Regular Article

ANALYTICAL
AND BIOANALYTICAL
CHEMISTRY
RESEARCH

Published by the
Iranian Chemical Society

***Anal. Bioanal. Chem. Res.**, Vol. 2, No. 1, 13-21, June 2015.*

Determination of Iron Species by Combination of Solvent Assisted-Dispersive Solid Phase Extraction and Spectrophotometry

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(Received 15 March 2015, Accepted 13 April 2015)

A simple, rapid and sensitive solvent assisted-dispersive solid phase extraction method was developed for the extraction of iron(II) prior to its spectrophotometric determination. The Fe(II) reacted with 2,4,6-tris(2-pyridyl)-1,3,5-triazine, neutralized with sodium dodecyl sulfate and extracted onto the fine particles of benzophenone which were formed upon rapid injection of a mixture of benzophenone as the sorbent and ethanol as the disperser solvent into the aqueous solution. After phase separation, the sedimented phase containing the complex was dissolved in ethanol and the analyte concentration was determined by measuring its absorption at 594 nm. Total iron was determined after the reduction of Fe(III) to Fe(II) with hydroxylamine hydrochloride. Under the optimized conditions, an enhancement factor of 32, the detection limit of 0.16 μg l^{-1}, and the relative standard deviation of 1.9% (n = 6) at 20 μg l^{-1} concentration level of Fe(II) were achieved. The method was successfully applied to the determination of iron species in water samples and total iron in infant dry formula milk, apple, rice, spinach and parsley samples.

Keywords: Iron speciation, Solvent assisted-dispersive solid phase extraction, Preconcentration, Spectrophotometry

INTRODUCTION

Iron is the fourth abundant element in the earth's crust and is an essential nutritional element for all of the known forms of life. It is a cofactor in many enzymes important for oxygen transport and electron transfer [1]. Iron occurs in +2 and +3 oxidation states in the biological and water samples [2]. The degree of chelating characteristic, oxidation states and solubility of iron influence its environmental and biological activity [3]. Therefore, it is important to develop simple, sensitive, selective, and rapid analytical procedures for the determination of iron species in biological and water samples.

An efficient separation and preconcentration method is often required before the determination of extremely low concentration levels of iron species through common analytical techniques. Various methods such as coprecipitation [4-6], liquid-liquid extraction (LLE) [7,8] and solid-phase extraction (SPE) [9-13] have been proposed for the separation and preconcentration of trace amounts of iron from different matrices. However, these pretreatment methods are often labor, time and reagent consuming and require large volumes of the sample and the solvent [14]. To overcome these drawbacks, Anastassiades and coworkers have introduced a new SPE method called dispersive solid phase extraction (DSPE) for the cleanup of environmental samples [15]. In comparison to traditional SPE, the DSPE method is simple, rapid, and cost-effective because it reduces the amount of the sorbent and the size of the sample and consumes low amounts of solvent [16]. This method is based on the dispersion of a small amount of sorbent in the aqueous sample and the analyte is quickly adsorbed onto the sorbent due to the high contact area. The sorbent containing the analytes is then separated from the sample by centrifugation. The method can be described as QuEChERS which stands for quick, easy, cheap, effective, rugged and

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safe [15]. DSPE method has been used for the separation of heavy metals, dyes, pesticide residues, pharmaceuticals and toxins [17-22]. In 2013, Jamali *et al*. reported a new mode of SPE called solvent-assisted dispersive solid phase extraction (SADSPE) for the extraction and preconcentration of cobalt prior to its determination by flame atomic absorption spectrometry [23]. Advantages of this method are its simplicity, easy operation, cost effectiveness, short term extraction, good enrichment factor and high extraction yield.

