ions, pH plays an important role in the formation of a complex with sufficient hydrophobicity. The effect of pH on the absorbance of Fe-APDC and Co-APDC complexes was investigated in the range of 2.0-9.0. As shown in Fig. 3, the absorbance of Fe-

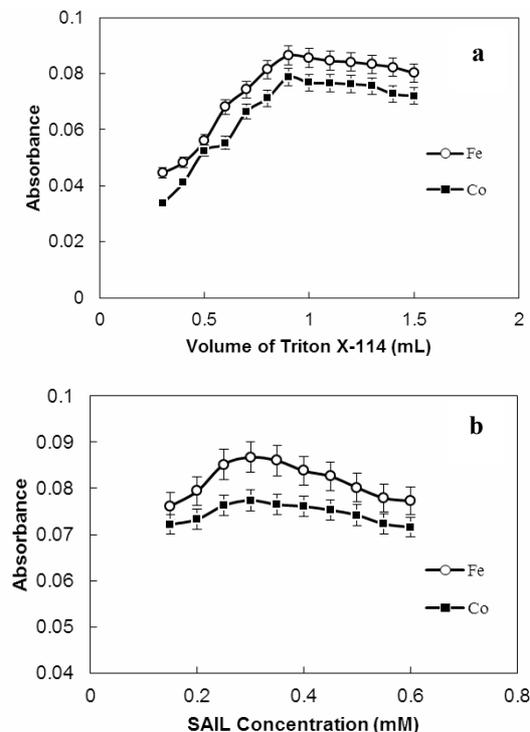


Fig. 2. (a) Effect of the amount of Triton X-114 (1.0%). Conditions: concentration of SAIL: 0.3 mM, concentration of APDC: 0.11 mM, NaCl: 0.75%, pH for Co: 6.0 and for Fe: 4.0, Co: 1.0 mg l⁻¹, Fe: 0.5 mg l⁻¹, and (b) Effect of SAIL concentration, conditions as (a) in the presence of 0.9 ml of 1.0% Triton X-114 and various concentrations of SAIL.

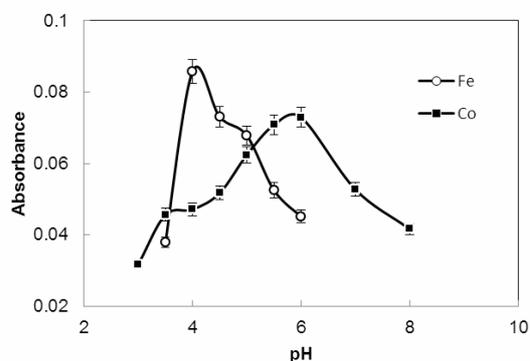


Fig. 3. Effect of pH. Conditions: concentration of SAIL: 0.3 mM, concentration of APDC: 0.11 mM, Triton X-114: 0.9 ml of 1.0% solution, NaCl: 0.75 %, Co: 1.0 mg l⁻¹, Fe: 0.5 mg l⁻¹.

APDC complex increases with increasing sample pH from 3.0 to 4.0 and then decreases at higher pHs. Thus, the optimum pH value was equal to 4.0, and this pH was used for the determination of iron ions throughout this work. On the other hand, the absorbance of Co-APDC complex was increased by increasing the sample pH from 3.0 to 6.0 and then decreased when the pH was higher than 6.0. Thus for optimizing the other factors affecting the cobalt ion extraction efficiency, the pH of solutions was adjusted to 6.0 as the optimal value. Reduction of absorbance at low pH values is probably the result of the dithiocarbamate ion protonation in an acidic solution [19], while the reduction of the analytical signal at high pH values can be attributed to the hydrolysis of cobalt and iron ions. According to Fig. 3, the optimal pH value for the simultaneous determination of these ions is 5.2, in which both ions have the maximum extraction efficiency at the same hydronium ion concentration.

Effect of Chelating agent Concentration

The concentration of APDC ligand, which was used as a complexing agent to increase the affinity of cobalt and iron ions to the hydrophobic extraction phase, was investigated. According to Fig. 4, for both complexes, it was found that the maximum absorbance would be observed when the concentration of APDC reaches 0.11 mM. At higher ligand concentrations there was no observable change in the absorbance. Therefore, the optimal concentration of APDC in the extraction system was chosen as 0.11 mM.

