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Development of a dispersive liquid–liquid microextraction method for iron speciation and determination in different water samples

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ABSTRACT

A novel, simple and efficient method for the iron (Fe) speciation and determination in different water samples was developed using dispersive liquid–liquid microextraction (DLLME) technique followed by spectrophotometric analysis. The procedure is based on complexation of Fe(II) with O-phenanthroline (O-Phen), the subsequent ion-association formation with picrate anion, then extraction of the complex using DLLME technique. Some important parameters such as the type and volume of extraction and dispersive solvents as well as the extraction time were investigated and optimized in detail. Under the optimum conditions, the calibration graphs were linear over the range of 0.025–1.0 $\mu g\,mL^{-1}$ with limit of detection of 7.5 $\mu g\,L^{-1}$. Relative standard deviation for five replicate determinations of Fe at 0.2 $\mu g\,mL^{-1}$ concentration level was calculated to be 1.2%. Average recoveries for spiked samples were determined to be between 90% and 108%. The method was applied to water samples and parenteral solutions and the amounts of Fe found in these samples using the proposed method were similar with those obtained by a standard method.

1. Introduction

Fe is widely distributed in nature and is one of the most important elements in environmental and biological systems [1]. Fe is an essential nutritional element for all life forms and biotic enzymes (such as catalase). It plays a central role in the biosphere and serves as the active center of proteins responsible for O_2 and electron transfer [1,2]. The environmental and biological effectiveness of Fe depends on its chemical properties, such as valence, solubility, and the degree of chelating characteristic [1,3]. Dissolved Fe in the natural water is found as both Fe(II) and Fe(III) forms with transformations between these states, which is of great interest in both atmospheric chemistry and oceanography [4]. Therefore, it is very important to develop sensitive methods for quantitative determination of trace Fe in various matrices.

Several techniques, such as spectrophotometry [4–7], atomic absorption spectrometry (AAS) [2,5,8–10], inductively coupled plasma-optical emission spectrometry (ICP-OES) [1,11], ICP-mass spectrometry (MS) [3,12,13], cathodic or anodic stripping Voltammetry [14,15], chromatography [16,17] and spectroscopic sensors [18] have been reported for the determination of Fe or its species. The direct determination of trace elements by spectroscopic methods, such as FAAS and ICP-OES, is often difficult because of insufficient sensitivity and selectivity of the used methods. For this reason, the preliminary separation and preconcentration of trace elements from the different matrices are required.

Several procedures such as: liquid–liquid extraction (LLE) [9,17], co-precipitation [13], solid phase extraction (SPE) [1–3] have been developed for the separation and preconcentration of contaminants such as Fe from environmental matrices. However, significant chemical additives, solvent losses, complex equipment, large secondary wastes, unsatisfactory enrichment factors and high extraction time limit the application of these techniques [19].

Recent research activities are being focused on the development of efficient, economical, and miniaturized sample preparation methods. Consequently different microextraction systems have been developed. For example a high performance and powerful microextraction technique termed as dispersive liquid–liquid microextraction (DLLME) has been developed by Assadi [20] and co-workers. In this method, an appropriate mixture of the extraction solvent and the disperser solvent is injected into the aqueous sample and a cloudy solution is formed. The cloudy state results from the formation of fine droplets of the extraction solvent which disperse in the sample solution. The cloudy solution is centrifuged and the fine droplets are settled at the bottom of the conical test tube. The analytes of interest are extracted from the initial solution

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and concentrated to a small volume of the settled phase. Determination of the analytes in the settled phase can be performed by conventional analytical techniques [21].

The ease of the operation, speed, lower sample volume, low cost, high recovery and high enhancement factor are some advantages of DLLME. The principles and the applications of this new technique have been reviewed recently [22,23], thus DLLME has been widely applied to the analyses of heavy metals, pesticide residues and so on [24–28]. However, to the best of our knowledge, this is the first report concerning Fe speciation using the DLLME method.

In this work, a DLLME methodology has been developed and optimized for the extraction and determination of Fe. The method is based on chemical complexation of Fe(II) by O-Phen and ion-association formation with picrate anion. DLLME technique was used to extract ion-association and the spectrophotometry was used to analyze the extracted product. Potential parameters affecting the DLLME and analytical performance are studied and optimized in detail. The Fe was selected for evaluation of the procedure due to its environmental and biological importance. The spectrophotometric method was used due to ease and low cost of operation. Using the developed method Fe can be analyzed in simple, rapid and inexpensive manner.

