

# Optimization of a new cloud point extraction procedure for the selective determination of trace amounts of total iron in some environmental samples

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A new, simple, and rapid cloud point extraction (CPE) procedure system, combined with flame atomic absorption spectrometry (FAAS), was developed for selective separation, preconcentration, and determination of trace amounts of total iron in some environmental samples. The complexing agent, N,N'-(2,2'-(ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(2-chloroacetamide) (EDBOCA), is selective at pH 5.0 for only Fe(II) and Fe(III) ions in the presence of Cu(II), Pb(II), Cd(II), Mn(II), Co(II), Cr(III), Cr(VI), Ni(II), Zn(II), Al(III), Mo(VI), Pd(II), Pt(IV), Au(III), and V(V) ions. The procedure is based on the complexation of Fe(III) ions with EDBOCA reagent in the presence of Triton X-114 (TX-114) as a non-ionic surfactant. The optimum conditions for the CPE of Fe(III) ions were investigated with respect to several experimental parameters such as pH of the solution, TX-114 and EDBOCA concentrations, incubation time and temperature, and centrifugation rate and time. The detection limit for Fe(III) ions based on the 3 times the standard deviation of the blanks (*N*:10) was found to be 1.22  $\mu\text{g L}^{-1}$ , while the relative standard deviation (RSD) was 4.2%. Environment Canada TM-25.3 and CRM-SA-C Sandy Soil C, as certified reference materials, were used, and spike tests were applied to validate the method. The method was applied to some real environmental samples to evaluate their total iron levels.

**Key Words:** Preconcentration, cloud point extraction, iron, flame atomic absorption spectrometry, Triton X-114

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## Introduction

Iron is known as one of the essential nutritional elements for many living organisms due to its role in most of metabolic processes, including oxygen and electron transport, and DNA synthesis. On the other hand, exposure to excess iron can cause several diseases or disorders such as endocrine problems, arthritis, diabetes, and liver disease.<sup>1,2</sup> According to the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for iron is 2.0 mg L<sup>-1</sup>.<sup>3</sup> Thus, the accurate and precise determination of iron ions in environmental samples is an important task in terms of protecting public health.

Flame atomic absorption spectrometry (FAAS), a low cost and simple method, is usually utilized in the determination of trace metal ions in environmental samples. However, the direct determination of analyte ions by FAAS sometimes becomes impossible because of the analyte levels' being lower than the limit of quantitation of the instrument and interfering effects of the matrix ions, and hence a separation and preconcentration step is usually required before the analysis of analyte ions.<sup>4</sup> Solid phase extraction,<sup>5</sup> liquid-liquid extraction,<sup>6</sup> coprecipitation,<sup>7</sup> ion-exchange,<sup>8</sup> and cloud point extraction (CPE)<sup>9</sup> have been utilized as separation and preconcentration techniques. Among them, CPE is considered the most versatile and simple method for separation and preconcentration of trace metal ions from aqueous solutions, because this technique provides some advantages such as safety, low cost, high extraction efficiency, easy disposal of the surfactants, and low toxicity of the utilized reagents compared with classical organic solvents.<sup>10</sup>

In CPE, nonionic surfactants such as Triton X-100, Triton X-114, and Tween 80 tend to form micelles in aqueous solutions and become turbid when heated to the cloud point temperature. Above the cloud point, the micellar solution separates into a surfactant rich phase, known as the coacervate phase with a small volume, and into a diluted aqueous phase, with a large volume. When the analyte ions, which are primarily present in the aqueous solution and bound to the micelles, form hydrophobic compounds with a chelating agent, they are extracted to the surfactant-rich phase, and hence they can easily be separated and preconcentrated by this way.<sup>11,12</sup>

In the present study, we applied CPE for the separation and preconcentration of Fe(III) ions from aqueous solutions by using Triton X-114 as a nonionic surfactant. An acetamide derivative, N,N'-(2,2'-(ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(2-chloroacetamide) (EDBOCA), was used for the formation of EDBOCA-Fe(III) complex. The selectivity of EDBOCA towards the quantitative recoveries of different metal ions (Cu(II), Pb(II), Cd(II), Mn(II), Co(II), Cr(III), Cr(VI), Fe(III), Fe(II), Ni(II), Zn(II), Al(III), Mo(VI), Pd(II), Pt(IV), and Au(III)) was checked in the pH range of 1.0-8.0, and the quantitative recovery values were obtained for only Fe(II) and Fe(III) ions in the presence of the other metal ions at pH 5. The factors influencing the efficiency of CPE such as effects of pH, Triton X-114 (TX-114) and EDBOCA concentrations, incubation time and temperature, and centrifugation rate and time were systematically studied. The developed CPE procedure was successfully applied to determine the total iron in some environmental samples after the method was validated.