To the best of our knowledge, there is no available paper on the separation/preconcentration of iron species by SADSPE. An attempt was made to develop a SADSPE methodology for the separation/preconcentration of iron(II) prior to its spectrophotometric determination in the present work. The Fe(II) in aqueous solution reacted with 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ) producing the cationic $Fe(TPTZ)_2^{2+}$ complex. Then, the $Fe(TPTZ)_2^{2+}$ formed an ion-association complex with the anionic surfactant sodium dodecyl sulfate (SDS) and was extracted onto the dispersed benzophenone particles. The fine particles of benzophenone were formed due to rapid injection of a mixture of benzophenone as the sorbent and ethanol as the disperser solvent into the aqueous solution. After centrifugation, the sedimented phase containing the complex was dissolved in ethanol and determined by spectrophotometry at the wavelength of 594 nm. The effect of various experimental parameters on the extraction was investigated. The method was eventually applied to the determination of iron species in water samples and the total iron in spinach, parsley, apple, rice and infant dry formula milk samples.

EXPERIMENTAL

Reagents

All the reagents used were of analytical reagent grade supplied by Merck (Darmstadt, Germany). Double distilled water was used throughout the experiments. The Fe^{2+} stock solution (1000 mg l^{-1}) was prepared through dissolving an appropriate amount of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 0.1 M H_2SO_4. The Fe^{3+} stock solution (1000 mg l^{-1}) was prepared by dissolving an appropriate amount of $Fe(NO_3)_3.9H_2O$ in 1% HNO_3. The working standard solutions were prepared daily by adequate dilution of the standard stock solutions.

The acetate buffer (1 M) was prepared by dissolving appropriate amounts of sodium acetate and acetic acid solutions in double distilled water and adjusting the pH to 4.5. The stock 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ) solution 5.0×10^{-3} M was prepared by dissolving 0.1236 g of the compound in a few drops of concentrated hydrochloric acid and diluting to 100 ml with distilled water. A 4.0×10^{-3} M solution of sodium dodecyl sulphate (SDS) was prepared by dissolving an appropriate amount of this reagent in water. A 1% (w/v) solution of benzophenone was prepared in pure ethanol. A 1% (w/v) hydroxylamine hydrochloride solution was prepared by dissolving 1.0 g of the reagent in double distilled water in a 100 ml volumetric flask. All the glassware used for the trace analysis was kept in 10% nitric acid solution for at least 24 h and subsequently rinsed twice with distilled water before use.

Apparatus

An Avantes photodiode array spectrophotometer model AvaSpec-2048 equipped with a source model of Ava Light-DH-S-BAL (Aventes, Eerbeek, The Netherlands) and a 1 cm quartz microcell used for the absorbance measurements. The pH measurements were carried out by means of a Metrohm pH meter (model 827, Herisau, Switzerland) using a combined glass calomel electrode. A centrifuge (Hitachi, Universal 320, Tuttlingen, Germany) was used in order to facilitate the phase separation.

Sample Preparation

The water samples were filtered through a 0.45 µm Millipore filter, the pH was adjusted to 4.5 upon the addition of acetate buffer solution and was treated according to the general procedure.

The apples, parsley and spinach were purchased from a local market in Yazd, Iran. They were then washed cleaned with tap water and double distilled water and were dried at 70 ºC. 100 mg of each dried sample was transferred into a silica crucible and was heated in a furnace for 6 h at 650 ºC. The residue was cooled at the room temperature, and was heated with 10 ml concentrated nitric acid and 3 ml of 30% H_2O_2 until brown fumes appeared and all the organic compounds were removed. The final residue was treated with 3 ml of concentrated hydrochloric acid and 2 ml of 70% perchloric acid and heated to dryness. The solid

residue was dissolved in water and was filtered. The pH was adjusted to 4.5 and the solution was transferred to a 100 ml flask and was diluted to the mark with distilled water [24].

100 mg of milk powder was treated with 5 ml of concentrated nitric acid and 2 ml of 30% hydrogen peroxide and was digested on an electric hot plate at 90 ºC for the analysis of infant dry formula milk. The temperature of this mixture was gradually augmented to 120 ºC until brown fumes appeared and the organic matrix of the sample was completely destroyed. When cooled, the solution was passed through a filter and the pH was adjusted to 4.5. The solution was then diluted with distilled water to 100 ml in a volumetric flask [25,26].

