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Separation, Preconcentration and Measurement of Inorganic Iron Species by Cloud Point Extraction and Flow Injection Flame Atomic Absorption Spectrometry

F. Shakerian, S. Dadfarnia* and A.M. Haji Shabani
Department of Chemistry, Faculty of Sciences, Yazd University, 89195-741 Yazd, Iran

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A sensitive and simple method for determination of iron species after separation/preconcentration by cloud point extraction (CPE) has been developed. When the temperature is higher than the cloud point extraction temperature (60 °C), the complexes of iron(II) and iron(III) species with ferron enter the surfactant-rich phase. Total amount of iron in the surfactant-rich phase was analyzed by FI-AAS, whereas, Fe(II) concentration was determined by a spectrophotometric method using mathematical equation to overcome the interference of Fe(III), when they are both present in the same solution. In this way the time-consuming and labor-intensive steps of preoxidation of Fe(II) or reduction of Fe(III) were eliminated. The parameters affecting could point extraction, such as concentrations of ferron and Triton X-114, pH, and equilibrium temperature were systematically investigated. Under the optimum conditions, the calibration curves were linear over the range of 10-250 and 5-150 μg l^{-1} for 20 and 40 ml preconcentration volume, respectively. The detection limit was 1.7 μg l^{-1}, and relative standard deviation (RSD) was 2.1% for 20 ml preconcentration volume. The method was applied to the determination of iron species in water samples and total iron in milk. The accuracy was determined by recovery experiment, independent analysis by furnace atomic absorption spectrometry and analysis of certified reference water.

Keywords: Cloud point extraction, Flame atomic absorption spectrometry, Ferron, Triton X-114, Iron Speciation, Total iron determination

INTRODUVTION

Iron is the most important transition element involved in living system, being vital to both plants and animals. Its versatility is unique. It is at the active center of molecules responsible for oxygen transport and electron transport and is found in such diverse metalloenzyme as nitrogenase, various oxidases, hydrogenases, reductases, dehydrogenases, deoxygenases and dehydrases. Iron involved in enormous range of function and the whole gamut of life forms, from bacteria to man. Iron has two readily inter converted oxidation states [1,2]. Excess concentration of iron is potentially toxic to human due to its pro-oxidant activity. Determination of oxidation state of iron in aquatic system is very important for environmental and biological studies because of the influence of the chemical forms on the bioavailability of iron and physicochemical and toxicological properties of other trace elements and organic substrates [3-5]. Expensive analytical methods such as inductively coupled plasma mass spectrometry (ICP-MS) [6], inductively coupled plasma optical emission spectrometry (ICP-OES) [7] and capillary electrophoresis (CE) [8] have been employed for the determination of Fe(II) and Fe(III). Flame atomic absorption spectrometry (FAAS) has been widely used for the

*Corresponding author. E-mail: sdadfarnia@yazduni.ac.ir

determination of metal ions [9-11]. Common availability of the instrumentation, simplicity of the procedures and the speed, precision and accuracy of the technique still make flame atomic absorption method an attractive alternate. However, the concentration of iron species in natural water (at μg l^{-1} level) are usually lower than the detection limits of common analytical methods and their determination is spectroscopically and chemically interfered with other major constituents; thus its determination necessitates the selection of a suitable preconcentration procedure [12].

Among the separation techniques used for the preconcentration step, cloud point extraction (CPE) has attracted considerable attention in the last decade mainly because it complies with the "green chemistry" principles [13-15]. The first report on the use of CPE for metal ion separation was done by Watanabe and co-workers [16]. Since then, the number of publications for CPE approaches concerning metal ions has been continually growing [17]. However, to the best of our knowledge, there is only one report for separation and speciation of iron in water samples using cloud point extraction and atomic spectroscopy measurement [18].

