Turkish Journal of Chemistry

http://journals.tubitak.gov.tr/chem/

Research Article

Turk J Chem
(2015) 39: 1059 – 1068

doi:10.3906/kim-1504-9

Spectrophotometric determination of iron species using ionic liquid ultrasound assisted dispersive liquid–liquid microextraction

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Received: 05.04.2015 • **Accepted/Published Online:** 02.06.2015 • **Printed:** 30.10.2015

Abstract: A simple and efficient method for speciation and determination of iron in different water samples was developed. The method is based on ionic liquid ultrasound assisted dispersive liquid–liquid microextraction (IL-USA-DLLME) followed by spectrophotometric determination. Fe(II) is complexed with 2,4,6-tri(2'-pyridyl)-l,3,5-triazine (TPTZ), neutralized through ion pair formation with sodium dodecyl sulfate (SDS) and extracted into 1-hexyl-3-methylimidazolium hexafluorophosphate [C_6MIM][PF_6]. Total iron amount was determined after reduction of Fe(III) to Fe(II) with hydroxylamine hydrochloride. The concentration of Fe(III) was determined from the difference of concentration of total iron and Fe(II). The important parameters such as the type and volume of the extraction solvent, pH, ligand concentration, and ionic-strength were optimized. Under the optimum conditions, the calibration graph was linear over the range of 5.0–140.0 μg L^{-1} with the detection limit of 0.2 μg L^{-1}. The relative standard deviation for five replicates measurement of 100 μg L^{-1} of Fe(II) was 1.5%. The proposed method was successfully applied to the determination of iron species in water samples.

Key words: Ionic liquid, dispersive liquid–liquid microextraction, ultrasound assisted, iron speciation, spectrophotometry

1. Introduction

Iron, a vital element in the environment and biology, is widely distributed in nature.[1] It is an important element for human, plants, animals, and biotic enzymes. Iron has a fundamental role in the biosphere and functions as the active center of proteins that transfer oxygen and electrons.[1,2] Iron exists as Fe(II) and Fe(III) species in natural water and knowledge about transformation between these states is of great importance in both aerosphere chemistry and oceanography.[3] Furthermore, determination of the oxidation states of iron in aquatic systems is very important from environmental and biological points of view as it influences the bioavailability of iron as well as the physicochemical and toxicological properties of other trace elements and organic substrates.[4–6] Thus, there is a great demand for development of a simple, fast, and sensitive method for trace element determination of the most important iron species (Fe(II) and Fe(III)) in water samples.[7] Various techniques including capillary electrophoresis,[8] inductively coupled plasma mass spectrometry (ICP-MS),[9] inductively coupled plasma optical emission spectrometry (ICP-OES),[10] flame atomic absorption spectrometry

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(FAAS),[11] polarography,[12] voltametry,[13] chemiluminescence,[14] and spectrophotometry[15] have been used for the determination of iron. Among these methods, spectrophotometry has the advantages of simplicity, availability, versatility, speed, accuracy, precision, and cost-effectiveness,[16] but it lacks the required sensitivity for direct determination of trace concentrations. Thus, for the determination of low amount of iron ions, a separation and preconcentration step is required. Different procedures, such as solid phase extraction,[11,17] stripping voltametry,[18] co-precipitation,[19] liquid–liquid extraction,[10,20,21] and cloud point extraction,[22,23] have been used for this purpose. Dispersive liquid–liquid microextraction (DLLME) based on injecting an appropriate mixture of extraction solvent and disperser solvent into aqueous sample solution by syringe was developed by Assadi et al.[24] in 2006. The main advantages of DLLME are simplicity, rapidity, low cost, use of micro amount of organic solvent, achievement of high recovery, and high enrichment factor.[25] DLLME has been widely used for the determination of heavy metals and organic compounds.[26,27] The principles and applications of this technique have been reviewed.[28] One of the drawbacks of DLLME is the use of organic solvents that are often volatile, flammable, and potentially toxic to humans and the environment.