## Experimental

### Apparatus and reagents

The determination of Fe(III) and also other metal ions, used for checking the selectivity of EDBOCA, were performed using a Unicam AA-929 model Flame Atomic Absorption Spectrometer. In order to adjust the desired pH value of the samples, a Hanna pH-211 (HANNA instruments, Romania) digital pH meter with

a glass electrode was used. The centrifugation of the solutions was performed with a Sigma 3-16P (Sigma Laborzentrifugen GmbH, Germany) model centrifuge. The digestion of the solid samples was carried out with a Milestone Ethos D (Milestone Inc., Italy) closed vessel microwave system. A Nüve BM 402 model thermostat bath, maintained at the desired temperature, was used for the CPE experiments.

In order to characterize EDBOCA, the IR spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer, using potassium bromide pellets.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in  $\text{CDCl}_3$ , and chemical shifts ( $\delta$ ) are reported relative to  $\text{Me}_4\text{Si}$  as internal standard. The mass spectra were measured on a Varian 711 and VG Zapspec spectrometer. Elemental analyses of this compound were performed using a LECO Elemental Analyzer (CHNS O932) and Unicam 929 AA spectrophotometer. The melting point was measured on an electrothermal apparatus.

The 1000 mg  $\text{L}^{-1}$  of stock solutions of  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{Cr}(\text{NO}_3)_3$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{FeSO}_4$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ,  $\text{Pd}(\text{NO}_3)_2$ ,  $\text{H}_2\text{PtCl}_6$ ,  $\text{V}_2\text{O}_5$  and  $\text{H}(\text{AuCl}_4)$ , which were used for checking the selectivity of EDBOCA, were purchased from Sigma and Aldrich. The  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ , and  $\text{Na}_2\text{HPO}_4$  salts, which were used for evaluating the interfering effects of some anions and cations, were purchased from Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland). The working metal ion solutions were prepared by diluting stock solutions of them. For preparing the stock and model solutions, distilled/deionized water was used. EDBOCA solution (0.2% (w/v)) was prepared in ethanol to use in the experiments. TX-114 (tert-octylphenoxy poly(oxyethylene)ethanol, molecular weight:  $537 \text{ g mol}^{-1}$ , cloud point:  $23 \text{ }^\circ\text{C}$ ), obtained from Merck, was used as the non-ionic surfactant. The solution of TX-114 was prepared as 4.0% (w/v) to use in the experiments. Environment Canada TM-25.3 and CRM-SA-C Sandy Soil C were obtained from High-Purity Standard Inc.

## Synthesis and characterization of EDBOCA

EDBOCA (Figure 1) was synthesized according to the literature.<sup>13</sup> 2,2'-(Ethylenedioxy)bis(ethylamine) (1.48 g, 10.0 mmol) was dissolved in dichloromethane (75 mL), and potassium carbonate (5.5 g, 39.8 mmol) was added. The mixture was cooled to  $0 \text{ }^\circ\text{C}$ , and a solution of chloroacetylchloride (2.3 mL, 28.7 mmol) in dichloromethane (30 mL) was added dropwise with stirring. The reaction was stirred at  $0 \text{ }^\circ\text{C}$  for 5 h. The reaction was then quenched with water (100 mL). The reaction was transferred to a separatory funnel, and the 2 phases were separated; the organic layer was washed with a 5% citric acid solution (50 mL) and then with water (100 mL). The organic phase was dried ( $\text{Na}_2\text{SO}_4$ ), and the solvents were removed under reduced pressure. The residue was recrystallized from ethyl acetate to afford the title compound as a colorless crystalline solid. Yield: (2.5 g, 82%); mp:  $89\text{--}90 \text{ }^\circ\text{C}$ . Anal. Calcd. ( $\text{C}_{10}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_4$ ) (%): C, 39.9; H, 6.1; N, 9.3. Found: C, 39.6; H, 6.2; N, 9.3. IR(KBr pellets): 3309 (NH), 2872, 1658 (C=O), 1547, 1449, 1413, 1272, 1141, 1043, 759.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta=7.02$  (2H, br, NH), 4.05 (4H, s,  $\text{COCH}_2\text{Cl}$ ), 3.62 (4H, s,  $\text{OCH}_2\text{CH}_2\text{O}$ ), 3.59 (4H, t,  $\text{OCH}_2\text{CH}_2\text{N}$ ), 3.54 (4H, t,  $\text{OCH}_2\text{CH}_2\text{N}$ ).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta=166.2$  (C=O), 70.5 ( $\text{OCH}_2\text{CH}_2\text{O}$ ), 69.6 ( $\text{OCH}_2\text{CH}_2\text{N}$ ), 42.9 ( $\text{COCH}_2\text{Cl}$ ), 39.7 ( $\text{OCH}_2\text{CH}_2\text{N}$ ). MS;  $m/z=302[\text{M}+1]^+$ .