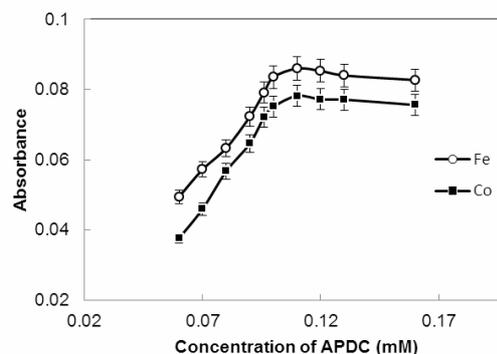


Fig. 4. Effect of the amount of APDC. Conditions: concentration of SAIL: 0.3 mM, Triton X-114: 0.9 ml of 1.0% solution, NaCl: 0.75%, pH for Co: 6.0 and for Fe: 4.0, Co: 1.0 mg l⁻¹, Fe: 0.5 mg l⁻¹.

Effect of Electrolyte

The variations in the analytical signal for both complexes as a function of the NaCl concentration were investigated (Fig. 5). It was observed that the analytical signal increased with the increase of NaCl amount up to 0.75% and then decreased in the range of 0.75-0.95%. A small amount of salt can decrease the solubility of the organic mixed-micellar phase in the aqueous phase, and salting-out occurs when the amount of salt surpass a certain limit. On the other hand, at higher salt concentrations, due to the increased solubility of the SAIL, the complete separation of the extracting phase would be impossible; hence a decrease in the extraction efficiency is obvious. Also, high concentration of salt can increase the density of water droplets accompanied by the extractant phase and hence disturb the phase separation [9,20]. Therefore, the NaCl content of the extraction mixture was adjusted to 0.75% as the optimum value.

Effects of Equilibration Temperature and Time

To achieve a quantitative separation of the extracting phase from the aqueous phase, it is necessary to maintain the extraction mixture at an appropriate temperature for a sufficient time period. Thus, to find the optimum conditions, the effects of the equilibration temperature and time were evaluated in the range of 20 to 80 °C and from 5 to 30 min, respectively. According to the obtained results, 45 °C equilibration temperature and 10 min incubation time were accepted as optimal conditions.

Centrifuging Conditions

The effect of the centrifugation time upon the extraction recovery of cobalt and iron was examined within the range of 5 to 20 min at 3000 rpm. A centrifugation time of 10 min at 3000 rpm was selected as optimal.

Interference Study

The effect of some foreign ions which may interfere in the simultaneous determination of cobalt and iron was studied. Thus, changes in the absorbance of cobalt and iron complexes were measured in the presence of different amounts of the probable interfering ions. A change of less than or equal to $\pm 5\%$ in the analytical signal was considered tolerable. Among the foreign ions tested, Ca^{2+} , Mg^{2+} , Cl^- ,

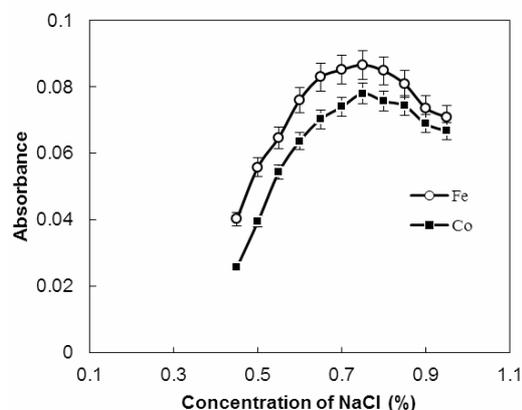


Fig. 5. Effect of NaCl concentration. Conditions: concentration of SAIL: 0.3 mM, concentration of APDC: 0.11 mM, Triton X-114: 0.9 ml of 1.0% solution, pH for Co: 6.0 and for Fe: 4.0, Co: 1.0 mg l⁻¹, Fe: 0.5 mg l⁻¹.