Room temperature ionic liquids (RTILs), with their unique physicochemical properties such as low toxicity and volatility, good solubility in organic solvents, and high thermal stability as well as good extractability for different organic compounds and metal ions, have recently gained increasing attention as environmentally friendly solvents to replace conventional organic solvents in extraction processes.[29−31]

Ultrasonic energy has been used as a powerful assistant in the acceleration of processes such as homogenization, formation of emulsion, and mass transfer between immiscible phases in separation and extraction procedures.[32,33] Ultrasound-assisted liquid–liquid extraction and ultrasound-assisted emulsification extraction procedures have been successfully used as the substitute of liquid–liquid extraction and in these methods the extraction equilibrium is attained in a short time.[32−34]

In this work the advantages of ionic liquids, ultrasound, and DLLME were combined and an ionic liquid ultrasound assisted dispersive liquid–liquid microextraction (IL-USA-DLLME) method for the preconcentration and speciation of iron in aqueous samples was developed. Fe(II) was complexed with 2,4,6-tri(2'-pyridyl)-l,3,5-triazine (TPTZ) and was neutralized through the formation of ion-association with sodium dodecyl sulfate (SDS). The hydrophobic ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate $[C_6MIM][PF_6]$ was chosen as the extraction solvent. After extraction, the extracted Fe(II) in the sediment phase was determined by spectrophotometric method. Total iron amount was determined after reduction of Fe(III) to Fe(II) with hydroxylamine hydrochloride. The concentration of Fe(III) was determined from the difference in the concentration of total iron and Fe(II). The effect of various experimental parameters on the extraction was investigated and the method was applied to the determination of Fe species in natural water samples.

2. Results and discussion

In the preliminary experiments it was observed that Fe(II) can form a colored cationic complex with TPTZ and after neutralization, it was quickly extracted into 1-hexyl-3-methylimidazolium hexafluorophosphate $[C_6MIM][PF_6]$. Hence, a separation/preconcentration method for speciation of iron based on IL-USA-DLLME method was designed and preconcentrated iron was measured at 589 nm.

The spectra of TPTZ, Fe-TPTZ complex in aqueous sample, and the extracted complex in ILs against the reagent blank are shown in Figures 1a–1c and they indicate that the molar absorptivity of the extracted complex significantly increased. In order to obtain high extraction efficiency, the parameters affecting iron complex formation and extraction were investigated and optimized.

2.1. Effect of pH

The pH of the aqueous phase may have an important effect on extraction yield by affecting metal complex formation and its subsequent extraction. The effect of pH on the extraction of iron complex was investigated in the range of 1.5–7.5. It was observed (Figure 2) that the maximum absorbance was achieved within the pH range of 3.5–6.5. The decrease in the signals at pH values greater than 7 might be related to the hydrolysis of iron species, whereas the decreases at lower pH values may be related to the competition of protons with iron species for complexation with TPTZ. Thus, a pH of 4.5 was chosen as the optimum pH in further studies.

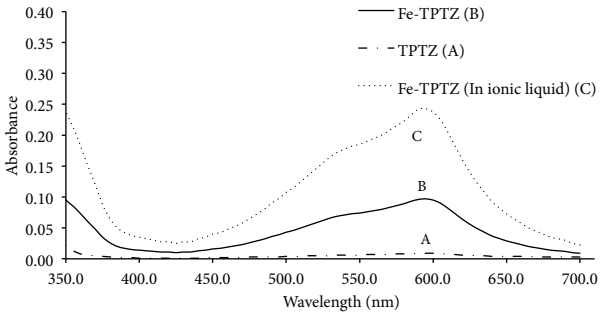

Figure 1. The absorption spectra of TPTZ (a), Fe(II)-TPTZ complex at pH 4.5 in aqueous phase (b), and Fe(II)-TPTZ complex in ionic liquid (c).