In 2002, Giokas and co-workers [18], reported speciation of Fe(II) and Fe(III) by the modified ferrozine method with FIA-spectrophotometry and flame atomic absorption spectrometry after cloud-point extraction. They used ammonium pyrrolidine dithiocarbamate (APDC) as a complexing agent for both species of iron in the CPE procedure. To differentiate the oxidation states of iron, they measured the absorbance of Fe(II)-ferrozine complex by spectrophotometry and used mathematical equations to overcome the interference of Fe(III) when they were both present in the same solution. They reported that, after the CPE, formation of the Fe(II)-ferrozine complex required ~10 min and the achievement of optimum conditions for the procedure is laborious.

In this study, 8-hydroxy-7-iodoquinoline-5-sulfonic acid (Ferron, $C_9H_6INO_4S$), as a classical ligand used for spectrophotometric determination of metal ions [19,20], was used as a complexing agent for cloud point extraction of both iron species. The procedure was applied to the speciation of iron in water and determination of total iron in water and milk samples.

EXPERIMENTAL

Apparatus

A Buck Scientific atomic absorption spectrometer (Model 210 VGP, USA) was used for all absorption measurements. An iron hollow cathode lamp and air-acetylene flame was used for all measurements. The operating conditions were as follows: wavelength 248.3 nm, slit width 0.2 nm, lamp current 8.2 mA. The absorbance time response was monitored on an x-t chart recorder (L-250) and quantitative analysis was based on measurement of the peak height of transient signals. The flow injection system consisted of a peristaltic pump (Ismatic, MS- REGLO/8-100 Switzerland) and a rotary injection valve (Rheodyne, CA, USA). A double beam spectrophotometer (Model 7800 JASCO, England) with matched cells of 1 cm path-length was used for absorbance measurements at 600 nm. A Varian Zeeman Spectra atomic absorption spectrometer Model 220Z equipped with autosampler was used for trace analysis and operated at conditions recommended by the manufactures.

Chemicals

All chemicals were of highest purity available from Merck and were used as received. Deionized water was used throughout all the experiments. A stock 1000 μg ml^{-1} of iron(II) or iron(III) was prepared by dissolving appropriate amount of $(NH_4)_2Fe(SO_4)_2.6H_2O$ or $Fe(NO_3)_3.9H_2O$ in water. Working solutions were prepared daily from the stock solutions by serial dilution. Ferron (Fluka) and Triton X-114 (Fluka) were used without further purification.

Preparation of Milk Sample

To 10 ml of human or cow's milk, few drops of concentrated nitric acid were added, and the sample was centrifuged for few minutes. Then the supernatant solution was taken, its pH was adjusted to ~5, and the resulting solution was diluted to 100 ml in a volumetric flask. The solution was then analyzed according to the given procedure.

For analysis of infant dry formula milk, 0.5 g of milk powder was dissolved in water. The protein was separated after addition of few drops of concentrated nitric acid. The pH of the supernatant was adjusted to ~5 and the resulting

solution was diluted to 250 ml. The sample was then treated according to the given procedure.

Water Samples

The water samples were filtered through a Millipore filter; the pH was adjusted and the resulting was treated according to the given procedure.

Procedure

For cloud point extraction, aliquots of 20.0 ml of the sample or standard solution (pH ~ 5) containing the analytes, 1.4×10^{-4} M ferron, 0.01 M tetra-*n*-butylammonium chloride (TBA-Cl) and triton X-114 (0.05% v/v) were kept in a thermostated water bath at 60 °C for 5 min. Then the solution was centrifuged for 5 min at 4000 rpm. At this stage, the aqueous and surfactant rich phase were separated. The phases were further cooled in an ice-water bath, which increase the viscosity of the surfactant-rich phase. The aqueous phase was easily decanted by simply inverting the tube. To decrease the viscosity of the surfactant-rich phase and facilitate sample handling, 350 µl of ethanol was added. The concentration of total iron was measured by injecting 100 µl of the solution into the FI-AAS at a flow rate of 2.5 ml min^{-1}. When determination of species of iron was desired, the absorbance of the extract was measured with a spectrophotometer at 600 nm, the concentration of total iron was determined by FI-AAS and the concentrations of Fe(III) and Fe(II) were obtained according to Eqs. (3) and (4), respectively.