The rice sample was thoroughly washed with distilled water, grounded and dried. 100 mg of the sample was weighed and added to a beaker; 10 ml of concentrated HNO_3 and 3 ml of H_2O_2 were added and the mixture was evaporated near to dryness on a heater-stirrer. The residue was solved in 10 ml of distilled water and filtered. The pH of the filtrate was adjusted to 4.5 while it was diluted to 100 ml with distilled water [27].

General Procedure

The pH of 20 ml of the sample or the standard solution containing 2.5-100.0 µg l^{-1} of iron(II) was adjusted to 4.5 with 1 ml of 1.0 M acetate buffer solution in a 25 ml glass screw-cap conical bottom centrifuge tube. Then, 0.2 ml of 5.0×10^{-3} M TPTZ and 0.3 ml of 4.0×10^{-3} M SDS were added and the contents were mixed. The iron ions in the aqueous solution were complexed with TPTZ and were neutralized through the ion-association with SDS. Then, 1.0 ml of the ethanol solution (as the disperser solvent) containing benzophenone (1.0%) (as the sorbent) was rapidly injected into the sample solution using a 1.0 ml syringe, and vortexed briefly for 10 s. A cloudy solution was produced in the test tube resulting from the dispersion of the fine particles of benzophenone in the bulk aqueous sample, and the complex was extracted into these fine particles. The mixture was centrifuged at 3800 rpm for 5 min, and the dispersed fine particles of benzophenone settled at the bottom of the conical test tube. The aqueous phase was simply decanted and the remained sediment phase was dissolved in 0.5 ml ethanol while the absorbance was measured at 594 nm against a reagent blank.

The total iron was determined after the quantitative reduction of Fe(III) to Fe(II) upon the addition of 0.5 ml of 1.0% hydroxylamine to a 20 ml of the sample and leaving the solution at room temperature for 15 min. Then, the pH of the solution was adjusted to 4.5 with 1.0 ml of the acetate buffer solution.

RESULTSAND DISCUSSION

The reagent 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ) reacts with Fe(II) and produces a sensitive violet complex of $Fe(TPTZ)_2^{2+}$ at pH of 4.5 convenient for its spectrophotometric determination [28]. The $Fe(TPTZ)_2^{2+}$ can be neutralized through an ion-association complex with anionic surfactant of SDS. The initial experiments indicated that when ethanol solution containing benzophenone dispersed throughout the aqueous solution of the complex, it quickly extracted into the fine particles of the sorbent. After the phase separation by centrifugation, the extracted complex was solved in a suitable organic solvent such as ethanol and was determined by the spectrophotometeric technique at the wavelength of 594 nm.

In order to obtain a high enrichment factor, different parameters affecting the complex formation of iron(II), its extraction and determination were investigated and optimized using the univariable approach.

Effect of pH

The pH of the solution has a critical role in the formation of complex between Fe(II) and TPTZ and its extraction into the fine particles of benzophenone. So, the effect of sample pH on the extraction of Fe(II) was studied by varying the pH within the range of 1.0-9.0. The pH was adjusted upon the addition of diluted hydrochloric acid or sodium hydroxide solution. Figure 1 shows the influence of the sample pH on the analytical signal intensity. As indicated, the maximum analyte absorbance was obtained in the pH range of 3.0-5.5. The decrease in the absorbance at pH < 3.0 is due to the competition between hydrogen ions and the analyte for the chelating agent,whereas the decrease at pH > 5.5 may be because of the hydrolysis of Fe(II). Therefore, pH 4.5 was selected for further studies.