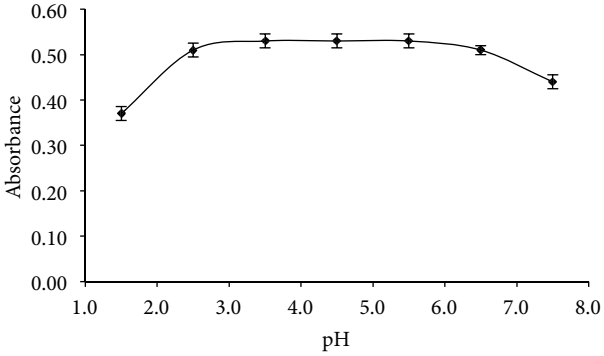

Figure 2. Effect of pH on the analytical signal. Conditions: sample volume, 8 mL; disperser solvent, 400 μL; extraction solvent, 60 μL; Fe^{2+} concentration, 100 μg L^{-1}; TPTZ concentration, 1.35 $\times$ 10^{-5} mol L^{-1}; SDS concentration, 5 $\times$ 10^{-5} mol L^{-1}, centrifugation time, 2 min; sonication time, 3 min.

2.2. Effect of TPTZ concentration

The extraction efficiency of iron complex was dependent on the TPTZ concentration. Figure 3 shows that the analytical signal was increased by an increase in the TPTZ concentration up to 1.1 $\times$ 10^{-5} mol L^{-1}, remained constant up to 1.35 $\times$ 10^{-5} mol L^{-1}, and then slightly decreased with a further increase in TPTZ concentration. The slight decrease in the high concentration of the ligand might be due to competition between complexing agent, which is in excess in the solution, and iron (II) complex for extraction into ionic liquid. Therefore, a TPTZ concentration of 1.35 $\times$ 10^{-5} mol L^{-1} was chosen for subsequent studies.

2.3. Effect of SDS concentration

In order to extract the cationic complex of Fe-TPTZ into IL, different anions such as I^-, ClO_4^-, and sodium dodecyl sulfate (SDS) was considered the counter ion in an effort to make a lipophilic ion pair. It was found that the bulky anionic surfactant of SDS was more effective for extraction of the complex into IL. Then the effect of the amount of SDS on the extraction efficiency was investigated by varying its concentration over the range of 2.0 $\times$ 10^{-5}–1.8 $\times$ 10^{-4} mol L^{-1}. The recovery of Fe(II) increased with an increase in the concentration of SDS up to a maximum value of 5.0 $\times$ 10^{-5} mol L^{-1} and then remained constant with further increases in SDS concentration. Thus 5.0 $\times$ 10^{-5} mol L^{-1} of SDS was selected as the optimal concentration.

2.4. Effects of the nature and volume of the disperser solvent

A disperser solvent should be miscible with both water and the extraction solvent. Therefore, acetone, acetonitrile, methanol, and ethanol were considered disperser solvents. For this purpose, the analyte was extracted into 120 μL of IL using 500 μL of different disperser solvents and it was found that with ethanol the analytical signal was higher than that of the other disperser solvents (Figure 4); therefore, ethanol was selected as the disperser solvent. Then the influence of ethanol volume in the range of 100–600 μL on extraction efficiency was investigated at the fixed volume of IL (120 μL). At low volumes of disperser solvent, IL was not completely dispersed and the extraction efficiency was low. The absorbance and extraction of analyte were maximized at 400 μL of ethanol and then slightly decreased at higher volumes of ethanol. The slight decrease in absorbance at higher volumes of ethanol was due to a slight increase in the solubility of the extraction solvent into the aqueous phase in the presence of ethanol, which causes a decrease in extraction efficiency. Thus, 400 μL of ethanol was selected as the optimal volume of the dispersive solvent.

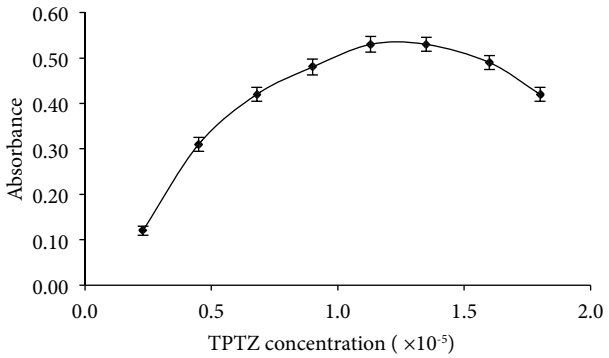

Figure 3. Effect of the TPTZ concentration on the analytical signal. Conditions: sample volume, 8 mL; disperser solvent, 400 μL; extraction solvent, 60 μL; pH, 4.5; Fe^{2+} concentration, 100 μg L^{-1}; SDS concentration, 5 $\times$ 10^{-5} mol L^{-1}, centrifugation time, 2 min; sonication time, 3 min.