RESULTS AND DISCUSSION

The separation and preconcentration of metal ions by cloud point extraction (CPE) often involve formation of a complex with sufficient hydrophobicity to be extracted into a small volume of the surfactant-rich phase. Ferron forms a greenish yellow complex with iron species which can be extracted into the surfactant rich phase. The concentration of total iron in the extract was determined by FI-FAAS.in the presence of tetra-*n*-butylammonium chloride The oxidation state of iron species was determined by following reasoning. According to Beer's law, when the light path is 1 cm, the mixture of complexes of Fe(II) and Fe(III) lead to the absorbance of:

$$A_1 = \varepsilon_{Fe(II)} C_{Fe(II)} + \varepsilon_{Fe(III)} C_{Fe(III)} \quad (1)$$

where A_1 is the absorbance of the mixture, $\varepsilon_{Fe(III)}$ and $\varepsilon_{Fe(II)}$ are the molar absorptivity coefficients, and $C_{Fe(II)}$ and $C_{Fe(III)}$ are the concentrations of the Fe species. If Fe(II) is oxidized to Fe(III) with an oxidizing agent, the absorbance of the solution will be:

$$A_2 = \varepsilon_{Fe(III)} (C_{Fe(II)} + C_{Fe(III)}) = \varepsilon_{Fe(III)} C_{Fe\ total} \quad (2)$$

Solving Eqs. (1) and (2) simultaneously will result in:

$$C_{Fe(III)} = [\varepsilon_{Fe(III)} \times A_1 - \varepsilon_{Fe(II)} \times A_2]/[\varepsilon_{Fe(III)}^2 - \varepsilon_{Fe(III)} \times \varepsilon_{Fe(II)}] \quad (3)$$

$$C_{Fe(II)} = [A_1 - A_2]/(\varepsilon_{Fe\ (II)} - \varepsilon_{Fe\ (III)}) \quad (4)$$

In this study, A_1 was determined by direct measurement of absorbance of the iron-ferron complexes in the extract at 600 nm, A_2 was calculated from Eq. (2) using total iron concentration obtained from FI-AAS analysis, and the concentration of iron species was calculated according to Eqs. (3) and (4). Furthermore, the negatively charged complex of ferron with iron species is hydrophilic, and a possible way to increase its lipophilicity is the neutralization of its charge by ion-pair formation. In an attempt to examine this possibility, the effect of different cations at a concentration of 0.05 M on CPE of iron-ferron complex was considered. As shown in Fig. 1, the size of the cation has a significant effect on the extraction efficiency of the analyte. It was found that the recovery of iron from the aqueous phase increases with an increase in the cation size and is maximized with tetra-*n*-butylammonium cation (TBA). A possible explanation for this observation is that the larger cations induce a greater degree of lipophilicity to the ternary adducts and, therefore, increases its extraction efficiency into the surfactant-rich phase. The small decrease in recovery with TBA-Br in comparison to TBA-Cl is due to competition of the large Br^- anion with ferron complex for ion-pair formation with TBA cation. Further experiments showed that 0.01-0.1 M TBA-Cl solutions are suitable for quantitative extraction of the iron complex. Subsequent studies were therefore, performed with samples prepared in 0.01 M of TBA-Cl.

It is known that recovery of metal ions in CPE preconcentration is influenced by different factors such as pH, concentrations of complexing agent and surfactant, equilibrium temperature and time. Systematic studies aimed at optimizing the analytical useful operation condition were

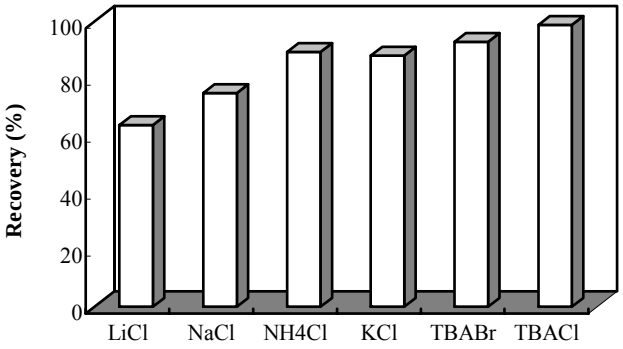

Fig. 1. Effect of different cations on the CPE of iron. Conditions: iron concentration, 125 µg l^{-1}; concentrated volume, 20 ml; Triton X-114, 0.05% (v/v); ferron, 1.4×10^{-4} M.