Effect of the Type and Amount of the Sorbent

The type of the sorbent used in SADSPE is an important

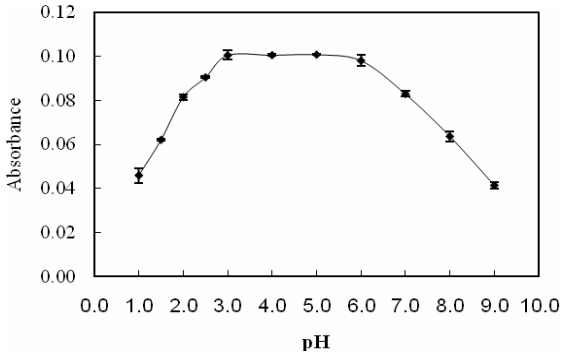

Fig. 1. Effect of pH on the analytical signal of iron(II). Conditions: sample volume, 20 ml; Fe(II) concentration, 10.0 μg l^{-1}; TPTZ concentration: 6.0×10^{-5} M; SDS concentration, 6.0×10^{-5} M; sorbent, 15 mg benzophenone; dispersive solvent, 1.0 ml ethanol.

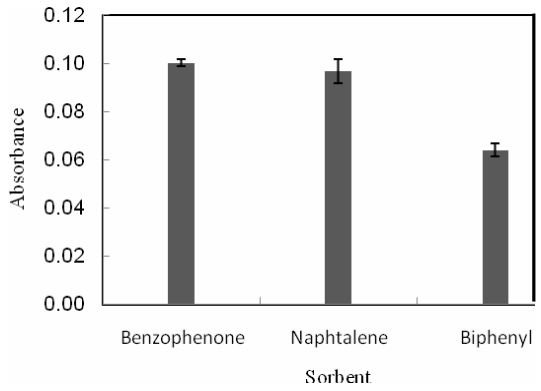

Fig. 2. The effect of type of sorbent on the analytical signal of iron(II). Conditions: sample volume, 10 ml; Fe concentration, 10.0 μg l^{-1}; TPTZ concentration, 6.0×10^{-5} M; SDS concentration, 6.0×10^{-5} M; dispersive solvent, 1 ml ethanol; pH = 4.5.

factor for the efficient extraction. The sorbent must have high affinity for the analyte, high solubility in the disperser solvent besides low solubility in aqueous phase. Accordingly, several sorbents including benzophenone, naphthalene and biphenyl were investigated for the extraction of Fe(II) applying the SADSPE method (Fig. 2). The experiments were performed by the use of 1.0 ml ethanol containing 15 mg of each sorbent. The signal obtained from the benzophenone for the Fe(II)-TPTZ complex was higher than the other sorbents. Therefore, benzophenone was chosen as the sorbent.

The amount of the sorbent is one of the most important factors affecting the extraction efficiency and the enrichment factor of the metal complexes in SADSPE. In order to select the optimum amount of the sorbent, several experiments were performed using 1.0 ml of ethanol and different amounts of benzophenone (3-30 mg). The results showed that by increasing the amount of the benzophenone up to 10 mg, the absorbance increased and then leveled off in larger amounts. Thus, 10 mg of the benzophenone was selected as the optimum amount of the sorbent for the subsequent experiments.

Effect of the Type and Volume of the Disperser Solvent

In SADSPE, the dispersive solvent must be miscible with both water and the sorbent and it permits the appropriate dispersion of the fine particles of the sorbent throughot the aqueous sample. Thus, for the sake of acquiring the most suitable disperser solvent, four types of disperser solvents including methanol, ethanol, acetone and acetonitrile were evaluated. A series of sample solutions were studied using 1.0 ml of each disperser solvent containing 10 mg of the benzophnone. Figure 3 shows that the analyte signal with methanol, ethanol and acetone, as the disperser solvents, was higher than with acetonitrile. Ethanol was selected as the dispersive solvent for the subsequent studies because of its low toxicity.

The effect of the volume of the disperser solvent on the absorbance of the extracted complex was also studied. For this purpose, different volumes of ethanol (0.5-2.0 ml) were examined (Fig. 4). The maximum absorbance was obtained when 1.0 ml of ethanol was used. Benzophenone was not completely dispersed at the low volume of ethanol and the absorbance was low. The slight decrease in the absorbance at large volume of ethanol is due to the increase in the solubility of the complex in the aqueous phase containing a high percentage of ethanol. Thus, 1.0 ml of ethanol was selected as the optimal volume of the disperser solvent.