2. Experimental

2.1. Apparatus

Spectrophotometric measurements were done on a Shimadzu UV–visible Recording Spectrophotometer (UV-160 model) and using 1.00 cm quartz micro-cells. A Hettich centrifuge (EBA 20) with 15 mL calibrated centrifuge tubes was used to accelerate the phase separation process. The pH values were controlled with a Corning M120 pH-meter.

2.2. Reagents

Stock standard solutions of Fe(III) and Fe(II) at a concentration of 1000 $\mu g\,mL^{-1}$ were prepared by dissolving analytical grade of $Fe(NH_4)(SO_4)_2{\cdot}12H_2O$ (Ridel De Haen, Germany) and $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ (E. Merck) in 1.0 M HCl, respectively. Working standard solutions were prepared fresh daily by stepwise dilution of these stock solutions with deionized water.

A 1% (m/v) hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) solution prepared by dissolving appropriate amount of $NH_2OH{\cdot}HCl$ (Fluka) in deionized water and diluted up to the mark. A 0.05 M solution of picric acid (E. Merck) was prepared by dissolving appropriate amount of this reagent in 5.0 mL of ethanol and 2.0 mL of 1.0 M NaOH solution and diluting to 25 mL with deionized water. A 0.05 M solution of O-Phen (E. Merck) was prepared by dissolving appropriate amount of this reagent in ethanol (E. Merck) and diluting to 25 mL with this solvent. These three solutions were kept at 4 °C.

A 1.0 M acetic acid–sodium acetate buffer solutions were used in the pH range of 3.0–5.5, while 0.1 M HCl was used to adjust pH below 3.0. Deionized water was generated in an R.100.M water deionizer (Absaz Co., Iran) and was used throughout. All the other reagents used in this work were analytical grade. All glass vessels used for analysis were kept in 10% solution of HNO_3 (analytical grade, Merck) for at least 24 h and subsequently washed twice with ultra pure water before use.

2.3. Real samples

Bottled mineral water samples and parenteral solutions were obtained from local sources and all solutions were stored in the dark at 4 °C until analysis without any previous treatment or filtration, whereas tap water samples were collected just before analysis.

2.4. Procedure for ion-association formation

From the Fe(III) standard solution (10 $\mu g\,mL^{-1}$) aliquot volumes were pipetted into 15-mL centrifuge tubes and mixed with 0.5 mL of 1.0 M acetate buffer solution at pH 4.5. Then 0.5 mL of 1% $NH_2OH{\cdot}HCl$ solution was added and the contents were mixed well and left to stand for 1 min. After reduction, the complexation was performed by adding 100 μL of 0.05 M O-Phen and 150 μL of 0.05 M picrate solution. The contents were mixed well after each addition and the tubes left to stand for 1 min. The contents were diluted to 7.0 mL and subjected to the DLLME.

2.5. Procedure for DLLME

Five hundred microliters of methanol (as disperser solvent) containing 70 μL of chloroform (as extraction solvent) was injected rapidly into a sample solution using a 2.0-mL syringe. A cloudy solution was rapidly produced, resulting from fine droplets, and the complex was extracted into these fine droplets. The mixture was centrifuged at 3500 rpm for 3 min and the dispersed fine droplets of chloroform were settled. The supernatant aqueous phase was readily decanted with a Pasteur pipette. The remained organic phase was diluted to 700 μL with ethanol and the absorbance measured at 510 ± 3 nm against a reagent blank.

2.6. Procedure for real samples

Aliquots of 5.0 mL of each sample were subjected to the chemical reactions and DLLME as described in Sections 2.4 and 2.5. Total Fe in the final solutions was measured using spectrophotometry.

Determination of Fe(II) in tap water was performed by the proposed method based on procedures described in Sections 2.4 and 2.5 without addition of $NH_2OH{\cdot}HCl$ solution. The concentration of Fe(III) in the sample solution could therefore be calculated by subtracting Fe(II) from total iron.