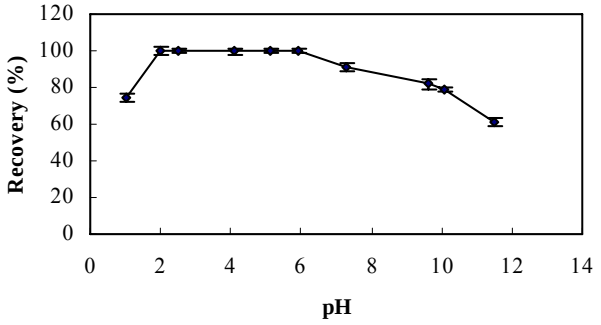

Fig. 2. Effect of pH on the CPE of iron. Conditions: iron concentration, 125 µg l^{-1}; concentrated volume, 20 ml; Triton X-114, 0.05% (v/v); TBT, 0.01 M; ferron, 1.4×10^{-4} M.

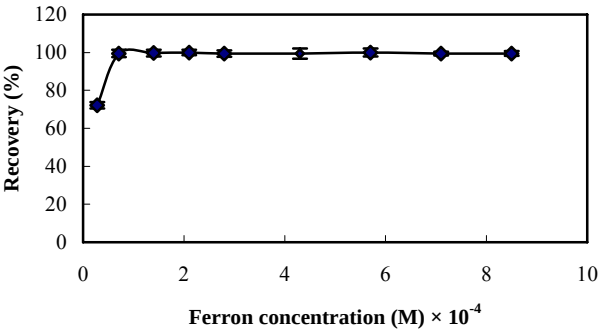

Fig. 3. Effect of ferron concentration on the CPE of iron. Conditions: iron concentration, 125 µg l^{-1}; concentrated volume, 20 ml; Triton X-114, 0.05% (v/v); pH ~ 5; TBT, 0.01 M.

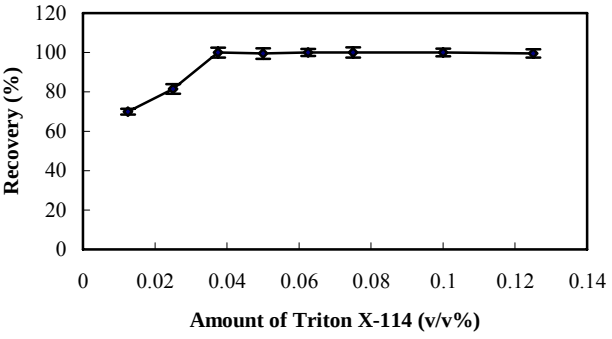

Fig. 4. Effect of Triton X-114 concentration on the CPE of iron. Conditions: iron concentration, 125 µg l^{-1}; concentrated volume, 20 ml; ferron, 1.4×10^{-4} M; pH ~ 5; TBT, 0.01 M.

therefore performed.

The extraction efficiency was dependent on sample pH. As shown in Fig. 2, maximum recovery for iron was achieved in a pH range of 2-6. The possibility of working in a wide pH range can be mentioned as one of the advantages of the method. The decrease in the extraction at pH > 6 is probably due to precipitation of iron as iron hydroxide, whereas, the decrease in extraction at pH < 2 is due to protonation of the ligand. A pH of ~5 was therefore selected for subsequent work.

The efficiency of analyte extraction was dependent on ferron concentration as shown in Fig. 3. For ligand concentrations greater than 7.1×10^{-5} M, the extraction was quantitative and independent of its concentration. A concentration of 1.4×10^{-4} M of ferron was selected as optimum for further studies.