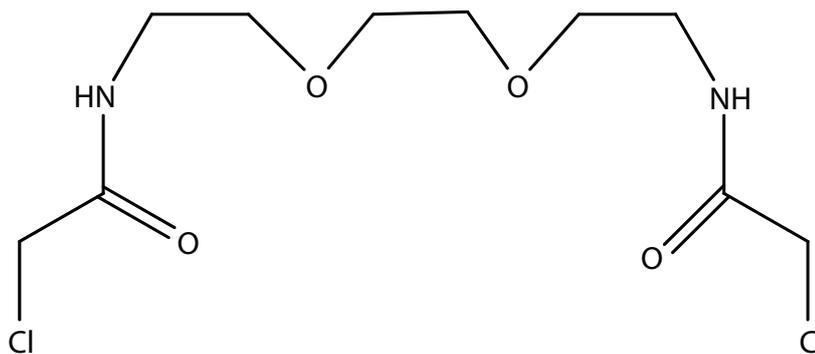


Figure 1. Chemical structure of EDBOCA.

### Preconcentration studies

For CPE experiments, 0.1% (w/v) of TX-114 (1.25 mL of TX-114 from 4.0% (w/v) solution of it) and 3.0 mg of EDBOCA (1.5 mL of EDBOCA from 0.2% (w/v) solution of it) were added into a 50 mL of aqueous solution containing 12.5  $\mu\text{g}$  of Fe(III) ions. The pH of the solution was adjusted to 5.0 by using dilute HCl or NaOH solutions. The mixture was kept in a thermo-stated bath at 60 °C for 30 min. The separation of the 2 phases was accelerated by centrifugation of the solution for 5 min at 2000 rpm. The viscosity of the surfactant-rich phase was increased by cooling the system in an ice-bath for 5 min. After decantation, the surfactant-rich phase that remained adhered to the tube was dissolved with 2.0 mL of conc.  $\text{HNO}_3$ . Then the final volume was completed to 5.0 mL with distilled/deionized water and the level of the Fe(III) ions was determined by FAAS. The recovery values of Fe(III) ions were calculated by using the following equation:

$$\%R = \frac{Q}{Q_o} \times 100, \quad (1)$$

where  $Q$  ( $\text{mg L}^{-1}$ ) is the Fe(III) concentration determined in solution after the preconcentration step and  $Q_o$  ( $\text{mg L}^{-1}$ ) is the Fe(III) concentration present in solution before the preconcentration step.

### Analysis of real samples

The present CPE method was applied for determination of total iron in sea, stream, and tap waters as liquid samples, and tobacco and black tea as solid samples. The method was also applied to Environment Canada TM-25.3 and CRM-SA-C Sandy Soil C reference materials for method validation.

The microwave digestion of the solid samples was performed according to the literature<sup>7</sup> after 0.750 g of tobacco and black tea and 0.100 g of CRM-SA-C Sandy Soil C samples being weighed into Teflon vessels. Then the volume of the samples was completed to 50 mL with distilled/deionized water and the developed CPE method was applied to them.

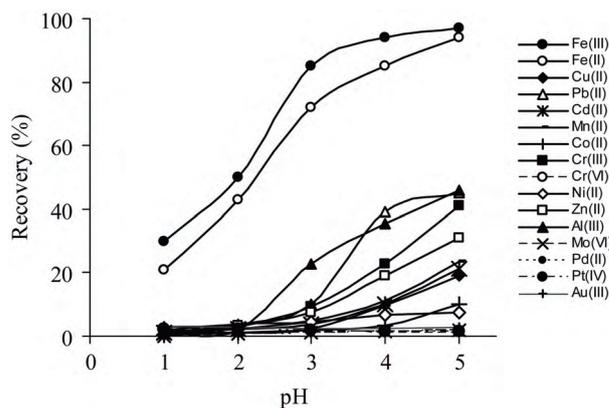
The preconcentration procedure was applied to 50 mL of Environment Canada TM-25.3 samples without any pretreatment. Other water samples were filtered and stored at 4 °C in a refrigerator in polyethylene bottles after acidifying with 1% (v/v)  $\text{HNO}_3$ , which was prepared by diluting 1.0 mL of conc.  $\text{HNO}_3$  to 100 mL with

distilled/deionized water. Before the analysis, the pH of the samples was adjusted to 5.0. Then the CPE procedure described above was applied.