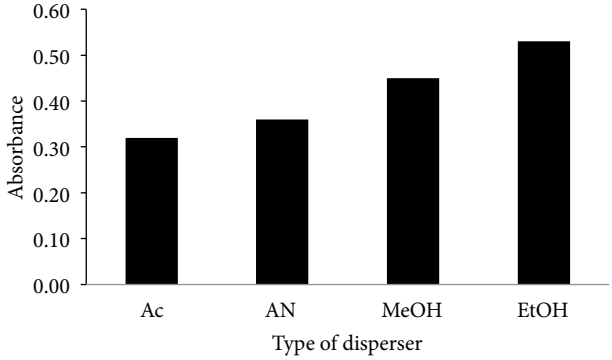

Figure 4. Effect of the type disperser solvent on the analytical signal. EtOH: ethanol, MeOH: methanol, Ac: acetone, ACN: acetonitrile. Conditions: sample volume, 8 mL; volume of disperser solvent, 400 μL; volume of extraction solvent, 60 μL; pH, 4.5; Fe^{2+} concentration, 100 μg L^{-1}; TPTZ concentration, 1.35 $\times$ 10^{-5} mol L^{-1}; SDS concentration, 5 $\times$ 10^{-5} mol L^{-1}, centrifugation time, 2 min; sonication time, 3 min.

2.5. Effect of volume of IL

One of the important factors affecting the enrichment factor and thereby the sensitivity of the method is the volume of extracting solvent. An increase in the ratio of the volume of the aqueous phase to the organic phase will increase the preconcentration factor, but it may reduce the extraction efficiency for a given extraction time. Thus, in order to increase the sensitivity of the IL-USA-DLLME, the effect of solvent volume on the extraction efficiency was investigated. For this purpose different volumes of $[C_6MIM][PF_6]$ (40–120 μL) were subjected to IL-USA-DLLME, keeping all the other variables constant. As indicated in Figure 5, by increasing the volume of IL up to 60 μL the analytical response increases and reaches its maximum. However, a further increase in $[C_6MIM][PF_6]$ volume causes a decrease in absorbance signal. Thus, 400 μL of ethanol is not sufficient to disperse the higher amount of IL into the fine droplets, which results in a decrease in the extraction efficiency and absorbance; similar results were observed before.[35,36] Thus, in order to obtain high sensitivity and enrichment factor, 60 μL of IL was chosen for subsequent experiments.

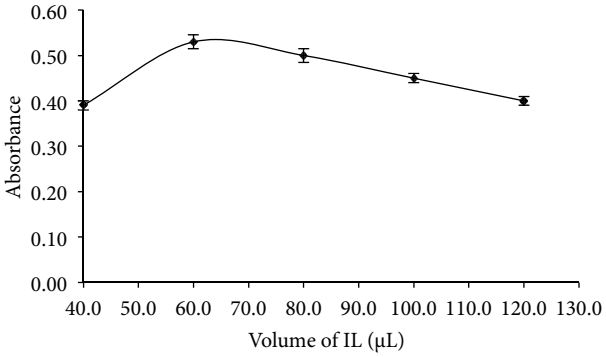

Figure 5. Effect of the extraction solvent (ionic liquid) volume on the analytical signal. Conditions: sample volume, 8 mL; disperser solvent, 400 μL; pH, 4.5; Fe^{2+} concentration, 100 μg L^{-1}; TPTZ concentration, 1.35 $\times$ 10^{-5} mol L^{-1}; SDS concentration, 5 $\times$ 10^{-5} mol L^{-1}, centrifugation time, 2 min; sonication time, 3 min.

2.6. Effect of ultrasound time

Dispersion is one of the most important stages for the successful performance of IL-USA-DLLME.[37] Thus, an adequate sonication time ensures complete dispersion of IL in the form of fine droplets into the sample solution, resulting in higher extraction efficiency. However, excessive sonication time may cause the generation of heat and an increase in the solubility of IL or decomposition of the complex, which both result in a decrease in extraction efficiency. Therefore, the effect of sonication time was investigated in the range of 1–8 min. The results showed that absorbance increases from 1 to 3 min and then decreased slowly with a further increase in sonication time. Hence, 3 min was chosen as the optimum sonication time.