A successful cloud point extraction should maximize the extraction efficiency by minimizing the phase volume ratio ($V_{org}/V_{aqueous}$), thus improving its concentration factor. Triton X-114 was chosen for the formation of surfactant rich phase due to its low cloud point temperature and high density of surfactant rich phase, which facilitates phase separation by centrifugation. Figure 4 shows the effect of the surfactant concentration in the range of 0.013-0.13 (V/V) on the extraction efficiency. As it is seen, at surfactant concentrations above 0.04%, the extraction of the ternary adduct of iron-ferron-TBA is quantitative in a single step process. A surfactant concentration of 0.05% was selected for subsequent work.

The efficiency of analyte extraction is dependent on the equilibration temperature above the cloud point and the incubation time. As shown in Fig. 5, complete extraction and efficient phase separation was achieved in a temperature range of 50-80 °C. Use of higher temperatures, however, resulted in a sharp decrease in recovery, which may be due to instability of the complex at high temperature. An equilibration temperature of 60 °C was selected as optimum. The dependence of extraction efficiency upon incubation time was studied in the range 1-15 min. The extraction was quantitative and independent of incubation time for incubation times greater than 5 min. An incubation time of 5 min was selected for further study.

Furthermore, the effect of rotating speed of the centrifuge on the extraction was studied in the range 3500-4500 rpm. It was found that for 5 min of centrifugation, 4000 rpm was sufficient for complete phase separation.

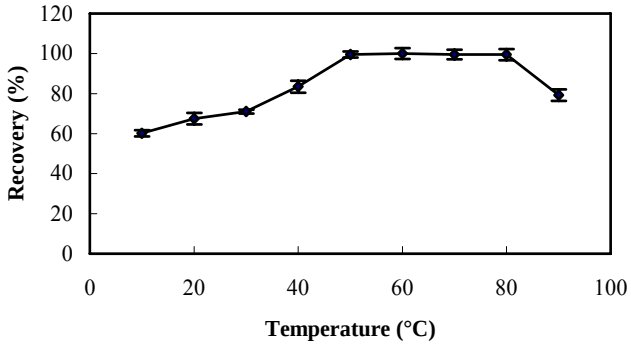

Fig. 5. Effect of equilibration temperature on the CPE of iron. Conditions: iron concentration, 125 μg l^{-1}; concentrated volume, 20 ml; ferron, 1.4×10^{-4} M; Triton X-114, 0.05% (v/v); pH ~ 5; TBT, 0.01 M.

Determination of Molar Absorption Coefficients

The determination of iron species necessitates the determination of molar absorption coefficient, ε, of both iron species under the specified experimental conditions. This was done by CPE at different concentrations of each iron species separately, followed by measurement of its absorption at 600 nm. The molar absorption coefficients of Fe(II) and Fe(III), obtained from the slope of the calibration graphs so constructed, were found to be 3.3×10^4 and 2.2×10^4 l mol^{-1} cm^{-1}, respectively.

Interference Studies

A possible concern was whether high enrichment factors could be realized for natural samples where other cations or anions might compete and impair the extraction efficiency. For this purpose, the effect of various cations and anions on the recovery of 2.5 μg of iron from 20 ml of aqueous sample solution was studied. A relative error of less than 5% was considered to be within the range of experimental error. The results of these studies (Table 1) indicate that the presence of

Table 1. Interference Study: Concentrated Volume 20 ml, Iron Concentration 125 μg l^{-1}