## Results and discussion

### Effect of pH on extraction efficiency

The solution pH plays a significant role in the formation of metal complexes with a chelating agent. The effects of pH on the recoveries of some metal ions were evaluated in the pH range of 1.0-8.0. At pH 5.0, only Fe(II) and Fe(III) ions were quantitatively recovered using the present CPE procedure, which indicates the selectivity of EDBOCA towards iron ions. Figure 2 was depicted for the recovery values of studied metal ions in the pH range of 1.0-5.0. This figure contains the conjoined data of 4 different experiments, which were applied to different metal ion solution mixtures. The first mixture contains 25  $\mu\text{g}$  of Fe(III), Cu(II), Mn(II), Co(II), Cr(III), and Ni(II); 50  $\mu\text{g}$  of Pb(II); 5  $\mu\text{g}$  of Cd(II); and 250  $\mu\text{g}$  of Pt(IV). The second mixture contains 25  $\mu\text{g}$  of Fe(III) and Cr(VI); 10  $\mu\text{g}$  of Zn(II); 50  $\mu\text{g}$  of Au(III) and Pd(II); and 200  $\mu\text{g}$  of Al(III) and Mo(VI). The third and fourth mixtures contain the same types and amounts of metal ions present in the first and second mixtures, respectively, the only difference is that the third and fourth mixtures contain Fe(II) ions instead of Fe(III) ions. After application of the CPE experiments for all of the mixtures at different pH values, the surfactant-rich phase was dissolved with 2.0 mL of conc.  $\text{HNO}_3$  and the final volume was completed to 10 mL with distilled/deionized water. The recovery values obtained above pH 5.0 are not shown in Figure 2, since both iron ions and other metal ions may be precipitated as their hydroxides after that pH value. All further CPE experiments were performed at pH 5.0 for Fe(III) ions.



**Figure 2.** Effect of pH on the recovery of metal ions (Sample volume: 50 mL, EDBOCA amount: 3.0 mg, TX-114 conc.: 0.1% (w/v), equilibrium temperature: 60 °C and incubation time: 30 min, centrifugation rate and time: 2000 rpm and 5 min).

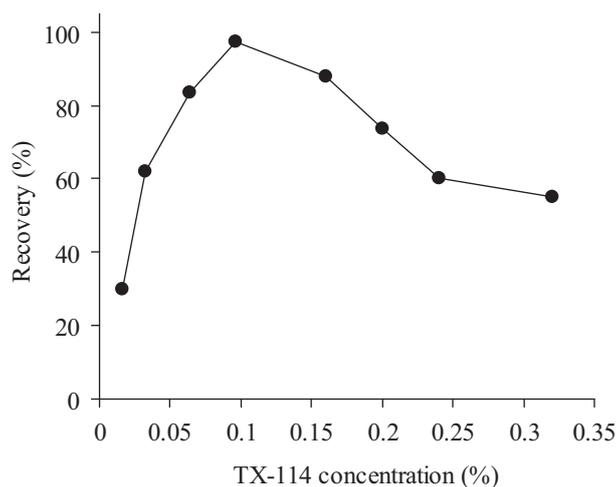
### Effect of TX-114 concentration

TX-114 was chosen as nonionic surfactant in the present study because of its low cost, commercial availability with high purity, and low toxicological properties, and also its high viscosity provides the opportunity for