Effect of the TPTZ Concentration

The effect of TPTZ on the extraction of Fe(II) in the concentration range of 4.0×10^{-6}-6.0×10^{-5} M was

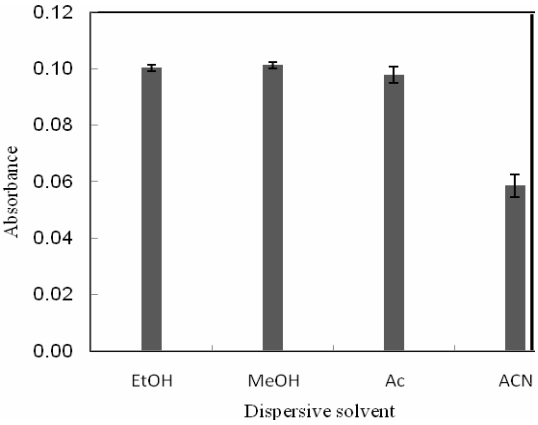

Fig. 3. Nature of dispersive solvent on the analytical signal of iron(II). Conditions: sample volume, 20 ml; Fe concentration, 10 µg l^{-1}; TPTZ concentration, 6.0×10^{-5} M; SDS concentration, 6.0×10^{-5} M; sorbent, 10 mg benzophenone; pH = 4.5.

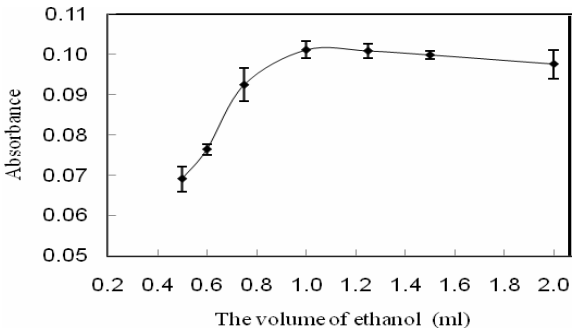

Fig. 4. The effect of the volume of dispersive solvent (ethanol) on the analytical signal of iron(II). Conditions: sample volume, 20 ml; Fe concentration, 10 µg l^{-1}; TPTZ concentration, 6.0×10^{-5} M; SDS concentration, 6.0×10^{-5} M; sorbent, 10 mg benzophenone; dispersive solvent, ethanol; pH = 4.5.

examined. Figure 5 shows the absorbance increased by increasing TPTZ concentration up to 2.0×10^{-5} M which reached a plateau. Therefore, a concentration of 5.0×10^{-5} M was chosen for the further experiments.

Effect of SDS Concentration

In order to extract the cationic complex of Fe(II)-TPTZ, the capability of some anions (picrate, perchlorate and SDS) as the counter-ions to make a hydrophobic ion pair was examined. The results showed that the anionic surfactant of SDS was more effective for the extraction of iron complex into the fine particles of the benzophenone. The effect of the SDS concentration on the extraction of iron(II) was investigated by varying its concentration over the range of 0.0-1.2 × 10^{-4} M. The results showed that the absorbance increased by increasing the SDS concentration up to 5.0×10^{-5} M, and then remained nearly constant. So, a concentration of 6.0×10^{-5} M SDS was chosen as the optimum value.

Effect of Extraction Time

In SADSPE, the extraction time is defined as the interval between the injection moment of the ethanol/benzopbenone mixture and the moment of the starting phase separation by centrifugation. The effect of the extraction time on the absorbance was investigated in the range of 30 s to 20.0 min under the optimum conditions. The results indicated that the extraction was relatively fast and the system reached equilibrium within 1 min. Thus, an extraction time of 1 min was selected for the further studies.

Effect of the Ionic Strength

In order to investigate the effect of the ionic strength on the extraction of Fe(II), some experiments were performed with different NaCl concentrations (0.0-1.0 M) while keeping other parameters constant. They all indicated that the ionic strength had no significant effect on the absorbance up to 0.6 M of NaCl. However, a further increase in salt concentration caused a decrease in absorbance which may be attributed to the dissociation and instability of the ion pair complex in high salt concentrations. Thus, the extraction experiments were carried out without the addition of salt.