Foreign ion	Molar ratio (ion/iron)	Recovery (%)	Foreign ion	Molar ratio (ion/iron)	Recovery (%)
Ni^{2+}	1000	100.9 ± 0.6	Pb^{2+}	1000	102.5 ± 0.5
Mn^{2+}	1000	97.9 ± 0.5	Al^{3+}	250	98.4 ± 0.8
Cd^{2+}	1000	98.6 ± 0.7	Ag^{+}	1000	96.5 ± 0.7
Zn^{2+}	1000	97.0 ± 0.8	Hg^{2+}	1000	97.4 ± 0.6
Cu^{2+}	1000	99.6 ± 0.5	Na^{+}	10000	100.9 ± 0.6
Ca^{2+}	1000	100.0 ± 0.6	Ba^{2+}	1000	98.4 ± 0.4
Mg^{2+}	1000	98.3 ± 0.7	Cl^{-}	10000	103.2 ± 0.5
Co^{2+}	250	99.3 ± 0.5	Br^{-}	10000	101.4 ± 0.7
Sr^{2+}	1000	101.3 ± 0.6	CO_3^{2-}	1000	98.6 ± 0.4
K^{+}	10000	98.6 ± 0.5	SO_4^{2-}	300	98.0 ± 0.5
Li^{+}	10000	99.1 ± 0.9			

high concentrations of other ions in the sample have no significant effect on the preconcentration of iron at trace levels. Thus the method offers a high selectivity for iron ions.

Basic Analytical Performance

In order to evaluate the ability of the system for quantification of iron at low levels, the extraction efficiency of CPE in separation and preconcentration of 2.5 μg of iron from different volumes of water (10-60 ml) was examined. The results of this study indicated that the extraction was quantitative up to a volume of 40 ml.

Two calibration curves were constructed by processing 20 and 40 ml of standard solution (in triplicate) under the optimum conditions of CPE. The graphs of absorbance, as peak height, *vs*. iron concentration were linear over the range 10-250 μg l^{-1} and 5-150 μg l^{-1} of iron, respectively. The calibration graph equations were Y = 0.375 C + 0.930 and Y = 0.743 C + 1.734 (where Y is peak height in mm and C is the iron concentration in μg l^{-1}) with correlation coefficients of 0.9999 and 0.9997, respectively.

The capability of the system for speciation of iron was investigated by cloud point extraction of mixtures of Fe(II) and Fe(III) from synthetic water solutions (containing Ca^{2+}, Na^{+}, Mg^{2+}, Cl^{-} and SO_4^{2-} at concentrations of 110, 30, 40, 250 and 60 ppm, respectively). The absorbance of the extract was measured at 600 nm, the concentration of total iron was determined by FI-FAAS and the concentration of iron species was determined by using Eqs. (4) and (5). The results given in Table 2 show that the recovery of both iron species is quantitative and, thus, the system is capable of iron speciation in the synthetic water sample.

The relative standard deviation of eleven replicate extractions and measurement of 2.5 μg of iron from 20 ml was 2.1%. The limit of detection based on three times the standard deviation of the blank signal with a sample volume of 20 ml was found to be 1.7 μg l^{-1} of iron. The preconcentration capability of the method was investigated by comparing the slope of calibration curve of the CPE method to that obtained without preconcentration. For the sampling volumes of 20 and 40 ml, a concentration factor of 75 and 149 were obtained, respectively. The analytical characteristics of the optimized method including linear range, limit of detection, reproducibility, and preconcentration factor are summarized in Table 3.

Table 2. Determination of Iron Species in Synthetic Water: Concentrated Volume 20 ml

Iron added (ng)		Recovery (%)	
Fe(II)	Fe(III)	Fe(II)	Fe(III)
-	500	-	103.0 ± 0.9
500		102.0 ± 0. 8	-
500	500	96.0 ± 0.6	106.0 ± 0.8
400	800	105.0 ± 0.7	96.3 ± 1.0
800	400	97.5 ± 0.9	101.2 ± 0.7

Table 3. Analytical Characteristics of the Method

Analytical property	20 ml	40 ml
Linear range (μg l^{-1})	10-250	5-150
Correlation coefficient (r)	0.9999	0.9997
concentration factor[a]	75	149
LOD (μg l^{-1})[b]	1.7	
R.S.D. (%) (n = 11)[c]	2.1	

[a]Determined as the ratio of slope of preconcentrated samples to that obtained without preconcentration. [b]Limit of detection; calculated as three times the standard deviation of the blank signal. [c]R.S.D. was determined for iron concentration of 125 μg l^{-1}.