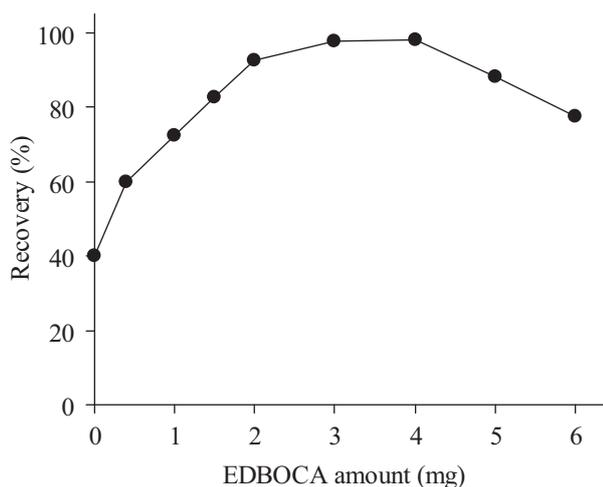
easy phase separation by centrifugation. The effect of TX-114 concentration was evaluated in the range of 0.02%-0.32% (w/v) (Figure 3). The extraction efficiency of Fe(III)-EDBOCA complex increased from 30.0% to 97.5%, as the TX-114 concentration was increased from 0.02% to 0.1% (w/v). The further increase in TX-114 concentration resulted in a decrease in Fe(III) recovery, because of an excessive increase in surfactant-rich phase volume. The reason for the lower recovery values at lower TX-114 concentrations may be related to the inadequacy of the volume of surfactant rich phase to entrap the Fe(III)-EDBOCA complex quantitatively.<sup>14,15</sup> As a result, the TX-114 concentration was optimized as 0.1% (w/v) for obtaining the quantitative recovery values.

### Effect of EDBOCA amount

The effects of amount of EDBOCA, as complexing agent, on the recoveries of Fe(III) ions were studied in the EDBOCA amount range of 0.0-6.0 mg (Figure 4). Under optimum conditions, the recoveries of Fe(III) ions were 40% without adding EDBOCA, which indicated that for the quantitative recoveries of Fe(III) ions EDBOCA is necessary. With increasing amount of EDBOCA from 0.0 to 4.0 mg, the recovery percentage of Fe(III) increased from 40% to 98%. However, when the amount of EDBOCA was beyond 4.0 mg, the extraction efficiency suddenly decreased. The decrease in extraction efficiency may be related to the stronger hydrophobicity of EDBOCA than the complex (Fe(III)- EDBOCA); hence more EDBOCA was entrapped in the surfactant-rich phase, as more complex remained in the aqueous phase.<sup>16</sup> Furthermore, when the amount of EDBOCA was increased beyond 4.0 mg, more volume of ethanol, as solvent of EDBOCA, enters the solution and prevents the formation of micelles, which causes the reduction in extraction efficiency.<sup>17</sup> Therefore, the EDBOCA amount was chosen as 3.0 mg for subsequent experiments.



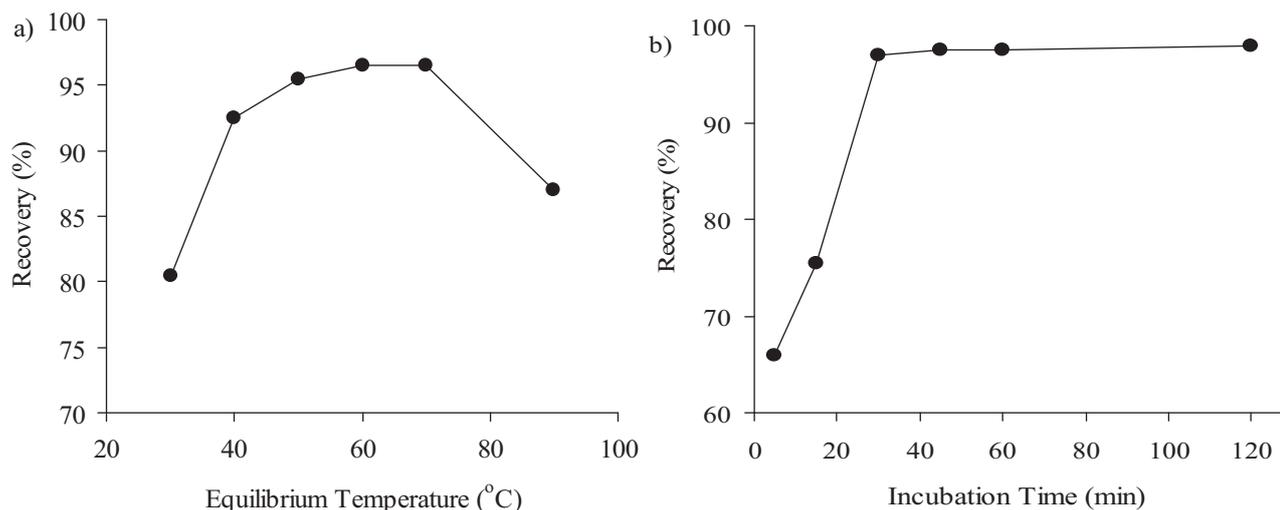
**Figure 3.** Effect of TX-114 concentration on the recovery of Fe(III) ions (Sample volume: 50 mL, Fe(III) quantity: 12.5  $\mu$ g, pH: 5.0, EDBOCA amount: 3.0 mg, equilibrium temperature: 60 °C and incubation time: 30 min).