3. Results and discussion

The spectrophotometric methods for determination or speciation of Fe are usually based upon the reduction of Fe(III) to Fe(II) and the subsequent complexation of Fe(II) with different agents, such as O-Phen, to achieve sensitive color products. In this work some reducing agents such as ascorbic acid, $NH_2OH{\cdot}HCl$ and their mixture were examined for the reduction of Fe(III). The results showed that sensitive color reaction was occurred when $NH_2OH{\cdot}HCl$ was used as a reducing agent. Fig. 1 shows the absorption spectrum of the formed complex after DLLME, which exhibits two absorption bands at 442 ± 3 and 510 ± 3 nm. It was observed that the intensity

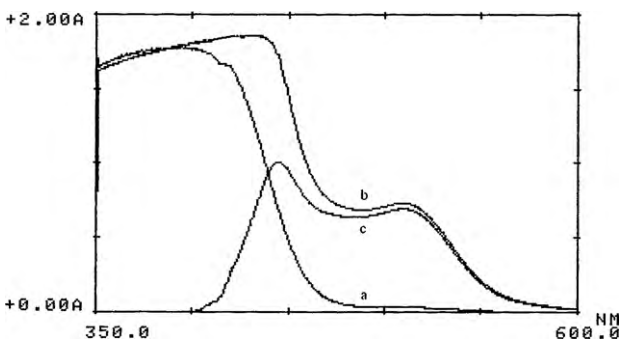

Fig. 1. Absorption spectra of: (a) reagents bank after DLLME, (b) ion-association after DLLME, (c) ion-association against reagents bank; *conditions*: 0.8 $\mu g\,mL^{-1}$ Fe(III), 0.5 mL of 1% $NH_2OH{\cdot}HCl$, 100 μL of 0.05 M O-Phen, 150 μL of 0.05 M picrate, conditions for DLLME have been mentioned in the text.

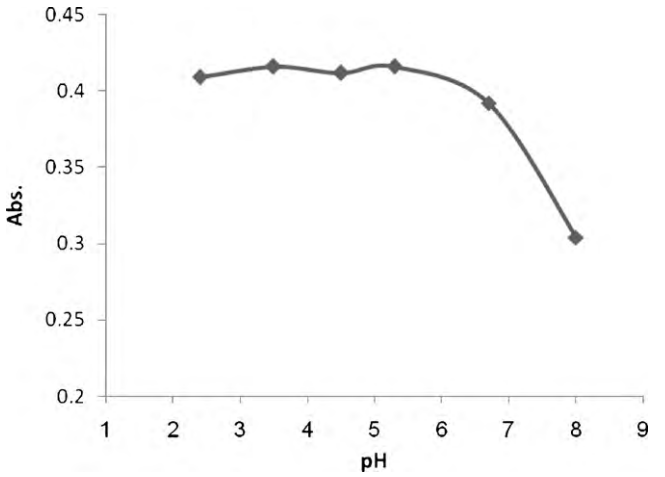

Fig. 2. Effect of pH on the analytical responses; conditions have been mentioned in the text.

and the shape of more sensitive band at 442 nm changed with rising concentration of picrate ion. Thus, this wavelength was an undesirable wavelength for analytical purpose [29]. Also, as can be seen from Fig. 1 the reagents did not show any significant absorbance in the analytical wavelength, *i.e.* 510 ± 3 nm. To obtain high sensitivity, it is necessary to investigate the effect of all parameters that could influence the chemical reactions and the performance of DLLME.

3.1. Effect of pH

The pH of the sample solution is one of the important factors affecting the formation of complexes and the subsequent extraction. The effect of pH on the DLLME extraction was studied over the pH range of 2.5–8. As can be seen in Fig. 2, the maximum absorbance was achieved over the pH range of 2.5–5.5. In more acidic media (pH < 2), the formation of the complex was incomplete owing to the reduction in the concentration of the picrate anion, which has a pK_a value of 1. While the raising of pH above this optimum range caused a gradual decrease in absorbance intensity probably due to hydrolysis of Fe(III). Therefore, pH 4.5 was selected for the further study.

3.2. Effect of the extraction and disperser solvent type

The type of extraction solvent used in DLLME is an important factor for efficient extraction. The solvent should be denser than water. Moreover it should have more capability for the extraction of interested compounds and lower solubility in water. Thus, chloroform, methylene chloride and carbon tetrachloride were studied as extraction solvent. On the other hand, the selection of a dispersive solvent is limited to solvents such as methanol, acetonitrile, ethanol and acetone, that are miscible with both water and extraction solvents.