Applications

The procedure was applied to the determination of total iron in tap water, spring water, rain water, river water (taken from Zayandeh Roud river, Isfahan/Iran), human milk, homogenized cow milk with different percentage of fat and infant dry formula milk. Reliability was checked by spiking experiments and comparing the results with data obtained by graphite furnace atomic absorption analysis. The results summarized in Table 4 indicate that, in all samples, the iron recovery is almost quantitative (97.0-102.5) and there is a satisfactory agreement between the results obtained by the proposed method and those by furnace atomic absorption spectrometry, at 95% confidence limit. The procedure was

Table 4. Determination of Total Iron in Real Samples

Sample	Iron (μg l^{-1})		Recovery (%)	GF-AAS
	Added	Found		
Tap water	0	64.5 ± 0.7	-	64.2 ± 0.5
	10	74.8 ± 0.5	103.0	
Spring water	0	19.7 ± 0.3	-	19.0 ± 2.0
	10	29.4 ± 0.6	97.0	
Rain water	0	42.3 ± 0.4	-	43.1 ± 1.6
	10	52.1 ± 0.7	98.0	
River water	0	69.3 ± 0.6	-	71.5 ± 2.6
	10	78.9 ± 0.4	96.0	
Human milk	0	823.0 ± 0.5	-	819.0 ± 2.6
	100	920.5 ± 0.7	97.5	
Cow milk (1.5% fat)	0	1440.0 ± 0.6	-	1443.3 ± 1.0
	100	1542.5 ± 0.4	102.5	
Cow milk (2.5% fat)[a]	0	756.0 ± 0.9	-	758.0 ± 3.0
	100	853.6 ± 0.4	97.6	
Cow milk (2.5% fat)[a]	0	872.0 ± 0.8	-	873.5 ± 3.5
	100	970.0 ± 0.5	98.0	
Infant dry formula milk[b]	0	71.9 ± 0.5	-	72.0 ± 1.5
	10	82.0 ± 0.7	101.0	

[a]Cow milk from different branch. [b]μg of iron per gram of sample.

also applied to the determination of iron in certified river water, CRM (SLRS-1) with iron concentration of 31.5 ± 2.1 μg l^{-1}. The amount of iron in SLRS-1 was found to be 31.9 ± 1.7 μg l^{-1}, which is in good agreement with the certified value. Thus the method is suitable for the type of samples examined.

The procedure was also applied to the speciation of iron in real water samples, and the accuracy of the method was examined by recovery experiment for both iron species. The results, summarized in Table 5, indicate that the recovery of iron species in all samples in quantitative. Thus, the procedure is reliable for determination of iron species in water samples, and total iron in milk and water samples.

CONCULUSIONS

It has been demonstrated that the complex of iron with ferron in the presence of tetra-*n*-butylammonium chloride salt can be quantitatively concentrated into surfactant rich phase in a single-step extraction. The feasibility of speciation of dissolved iron in water samples on the basis of cloud-point extraction of both species with ferron, followed by spectrophotometric and atomic absorption spectroscopy detection has been demonstrated. Simplicity, high sensitivity, low cost, safety, and freedom from interferences are significant advantage of the proposed cloud point extraction.

The proposed method, in comparison to a previously proposed CPE method for iron speciation [18], has the advantage of using ferron as both the complexing and the colorimetric reagent, and its applicability for total iron determination in milk samples.

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Table 5. Determination of Iron Species in Water Samples

Sample	Iron added ($\mu g\ l^{-1}$)		Iron found ($\mu g\ l^{-1}$)		Recovery (%)	
	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
Tap water	-	-	16.0	48.5		
	10	10	25.5	58.8	95.0	103.0
Rain water	-	-	5.5	36.7		
	10	10	16.0	46.5	105.0	98.0
River water	-	-	21.5	47.7		
	10	10	31.3	57.4	98.0	97.0
Spring water	-	-	1.0	18.5		
	10	10	11.5	28.1	105.0	96.0

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