**Figure 4.** Effect of EDBOCA amount on the recovery of Fe(III) ions (Sample volume: 50 mL, Fe(III) quantity: 12.5  $\mu$ g, TX-114 conc.: 0.1% (w/v), equilibrium temperature: 60 °C and incubation time: 30 min, centrifugation rate and time: 2000 rpm and 5 min).

### Effect of equilibrium temperature and time

The extraction efficiency is strongly affected by the temperature and incubation time. It is desirable to carry out the CPE experiments in the shortest possible incubation time and at the lowest equilibration temperature.<sup>18</sup> The effects of equilibration temperature were evaluated in the range of 30-90 °C (Figure 5(a)). The quantitative recovery values were obtained in the temperature range of 50-70 °C. The decrease in the extraction efficiency beyond 70 °C may be related to the decomposition of the Fe(III)-EDBOCA complex. Hence, the optimum equilibration temperature was selected as 60 °C. The effects of incubation time were evaluated in the range of 5-120 min (Figure 5(b)), and it was found that an incubation time of 30 min was sufficient for quantitative extraction.



**Figure 5(a).** Effect of equilibrium temperature on the recovery of Fe(III) ions (pH: 5.0, Fe(III) quantity: 12.5  $\mu\text{g}$ , TX-114 conc.: 0.1% (w/v), EDBOCA amount: 3.0 mg, incubation time: 30 min **(b)** Effect of incubation time on the recovery of Fe(III) ions (pH: 5.0, Fe(III) quantity: 12.5  $\mu\text{g}$ , TX-114 conc.: 0.1% (w/v), EDBOCA amount: 3.0 mg, equilibrium temperature: 60 °C).

### Effect of centrifugation rate and time

The effects of centrifugation rate and time were evaluated in the range of 1500-3500 rpm and 5-30 min, respectively. For complete phase separation, a centrifugation rate of 2000 rpm and centrifugation time of 5 min were found to be optimum.

### Interference study

In order to evaluate the usage of the presented CPE procedure in analytical applications, the effects of the potential interfering species were tested by contacting known amounts of some anions and cations with 12.5  $\mu\text{g}$  of Fe(III) ions, under the optimal conditions. Then the CPE procedure was applied for all the interfering ions, separately. The results indicated that the Fe(III) recoveries were almost quantitative in the presence of most

of the interfering ions. Moreover, some of the transition metals did not interfere with the recoveries of Fe(III) ions (Table 1).

**Table 1.** Effects of some foreign ions on the recovery of Fe(III) ions (pH: 5.0, sample volume: 50 mL, Fe(III) quantity: 12.5  $\mu\text{g}$ , EDBOCA amount: 3.0 mg, TX-114 conc.: 0.1% (w/v), equilibrium temperature: 60 °C, incubation time: 30 min, centrifugation rate and time: 2000 rpm and 5 min).

Ions	Added as	Conc. ( $\text{mg L}^{-1}$ )	Fe(III) recovery (%)
$\text{Na}^+$	NaCl	5000	$95.8 \pm 2.5$
$\text{K}^+$	KCl	1000	$93.7 \pm 1.7$
$\text{Ca}^{2+}$	$\text{CaCl}_2$	1000	$99.7 \pm 1.0$
$\text{Mg}^{2+}$	$\text{Mg}(\text{NO}_3)_2$	1000	$93.0 \pm 2.5$
$\text{CO}_3^{2-}$	$\text{Na}_2\text{CO}_3$	1000	$91.0 \pm 2.1$
$\text{SO}_4^{2-}$	$\text{Na}_2\text{SO}_4$	1000	$97.0 \pm 2.5$
$\text{NH}_4^+$	$\text{NH}_4\text{NO}_3$	1000	$101.0 \pm 1.1$
$\text{HPO}_4^{2-}$	$\text{Na}_2\text{HPO}_4$	1000	$90.2 \pm 3.9$
$\text{Al}^{3+}$ , $\text{Cd}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Pb}^{2+}$ , $\text{V}(\text{OH})_4^+$ , $\text{Co}^{2+}$	*	25	$95.5 \pm 1.4$
Mixed <sup>a</sup>			$97.0 \pm 1.8$

\* $\text{V}(\text{OH})_4^+$  added as  $\text{V}_2\text{O}_5$ , other ions added as their nitrate salts.