In this study, all combinations of chloroform, methylene chloride and carbon tetrachloride (60 μL) as extraction solvents and methanol, acetonitrile, ethanol and acetone (500 μL) as dispersive solvents were tested. In the case of methylene chloride only with acetone as dispersive solvent, a two-phase system was achieved. With carbon tetrachloride and chloroform, a two-phase system was formed with all four dispersive solvents but in the case of carbon tetrachloride low signals was observed, probably due to little extractability of the product in this solvent. While in the case of chloroform with methanol more stable two-phase systems and higher signals were observed (see Fig. 3). Thus chloroform and

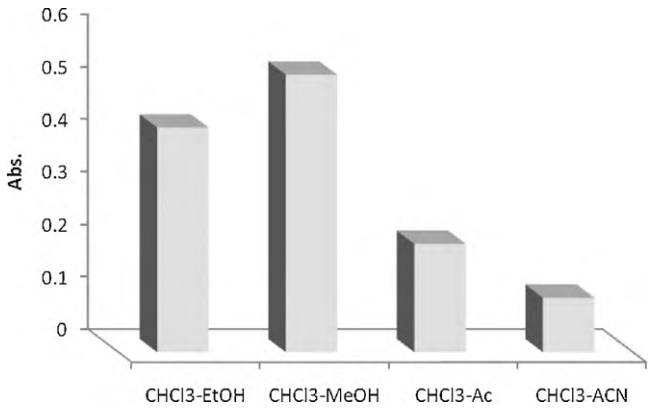

Fig. 3. Effect of the type of extraction and dispersant solvent on the analytical signals, $CHCl_3$: chloroform, EtOH: ethanol, MeOH: methanol, Ac: acetone, ACN: acetonitrile; other conditions have been mentioned in the text.

methanol was selected as extraction and disperser solvents, respectively, in subsequent experiments.

3.3. Effect of the extraction and disperser solvent volume

The effect of the volume of the extraction solvent on the analytical signals was investigated. Experiments were performed with different volumes of chloroform (in the range of 40–90 μL) as the extraction solvent by fixing the volume of the methanol at 500 μL. Fig. 4 indicates that the absorbance increased by increasing the volume of the chloroform to 70 μL and then remained approximately constant by further increasing of its volume between 70 and 90 μL. Thus 70 μL of chloroform was used in other experiments. In order to examine the effect of the disperser solvent volume, solutions containing different volumes of methanol (in the range of 400–800 μL) containing 70 μL of chloroform were subjected to the same DLLME procedure. As can be seen from Fig. 5, the absorbance reached to its maximum value at 500 μL of the methanol and then gradually decreased by further increasing of its volume, probably due to increasing of the dissolution of the extraction solvent in water and thus lower extraction efficiency of the product.

3.4. Effect of the $NH_2OH{\cdot}HCl$ concentration

The influence of the $NH_2OH{\cdot}HCl$ concentration on the analytical signals was examined by varying volumes of 1% $NH_2OH{\cdot}HCl$ (in the range of 0.1–1.5 mL). As shown in Fig. 6 the absorbance

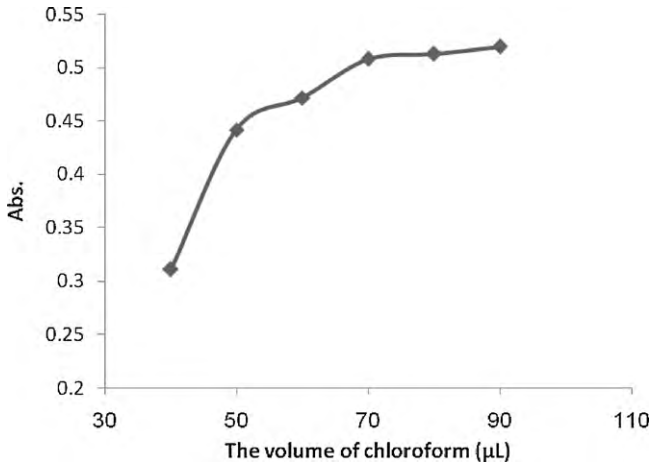

Fig. 4. Effect of the extraction solvent (chloroform) volume on the analytical signals, other conditions have been mentioned in the text.