Effect of Sample Volume

Demonstration of the capability of the method in the determination of the trace amounts of the analyte in the large sample volume is an important aspect of the method development. For this purpose, different volumes of the sample solution (5.0-30.0 ml) containing 0.5 µg of iron(II) were treated according to the given procedure. The result of

this study revealed that the absorbance and the extraction efficiency were maximum up to the sample volume of 20.0 ml and then decreased by the further increase in the sample volume.

Influence of Potential Interfering Species

Some experiments were carried out to examine the influences of coexisting ions on the extraction of analyte from 20 ml of aqueous sample. Various coexisting ions were added to the solution containing 50 μg l^{-1} of Fe(II) in these experiments and the recommended procedure was applied. A relative error of less than ±5% was considered to be within the range of the experimental error. Table 1 illustrates the results of this investigation. The ions

Table 1. Effect of Divers Cations and Anions on the Recovery of Iron(II) (50 μg l^{-1})

Ion	Molar ratio (ion/Fe(II))	Recovery (%)	Ion	Molar ratio (ion/Fe(II))	Recovery (%)
NH_4^+	1000	100.0	Ni^{2+}	50	95.3
Na^+	1000	100.2	Co^{2+}	30	97.8
K^+	1000	103.2	Cu^{2+}	20	100.5
Mg^{2+}	1000	99.4	Cl^-	1000	100.2
Sr^{2+}	1000	101.5	NO_3^-	1000	100.6
Ca^{2+}	1000	97.8	Br^-	1000	102.1
Ba^{2+}	1000	100.5	SO_4^{2-}	1000	96.8
Cr^{3+}	500	105.1	$S_2O_3^{2-}$	500	99.2
Zn^{2+}	500	98.3	PO_4^{3-}	500	97.5
Cd^{2+}	100	99.0	$C_2O_4^{2-}$	50	101.2
Pb^{2+}	100	98.2	F^-	50	100.5

Table 2. Determination of Fe(II) and Fe(III) in Different Water Samples

Sample	Spiked (μg l^{-1})		Found (μg l^{-1})[a]		Recovery (%)	
	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
Tab water	-	-	9.2 ± 0.3	33.1 ± 1.2	-	-
	10	10	19.4 ± 0.7	42.8 ± 1.5	102.0	97.0
	20	20	28.5 ± 1.1	52.8 ± 0.8	96.5	98.5
Well water	-	-	14.2 ± 0.5	7.4 ± 0.3	-	-
	10	10	23.8 ± 0.7	17.3 ± 0.5	96.0	99.0
	20	20	33.8 ± 1.2	26.9 ± 0.5	98.0	97.5
River water	-	-	18.7 ± 0.4	43.5 ± 0.9	-	-
	10	10	28.5 ± 0.5	53.4 ± 1.4	98.0	99.0
	20	20	37.8 ± 0.8	64.2 ± 2.1	95.5	103.5

[a]Mean and standard deviation of three independent analyses.

considered at the mole ratio given in the table did not show any interference in the measurement of the analyte. Thus, the procedure is relatively selective for the analyte.

Analytical Performance

The analytical performance of the developed method was evaluated by processing 20 ml of the standard solutions of the iron(II) under the optimum conditions. The calibration graph was linear in the concentration range of 2.5-100.0 μg l^{-1} of iron(II). The equation of the calibration graph was A = 0.0105C-0.0139 (where A is the absorbance and C is the concentration of Fe(II) as μg l^{-1}) with a correlation coefficient of 0.9991.

The detection limit defined as $3S_b/m$ (where S_b and m are the standard deviation of the blank and the slope of the calibration graph, respectively) was found to be 0.16 μg l^{-1}. The relative standard deviation (RSD) for six replicate measurements at 20 μg l^{-1} of Fe(II) was 1.9%. The enhancement factor (EF) calculated as the ratio of the slopes of the calibration graphs constructed from aqueous solutions submitted to the proposed extraction method and that achieved without preconcentration was 32.