2.7. Effect of centrifugation time

Centrifugation is a vital step for separating IL from the aqueous phase. In order to achieve the best extraction efficiency and speed, the effect of centrifugation time in the range of 1–5 min at 5000 rpm on the extraction of Fe(II) with IL-USA-DLLME was investigated. The absorbance was found to increase with an increase in the centrifugation time up to 2 min and then remained constant with further increases in centrifugation time. This phenomenon can be attributed to the incomplete sedimentation of IL at shorter centrifugation times. Therefore, 2 min was selected as the optimum time for centrifugation.

2.8. Effect of common salt

The effect of ionic strength on IL-USA-DLLME performance was investigated by performing several experiments with different NaCl concentrations (0.0–0.6 mol L^{-1}) while keeping the other experimental parameters constant. The results confirmed that salt addition had no significant effect on extraction efficiency up to 0.4 mol L^{-1}. Thus the method can be used for the separation and determination of iron species from saline samples.

2.9. Effect of sample volume

Sample volume is an important factor to be studied when real samples are analyzed by a preconcentration method. In order to obtain the maximum preconcentration factor, the effect of sample volume was investigated in the range of 5–20 mL for 100 μg L^{-1} Fe(II). The results showed that the analytical signal was constant up to 8 mL of sample volume and then decreased. This decrease can be related to the increase in dissolution of IL in higher volumes of aqueous phase.

2.10. Speciation of iron

In order to extract Fe(III), it was reduced to Fe(II) and was subsequently complexed with TPTZ. Hydroxylamine was selected as the reducing agent and its concentration for effective reduction of Fe(III) to Fe(II) was optimized by extracting 8 mL of Fe(III) at a concentration of 100 μg L^{-1} in the presence of varying amounts of hydroxylamine (0.02–0.18 mol L^{-1}). The results showed that Fe(III) could be quantitatively reduced when the hydroxylamine concentration was 0.11 mol L^{-1}. Furthermore, the capability of the method for speciation of iron was investigated by processing synthetic water of Fe(III) and Fe(II) according to the given procedure. The results in Table 1 reveal that the recovery of both species of iron is quantitative; thus the system is capable of speciation of iron.

Table 1. Recovery of Fe(II) and Fe(III) cations from 8 mL of synthetic water at pH 4.5.

Added (μg L^{-1})		Found (μg L^{-1})[a]		Recovery (%)	
Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
100	0	101.6 ± 3.0	-	101.6	-
75	25	73.6 ± 3.0	24.1 ± 3.0	98.1	96.4
25	75	24.3 ± 4.0	77.3 ± 4.0	97.2	103.1
50	50	48.3 ± 3.0	48.1 ± 3.0	96.6	96.2
0	100	-	96.4 ± 4.0	-	96.4

[a]Mean and standard deviation of three measurements.

2.11. Interference study

The selectivity of the method was evaluated for the determination of iron in the presence of other common ions in water matrices. The effect of different ions was studied on the extraction and determination of 10 μg L^{-1} Fe(II). A relative error of less than ±5% was considered to be within the range of the experimental error. The results (Table 2) showed that the examined ions at the given mole ratio cause no significant interference in the extraction and determination of iron. Thus, the system has high selectivity for iron ions.

2.12. Analytical figures of merit

Under the optimum conditions, a calibration graph was obtained by analyzing 8.0 mL of standard solutions of Fe(II). The calibration graph was linear over the range of 5.0 to 140.0 μg L^{-1}. The regression equations for iron with and without preconcentration were A = 0.00513C + 0.0089 (R^2 = 0.9993) and A = 0.00027C + 0.046 (R^2 = 0.9997), respectively, where A is the absorbance and C is iron concentration in μg L^{-1}. The limits of detection (LOD) and the limits of quantification (LOQ), defined as the ratio of three and ten times the standard deviation of the blank signal over the slope of the calibration curve, respectively, were 0.2 μg L^{-1} and 0.7 μg L^{-1}. The relative standard deviation (RSD%) for five replicate determinations of Fe(II) at 100 μg L^{-1} concentration was 1.5%. The enhancement factor, defined as the slope ratio of the calibration curve of the extraction method to that obtained without preconcentration, was 19.0.