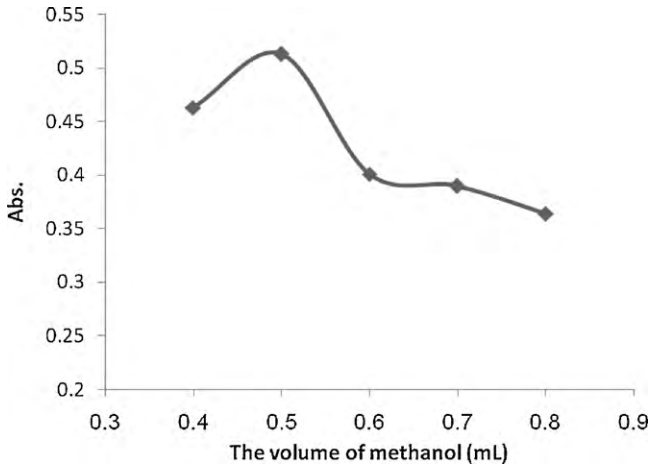

Fig. 5. Effect of the dispersant solvent (methanol) volume on the analytical signals, other conditions have been mentioned in the text.

rose with increasing concentration of $NH_2OH{\cdot}HCl$ reaching to its constant value at 0.25–0.75 mL. After this optimum range further increase in volume of reagent caused slight decrease in absorbance. The 0.5 mL of 1% $NH_2OH{\cdot}HCl$, corresponding to its maximum value, was used for other experiments.

3.5. Effect of the O-Phen and picrate concentration

The effect of O-Phen concentration on the absorbance was examined using increasing volumes of 0.05 M O-Phen from 50 to 1000 μL. The results showed that the change of O-Phen concentration in the studied range has little effect on analytical signals, thus the volume of 100 μL, corresponding to its maximum value, was used in other experiments.

Also, the effect of picrate concentration was investigated over the range of 50–300 μL of 0.05 M picrate solution. The absorbance rose with increasing concentration of picrate reaching its maximum value at 150 μL. Larger volumes caused decrease in absorbance (see Fig. 7) thus, 150 μL of picrate was selected.

3.6. Effect of extraction time

In DLLME, extraction time is defined as interval time between the injection of the mixture of solvents and the starting of centrifuge. The effect of extraction time was examined in the range of 30 s to 15 min with the constant experimental conditions. The obtained results showed that the extraction time had no significant influence on the signal. Because of the infinitely large surface area between extraction solvent and aqueous phase after the formation of cloudy solution, the complex diffuses quickly into the extraction solvent. Therefore, the DLLME method was time-independent, which was the most important advantage of this technique. In this method, the most time-consuming step, which took about 3 min, was the centrifuging of sample solution in the extraction procedure.

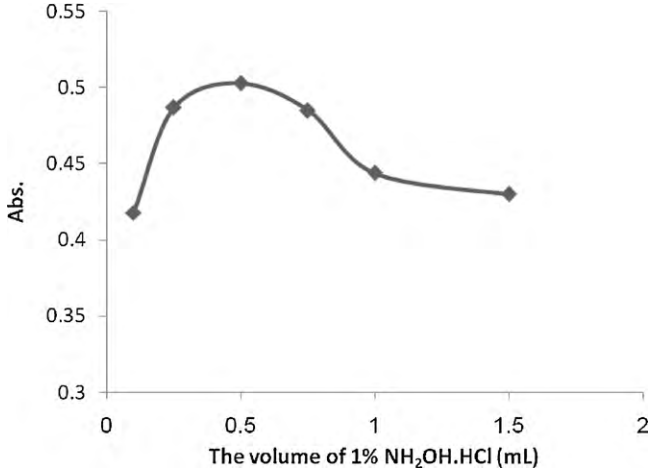

Fig. 6. Effect of $NH_2OH{\cdot}HCl$ concentration on the analytical responses; conditions have been mentioned in the text.

Table 1
Tolerance limits of interfering species in the determination of 200 μg L^{-1} of Fe(III).

Interferent-to-anlyte ratio	Interference species
1000:1	As^{3+}, Sn^{2+}, Bi^{3+}, Li^{+}, Na^{+}, K^{+}, Cl^{-}, F^{-}, I^{-}, ClO_4^{-}, CO_3^{2-}, SO_4^{2-}, NO_3^{-}, tartrate, urea, citrate
500:1	Pb^{2+}, Mn^{2+}, Cr^{3+}, glycine, oxalate, thiourea
100:1	Ba^{2+}, Ca^{2+}, Mg^{2+}, PO_4^{3-}
50:1	Al^{3+}, Zn^{2+}, Ni^{2+}, Cu^{2+},Cd^{2+}, Co^{2+}, Hg^{2+}
5:1	EDTA, SCN^{-}