<sup>a</sup> 5734  $\text{mg L}^{-1}$   $\text{Na}^+$ , 8388  $\text{mg L}^{-1}$   $\text{Cl}^-$ , 2282  $\text{mg L}^{-1}$   $\text{NO}_3^-$ , 250  $\text{mg L}^{-1}$   $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{HPO}_4^{2-}$ , 10  $\text{mg L}^{-1}$   $\text{Al}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{V}(\text{OH})_4^+$ , and  $\text{Co}^{2+}$ .

## Analytical performance of the method

The limit of detection (LOD), the concentration giving a signal equivalent to 3 times the standard deviation of 10 replicate analyses of the blank samples, was found to be 1.22  $\mu\text{g L}^{-1}$  for Fe(III) ions when the sample volume was 50 mL and the final volume was 5.0 mL (preconcentration factor is 10). The relative standard deviation (RSD), which reflects the precision of the method, was found to be 4.2% after the CPE experiments were repeated 10 times with 12.5  $\mu\text{g}$  of Fe(III) ions in 50 mL of aqueous solution under optimum conditions. The linear range for iron determination by FAAS was found to be in the range of 0.2-5.0  $\text{mg L}^{-1}$ .

## Method validation and application to real samples

The accuracy of the CPE method was tested by spiking different amounts of the Fe(III) ions in 50 mL of sea water (Black Sea, Trabzon, Turkey), stream water (Şana Stream, Trabzon, Turkey), and tap water (Karadeniz Technical University, Trabzon, Turkey) as liquid samples (Table 2), and in 0.750 g of microwave digested black tea and tobacco samples (Table 3). The obtained results showed the applicability of the new CPE method in separation and preconcentration of iron ions in environmental liquid and solid samples.

The certified values for the components of Environment Canada TM-25.3 and CRM-SA-C Sandy Soil C, which were used for accuracy tests, are given in Table 4(a) and Table 4(b), respectively. As can be seen, in

Environment Canada TM-25.3, the certified iron ion value is  $29.5 \mu\text{g L}^{-1}$  and the found value is  $28.4 \pm 2.4 \mu\text{g L}^{-1}$  (96% recovery), and in CRM-SA-C Sandy Soil C the certified iron ion value is  $13.9 \pm 1.2 \text{ mg g}^{-1}$  and the found value is  $13.8 \pm 0.7 \text{ mg g}^{-1}$  (99% recovery). The good agreement obtained between the analytical and certified values also supported the accuracy of the method.

**Table 2.** Spiked recoveries of Fe(III) ions from water samples ( $N$ : 3, pH: 5.0, sample volume: 50 mL, EDBOCA amount: 3.0 mg, TX-114 conc.: 0.1% (w/v), final volume: 5.0 mL).

Added Fe(III) ( $\mu\text{g}$ )	Sea water		Stream water		Tap water	
	Found ( $\mu\text{g}$ )	Recovery (%)	Found ( $\mu\text{g}$ )	Recovery (%)	Found ( $\mu\text{g}$ )	Recovery (%)
0.0	ND*	-	ND	-	ND	-
5.0	$5.3 \pm 0.2$	106	$5.1 \pm 0.3$	102	$4.8 \pm 0.2$	96
10.0	$9.8 \pm 0.5$	98	$9.3 \pm 0.4$	93	$9.7 \pm 0.6$	97

\*Not detected

**Table 3.** Spiked recoveries of Fe(III) ions from solid samples ( $N$ : 3, pH: 5.0, EDBOCA amount: 3.0 mg, TX-114 conc.: 0.1% (w/v), sample quantities: 0.750 g of black tea and tobacco, final volume: 5.0 mL).

Added Fe(III) ( $\mu\text{g}$ )	Black tea		Tobacco	
	Found ( $\mu\text{g}$ )	Recovery (%)	Found ( $\mu\text{g}$ )	Recovery (%)
0.0	$97.0 \pm 3.5$	-	$78.4 \pm 0.9$	-
10.0	$107.7 \pm 2.4$	107	$87.5 \pm 1.3$	91

**Table 4.** (a) The certified values for the components of Environment Canada TM-25.3 (b) The certified values for the components of CRM-SA-C Sandy Soil.