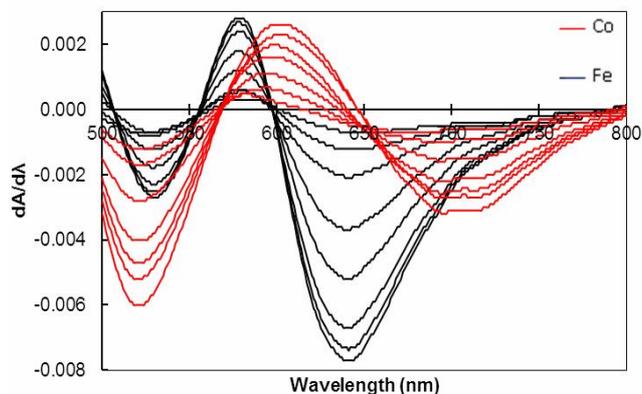


Fig. 6. First-order derivative spectra of Fe-APDC and Co-APDC complexes with varying concentration of the corresponding.

Na^+ , NO_3^- , Mn^{2+} , Hg^{2+} , Pb^{2+} , Cr^{3+} , Zn^{2+} , Ni^{2+} did not interfere at concentrations up to 1000 times greater than analytes. Only Cu^{2+} ion at concentrations of more than 50 times of the analytes had an interfering effect. The above results show the advantages of implementing measurements in the visible region, as APDC complexes of most of the investigated ions show absorption bands at the ultraviolet side of the spectrum; thus, it is possible to have a more selective determination.

Derivative Spectra

The spectra in the first-order derivative state were studied by the zero-crossing method to find the appropriate wavelengths for drawing calibration curves. Two sets of mixtures were prepared: one for standard solutions containing various amounts of cobalt in the presence of 0.2 mg l^{-1} of iron and a second for standard solutions containing various amounts of iron in the presence of 0.2 mg l^{-1} of cobalt. As shown in Fig. 6, zero-crossing wavelengths of Co(II) and Fe(II) complexes are obtained at 567 and 598 nm, respectively. Thus by measuring the absorbance of the iron-APDC complex at 567 nm, it is possible to obtain the concentration of iron without the interference of cobalt ions. On the other hand, accurate measurement of the concentration of cobalt would be possible at the zero-crossing wavelength of the iron-APDC complex (598 nm). Thus, two calibration curves were obtained for each complex at the corresponding zero-crossing wavelengths. The analytical features of the calibration graphs are summarized in Table 1.

Analytical Performance

Using measurements performed under the above optimal conditions, the calibration graphs for the determination of the pursued analyte ions were obtained (Table 1). The calibration curves were linear between 0.15 and 2.0 mg l^{-1} ($r = 0.9987$) for cobalt and 0.05 - 0.75 mg l^{-1} ($r = 0.9969$) for iron ions at the measuring wavelengths of 598 and 567 nm, respectively. The limit of detection ($3s_b/m$, where s_b is the standard deviation of the blank and m is the slope of the calibration curve) was obtained as 0.07 mg l^{-1} for cobalt and 0.01 mg l^{-1} for iron ions. The enhancement factors were calculated by dividing the slopes of calibration curves after and before the pre-concentration of the analytes. The relative standard deviation was obtained by measuring the concentration of analyte ions in eight 0.5 mg l^{-1} replicate samples. As shown in Table 1, the RSDs values resulted from the measurements of both ions were less than 4%. Table 2 summarizes the comparison of the analytical characteristics of the proposed method with the previously reported works for the simultaneous determination of cobalt and iron.

Table 1. Analytical Features of the Proposed method

Analyte	Linear range (mg l^{-1})	Regression equation	Regression coefficient	Limit of detection (mg l^{-1})	Enhancement factor	RSD (%)*
Co	0.15-2.0	$Y = 0.0013X - 7E-06$	0.9987	0.07	20.4	3.8%
Fe	0.05-0.75	$Y = 0.0027 X - 9E-05$	0.9969	0.01	20.4	3.9%

* 0.5 mg l^{-1} solution of analyte, $n = 8$.

Table 2. Comparison of the Analytical Features of the Proposed Method with the other Reports in the Literature