2.13. Comparison with other methods

Determination of iron species in water samples by the developed IL-USA-DLLME was compared with the other reported liquid phase microextraction methods for the determination of iron and the results are shown in Table 3. The enrichment factor of IL-USA-DLLME was higher and consequently its detection limit was lower than

those of the other reported methods even though some of them used the more sensitive instrument of FAAS for iron quantification.

Table 2. Effect of diverse ions on the extraction and determination of 10 μg L^{-1} Fe(II).

Interfering species	Molar ratio (ion/Fe^{+2})	Recovery (%)[a]
Ca^{2+}	1000	101.0 ± 4.0
Li^{+}	1000	101.5 ± 2.0
Al^{3+}	1000	105.0 ±5.0
Mg^{2+}	1000	95.5 ± 2.5
Cr^{3+}	1000	96.5 ± 3.0
PO_4^{3-}	1000	101.0 ± 3.0
F^{-}	1000	102.6 ± 2.5
Br^{-}	1000	102.0 ± 3.0
CO_3^{2-}	1000	98.0 ± 4.0
NO_2^{-}	1000	99.5 ± 3.0
I^{-}	1000	103.6 ± 3.0
S^{2-}	1000	98.0 ± 4.2
Mn^{2+}	1000	97.1 ± 2.8
Zn^{2+}	200	105.0 ± 2.4
Cd^{2+}	40	96.3 ± 1.5
Pb^{2+}	40	102.5 ± 2.5
Co^{2+}	30	105.0 ± 6.0
Cu^{2+}	30	102.1 ± 1.8
Ni^{2+}	20	103.0 ± 1.1

[a] Mean and standard deviation of three measurements.

Table 3. The analytical characteristics of some extractive methods for iron speciation.

Method	EF[a]	Dynamic range (μg L^{-1})	RSD%	LOD[b] (μg L^{-1})	Detector	Ref.
LEE	12.5	25–150	7.0	9.0	FFAS	20
DLLME	10.0	25–1000	1.2	7.5	UV-Vis	21
IL-DLLME	15.02	10–700	3.1	2.4	FFAS	38
DLLME	15.0	50–1000	1.4	4.5	FAAS	39
DLLME-SFO	-	25–250	3.2	4.8	FASS	11
IL-USA-DLLME	19.0	5–140	1.5	0.2	UV-Vis	This work

[a]Enhancement factor.

[b]Limit of detection.

2.14. Analysis of real samples

The proposed method was applied to the determination of Fe(II) and Fe(III) in 8 mL of mineral water, and drum water of Yazd power plant and the results are listed in Table 4. In order to validate the applicability of the proposed method, aliquots of 8.0 mL of different water samples were spiked with different concentration levels of Fe(II) or Fe(III) and recovery experiments were carried out. The results summarized in Table 5 show that the recoveries of the spiked samples are good (95.0%–104.0%). Thus the method has good accuracy for iron speciation in the matrix types examined.

Table 4. The concentration of Fe(II) and Fe(III) in the various samples.

Sample	Found (μg L^{-1}) [a]	
	Fe(II)	Fe(III)
Low pressure supper heat steam	39.0 ± 1.0	49.0 ± 3.5
High pressure supper heat steam	43.5 ± 3.0	63.2 ± 3.5
Mineral water	N.D.[b]	34.4 ± 1.5

[a]The results are mean and standard deviation of three measurements.
[b]Not detected.

Table 5. Analytical results for determination of Fe(II) and Fe(III) in water samples.

Sample	Spiked (μg L^{-1})		Recovery (%)	
	Fe(II)	Fe(III)	Fe(II)	Fe(III)
Low pressure supper heat steam	100	100	102.0	98.0
	120	120	96.7	103.0
High pressure supper heat steam	100	100	97.5	96.3
	120	120	103.0	103.6
Mineral water	100	100	95.0	104.0
	120	120	96.0	97.2

The results are mean and standard deviation of three measurements.