(a)

Element	Conc. ( $\mu\text{g L}^{-1}$ )	Element	Conc. ( $\mu\text{g L}^{-1}$ )	Element	Conc. ( $\mu\text{g L}^{-1}$ )
Al	24.6	Fe	29.5	Ti	24.6
Sb	23.7	Pb	27.8	W	8.4*
As	27.6	Li	25.6	U	27.4
Ba	26.8	Mn	25.4	V	26.3
Be	26.0	Mo	28.8	Zn	41.9
Bi	22.4*	Ni	15.5		
B	32.4	Rb	10*		
Cd	24.0	Se	27.9		
Cr	24.5	Ag	22.0		
Co	28.0	Sr	69.9		
Cu	27.6	Tl	29.9		
Ga	5.4*	Sn	24.4		

\*Not certified values, given for information only

**Table 4.** Continued.

(b)

Element	Conc. (mg g <sup>-1</sup> )	Element	Conc. (μg g <sup>-1</sup> )	Element	Conc. (μg g <sup>-1</sup> )
Al	6.18 ± 0.36	Ag	24.6 ± 1.6	Ni	48.4 ± 3.0
Ca	12.9 ± 0.4	As	67.7 ± 4.2	Pb	120 ± 8
Fe	13.9 ± 1.2	Au	(25)*	Pd	(4)*
K	0.19 ± 0.03	B	(20)*	Pt	(17)*
Mg	0.92 ± 0.03	Ba	12.4 ± 0.5	Sb	(14)*
Mn	0.317 ± 0.025	Be	2.3 ± 0.2	Se	107 ± 7
Na	0.43 ± 0.03	Cd	109 ± 8	Sn	(50)*
P	(0.96)*	Co	12.4 ± 0.6	Sr	38.5 ± 1.4
Ti	0.043 ± 0.004	Cr	54.1 ± 4.2	Tl	51.0 ± 2.0
S	(0.35)*	Cu	63.6 ± 4.0	V	60.2 ± 4.0
		Li	70.3 ± 4.0	Zn	607 ± 30
		Mo	53.6 ± 4.0	Hg	(5)*

\*Not certified values, given for information only

After the accuracy of the presented method was tested, the CPE procedure was applied to black tea and tobacco samples, and the concentrations of total iron ions were found to be 129.0 ± 3.5 and 104.5 ± 0.9 μg g<sup>-1</sup>, respectively.

## Conclusions

The developed CPE procedure, based on the complexation of Fe(III) ions with N,N'-(2,2'-(ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(2-chloroacetamide) (EDBOCA) reagent in the presence of non-ionic surfactant of Triton X-114, provides a versatile, simple, rapid, and low cost methodology for selective separation and preconcentration of total iron ions in aqueous solutions. One of the main advantages of the method can be

**Table 5.** Optimization parameters for the quantitative recovery of Fe(III) ions.

Optimization parameters	
pH	5.0
TX-114 concentration	0.1% (w/v)
EDBOCA amount	3.0 mg
Incubation time	30 min
Equilibrium temperature	60 °C
Centrifugation rate	2000 rpm
Centrifugation time	5 min
Final volume	5.0 mL

Table 6. Previous studies in the literature on the CPE of iron ions.

Analyte and method	Complexing agent	pH	PF	LOD ( $\mu\text{g L}^{-1}$ )	RSD (%)	Technique	Ref.
Fe(II)-speciation-CPE	2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP)	5.0	20	0.8 for Fe(II) 1.0 for Fe(III)	2.0 for Fe(II) 2.6 for Fe(III)	UV/Vis spectrophotometry	19
Fe(III)-Flow Injection CPE	Eriochrome Cyanine R	4.5	-	0.33	1.9	FAAS	20
Fe(III)-CPE	2-phenyl-1H-benzol[d]imidazole	8.5	30	2.8	3.6	FAAS	21
Fe(III)-CPE	1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP)	5.5	-	0.08	4.2	GFAAS	22
Fe(III)-Flow Injection CPE	2-(5-bromo-2-pyridylazo)-5-diethylaminophenol	9.0	200	0.48	<1	Capillary electrophoresis (CE) with UV detection	23
Fe(III)-CPE	N,N'-(2,2'-(ethane-1,2-diy)bis(oxy))bis(ethane-2,1-diy))bis(2-chloroacetamide) (EDBOCA)	5.0	10	1.22	4.2	FAAS	This work

considered the selectivity of EDBOCA towards iron ions at pH 5.0 in the presence of most of the metal ions. Quantitative recovery values were obtained for Fe(III) ions after the experimental parameters were optimized as given in Table 5. Some of the reported studies in the literature related with the CPE of iron ions<sup>19–23</sup> are given in Table 6. The present CPE method is superior to those reported CPE methods in the literature as there is no need to use complex and expensive instruments. The procedure was successfully applied to real samples for the determination total iron levels with acceptable accuracy and precision.

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