Table 3. Analytical Results for Fe in Food Samples

Samples	Added (μg g^{-1})	Found (μg g^{-1})[a]	Recovery (%)	GF-AAS (μg g^{-1})
Spinach	0	75.4 ± 1.7	-	76.1 ± 2.5
	10	85.2± 2.1	98.0	
Parsley	0	58.7 ± 1.5	-	58.3 ± 1.8
	10	68.3 ± 1.3	96.0	
Infant dry formula	0	69.8 ± 2.5	-	68.5 ± 2.8
milk	10	79.9 ± 0.8	101.0	
Rice	0	26.4 ± 0.7	-	27.0 ± 0.5
	10	35.9± 1.1	95.0	
Apple	0	15.1 ± 0.5	-	15.6 ± 0.8
	10	24.8 ± 1.3	97.0	

[a]Mean and standard deviation of three independent analyses.

Table 4. Characteristic Performance Data of the Proposed Method and other Preconcentration Techniques for Spectrophotometric Determination of Iron

Method	Complexing agent	EF or PF	LOD (μg l^{-1})	RSD (%)	Extraction time (min)	Ref.
CPE	5-Br-PADAP	20	0.8	2	5	[29]
FI-SPE	Thiocyanate	-	0.75	1.2	2	[30]
FI-SPE	SPDA	36	18	3.1	1.5	[31]
FI-SPE	DPD	-	0.01	-	2.4	[32]
CPE	TAN	30	1	-	-	[33]
DLLME	O-Phen	5	7.5	1.2	3	[34]
DLLME-SFO	TTA	125	25	4.2	1	[35]
SADSPE	TPTZ	32	0.16	1.9	1	This work

EF: enrichment factor; PF: preconcentration factor; LOD: limit of detection; RSD: relative standard deviation; 5-Br-PADAP: 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol; SPDA: N,N-bis(salicylidene)-1,3-propanediamine; DPD: N,N-dimethyl-p-phenylenediamine; TAN: 1,2-tiazolylazo-2-naphthol; TTA: 2-thenoyltrifluoroacetone; TPTZ: 2,4,6-tris(2-pyridyl)-1,3,5-triazine.

Analysis of Real Samples

The method was applied to the determination of iron species in tap water, well water, and river water (Zayandeh Roud River, Isfahan, Iran). The reliability of the method was checked through the recovery experiments. The results are listed in Table 2. Good recoveries (95.5-103.5%) indicate the applicability of the method for the speciation of iron in water samples.

The procedure was also applied to the determination of the total iron in spinach, parsley, apple, rice and infant dry formula milk samples. The validity of the method was verified through the recovery experiments as well as the comparison of the results with the data obtained by electrothermal atomic absorption spectrometry. The results summarized in Table 3 showed that satisfactory recoveries in the range of 95.0-101.0% were achieved and there is no significant difference between the results of the developed method and the electrothermal atomic absorption spectrometry at the 95% confidence level. Thus, the proposed method is reliable for the determination of iron in a wide range of samples.

Comparison to other Methods

The presented method was compared with the previously reported preconcentration methods for the speciation and determination of trace levels of Fe(II) and Fe(III). The results have been shown in Table 4. The developed method with low LOD, good repeatability, high preconcentration factor, and low extraction time is apparently comparable or even better than most of the other reported methods of the Table 4.

CONCLUSIONS

This paper deals with a new SADSPE technique combined with spectrophotometry for the extraction, preconcentration and determination of trace amounts of iron species. As the extraction equalibrium is acheived very quickly, the proposed method has the extraction time of approximately 1 min which is lower or comparable to the previously reported methods including LLE, SPE, CPE and DLLME. The method has the adequate accuracy, good precision and selectivity and allows the determination of iron species in water samples at $\mu g\ l^{-1}$ levels. Other advantages of the method are the easy operation and simplicity, speed of analysis, use of small amount of sorbent and sample, high tolerance to interference ions, inexpensive, and environmentally friendly.

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