2.15. Conclusion

In this study a simple and sensitive method for the speciation of trace amounts of inorganic iron species by IL-USA-DLLME combined with spectrophotometry was developed. An ultrasonic bath was used to increase the dispersion of ionic liquid droplets and enhance the speed of mass transfer of analyte from the aqueous phase to the ionic liquid. In the developed method, the sample preparation time and the consumption of volatile organic solvents were minimized. With the use of IL environmental pollution was limited to a very small amount, which is particularly attractive, as the green chemistry concept has been employed.

Other advantages of the method are its low cost, no need for sophisticated extraction apparatuses, and providing an alternative to techniques such as ETAAS and ICP-AES for the determination of iron at μg L^{-1} level in the matrix types examined.

3. Experimental

3.1. Reagent and glassware

All the chemicals used were of analytical reagent grade and were obtained from Merck (Darmstadt, Germany). All the solutions were prepared with doubly distilled water. Stock standard solutions of Fe(II) and Fe(III) at a concentration of 1000 mg L^{-1} were prepared by dissolving appropriate amounts of $Fe(NH_4)_2(SO_4)_2.6H_2O$ and $Fe(NH_4)(SO_4)_2.12H_2O$ in 0.1 mol L^{-1} H_2SO_4, respectively. The working standard solutions were prepared daily by appropriate dilution of the stock standard solutions. A 10% (w/v) hydroxylamine hydrochloride ($NH_2OH.HCl$) solution was prepared by dissolving an appropriate amount of the reagent in doubly distilled water. A 3×10^{-3} mol L^{-1} solution of sodium dodecyl sulfate (SDS) was prepared by dissolving 0.01 g of the reagent in doubly distilled water. A stock solution of acetate buffer (2 mol L^{-1}) was prepared by dissolving appropriate amounts of sodium acetate and acetic acid solutions in doubly distilled water and adjusting the

pH to 4.5. A stock 2,4,6-tri(2'-pyridyl)-l,3,5-triazine (TPTZ) solution (3×10^{-4} mol L^{-1}) was prepared by dissolving an appropriate amount of TPTZ in 0.1 mol L^{-1} HCl in a 25 mL volumetric flask.

3.2. Apparatus

Spectrophotometric measurements were done by double beam Cary 100 spectrophotometer (Varian, Australia) with matched cells of 1 cm path length. A 300 μL quartz micro-cell with 10 mm light path were prepared from Hellma (Mullheim, Germany). A 0.5 mL syringe was prepared from Hamilton (Reno, NV, USA). All pH measurements were done with an AZ 86502 pH-meter (China) equipped with a combined glass calomel electrode. An EBA20 model centrifuge (Hitachi, Universal 320, Tuttlingen, Germany) was used for the phase separation. The samples were ultrasonically irradiated in a water bath at 550 W and 60 kHz using an ultrasonic bath (Elmasonic, Singen/Htw, Germany).

3.3. Procedure

Eight milliliters of real sample or standard solution containing Fe(II) not more than 1.12 μg was transferred into a 15 mL conical bottom glass centrifuge tube. Its pH was adjusted to 4.5 by adding 2 mL of acetate buffer. Then 360 μL of 3×10^{-4} mol L^{-1} TPTZ as the complexing agent and 120 μL of 3×10^{-3} mol L^{-1} SDS as the counter ion were added and the mixture was gently shaken for several seconds. A mixture containing 400 μL of ethanol (as the disperser solvent) and 60 μL of $[C_6MIM][PF_6]$ (as the extraction solvent) was rapidly injected into the solution; the tube was then immersed in an ultrasonic water bath and sonicated at 550 W for 3 min. In this stage a cloudy solution was formed and the analyte was extracted into fine droplets of $[C_6MIM][PF_6]$. The tube was transferred into an ice bath for 4 min and the mixture was centrifuged at 5000 rpm for 2 min. The aqueous phase was withdrawn with a syringe, the remaining IL phase was diluted to 300 μL with ethanol, and its absorbance was measured at 589 nm against the reagent blank.

Total dissolved iron was determined by effective reduction of Fe(III) to Fe(II) upon addition of 0.6 mL of the hydroxylamine hydrochloride solution prior to the extraction procedure. The concentration of Fe(III) was calculated by subtracting the concentration of Fe(II) from total iron concentration.

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