Pre-concentration method	Determination technique	Linear range for cobalt	Linear range for iron	LOD for cobalt	LOD for iron	Ref.
CPE	Spectrophotometry	5.89 - $35.4 \text{ (mg l}^{-1}\text{)}$	0.14 - $0.84 \text{ (mg l}^{-1}\text{)}$	$6.18 \text{ (}\mu\text{g l}^{-1}\text{)}$	$1.54 \text{ (}\mu\text{g l}^{-1}\text{)}$	[21]
CPE	Spectrophotometry	2 - $250 \text{ (ng ml}^{-1}\text{)}$	-	-	-	[22]
SPE ^a	FAAS ^b	-	-	$3.3 \text{ (}\mu\text{g l}^{-1}\text{)}$	$1.25 \text{ (}\mu\text{g l}^{-1}\text{)}$	[23]
CPE	Spectrophotometry	20 - $200 \text{ (}\mu\text{g l}^{-1}\text{)}$	-	$7.5 \text{ (}\mu\text{g l}^{-1}\text{)}$	-	[24]
CPE	FO-LADS ^c	-	5 - $200 \text{ (}\mu\text{g l}^{-1}\text{)}$	-	$0.5 \text{ (}\mu\text{g l}^{-1}\text{)}$	[25]
CPE	Spectrophotometry	0.05 - $10 \text{ (mg l}^{-1}\text{)}$	-	$0.012 \text{ (mg l}^{-1}\text{)}$	-	[26]
SAIL-Assisted CPE	Spectrophotometry	0.15 - $2.0 \text{ (mg l}^{-1}\text{)}$	0.05 - $0.75 \text{ (mg l}^{-1}\text{)}$	$0.07 \text{ (mg l}^{-1}\text{)}$	$0.01 \text{ (mg l}^{-1}\text{)}$	This work

^aSolid phase extraction. ^bFlame atomic absorption spectrometry. ^cFiber optic linear array detection spectrophotometry.

Table 3. Simultaneous Determination of Iron and Cobalt Ions in Synthetic Binary Mixtures and Permendur Alloy

Sample	Concentration		Found ^a		Recovery (%)	
	Fe	Co	Fe	Co	Fe	Co
Synthetic mixture 1	0.50 (mg l ⁻¹)	0.70 (mg l ⁻¹)	0.51 ± 0.02 (mg l ⁻¹)	0.69 ± 0.03 (mg l ⁻¹)	102.0	98.6
Synthetic mixture 2	0.20 (mg l ⁻¹)	0.50 (mg l ⁻¹)	0.19 ± 0.01 (mg l ⁻¹)	0.49 ± 0.02 (mg l ⁻¹)	95.0	98.0
Permendur 49 alloy ^b	49%	49%	48 ± 1.9%	48 ± 1.8%	98.0	98.0

^aAverage of three determinations ± S.D. ^bMeasurements were made on a 1.0 mg l⁻¹ solution of the dissolved alloy.

Table 4. Determination of Iron and Cobalt Ions in Real Water Samples

Sample	Amount added (mg l ⁻¹)		Amount found (mg l ⁻¹) ^a		Recovery (%)	
	Iron	Cobalt	Iron	Cobalt	Iron	Cobalt
Tap water	0.0	0.0	N.D. ^b	N.D.	-	-
	0.30	0.40	0.30 ± 0.01	0.41 ± 0.01	100.0	102.5
	0.50	0.60	0.49 ± 0.02	0.61 ± 0.02	98.0	101.7
Rain water	0.0	0.0	N.D.	N.D.	-	-
	0.30	0.40	0.29 ± 0.01	0.39 ± 0.01	96.7	97.5
	0.50	0.60	0.48 ± 0.02	0.62 ± 0.02	96.0	103.3

^aAverage of three determinations ± S.D. ^bNot detected.

Analysis of Real Samples

The proposed procedure has been applied to the determination of Co(II) and iron(II) ions in synthetic samples as well as standard reference material and environmental water samples. In addition, measurement of spiked samples was made to assay the accuracy of the analyses. The recovery results were varied between 97.0 to 102.0 percent that shows the validity of the proposed method. The obtained results are summarized in Tables 3 and 4.

CONCLUSIONS

A simple, accurate, and sensitive SAIL-based pre-concentration method was proposed for the simultaneous determination of cobalt and iron ions by visible spectrophotometry. The interference of each ion in the determination of the other was canceled by using derivative spectroscopy. The first-order derivative spectra enabled us to determine the investigated analyte ions in the presence of

each other. In addition, the presence of SAIL in the cloud point extraction process provides suitable conditions to have a complete and easy phase separation stage, which directly affects the repeatability and accuracy of the final results. Therefore, the combination of SAIL-based mixed-micellar CPE and derivative spectroscopy can be used as a sensitive and selective procedure for the determination of interested analytes. The proposed method was applied successfully to the simultaneous measurement of iron and cobalt content of different real samples.

ACKNOWLEDGMENTS

Support of this work by the Arak university research council is appreciated.

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