3.7. Interferences

The influence of the common coexisting ions in natural water samples on the analytical signals was investigated. In these experiments, solutions containing 200 μg mL^{-1} of Fe(III) and the interfering ions were treated according to the recommended procedure. The tolerance limits of the coexisting ions, defined as the largest amount that caused an error in the absorbance value of no longer than ±5%, are given in Table 1. As can be seen from this table, the common cations and anions present in natural water possess no adverse effects on the assaying of Fe. Metal ions of the 3d series can be tolerated at levels indicated in this table provided that sufficient O-Phen is added since these cations can react with O-Phen and picrate to form yellow complexes. As the concentrations of these ions are generally similar to concentrations of Fe, their interference at given ratios can be considered negligible. Among the complexing agents examined, only EDTA and cyanide interfered.

3.8. Effect of salt addition

The effect of salt in this experiment was performed by adding different amounts of NaCl, from 0% to 5% (w/v), and other experimental conditions were kept constant. With the increase of the ionic strength, the signals were constant at first but decreased gradually by further increase of the salt concentration. This effect can be probably attributed to the dissociation and un-stability of the ion-pair complex in higher salt concentrations, *i.e.* higher than 1000:1 interferent to analyte ratio. Based on the above experimental data, no addition of salt was employed in all subsequent experiments.

3.9. Analytical performance

Calibration graphs were obtained by DLLME of 7.0 mL of standard solutions containing known amount of the Fe and under the experimental conditions specified in the procedure. The remained phase (≈100 μL) was diluted to 0.7 mL with ethanol and the absorbance was measured. Thus, the theoretical and experimental preconcentration factors of 70 and 10 were achieved. The linear concentration range was from 0.025 to 1.0 μg mL^{-1} of Fe with linear regression equation as:

$$\text{Abs.} = 0.724C + 0.015, \quad r = 0.998,$$

where Abs. is the absorbance intensity, C is the concentration of Fe as μg mL^{-1} and r is correlation coefficient.

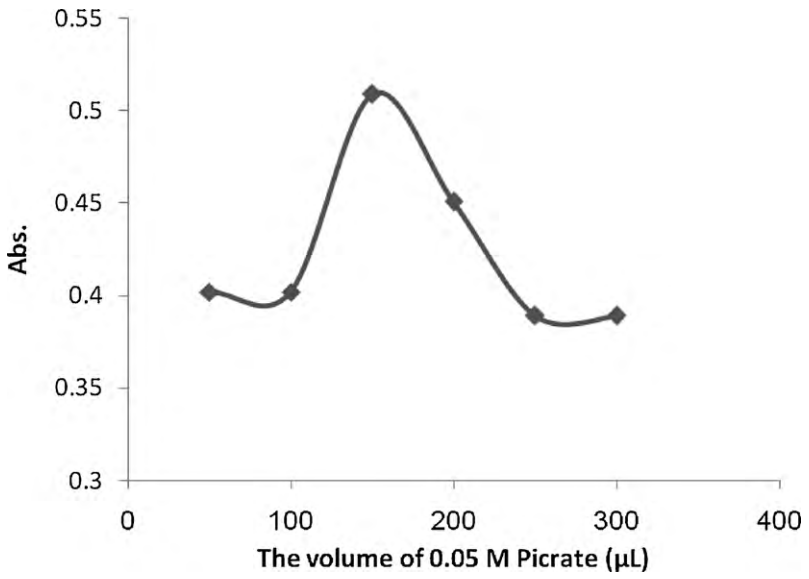

Fig. 7. Effect of picrate concentration on the analytical responses; conditions have been mentioned in the text.

Table 2
Analytical characteristics of the different extractive methods.

Method	Extraction method	Concentration range	r	RSD%	Mean recovery (%)	Concentration factor	LOD	Reference
ICP-OES	SPE	50–1000 μg L^{-1}	–	–	88–105.8	156	0.053 μg L^{-1}	[1]
FAAS	SPE	0.2–10 μg mL^{-1}	0.997	1.4	100–104	10	19 μg L^{-1}	[2]
ICP-MS	SPE	–	–	5.6 and 4.3	97–105	10	0.24–0.48 μg L^{-1}	[3]
FAAS	CPE	10–250 μg L^{-1}	0.9999	2.1	97–102.5	75	1.7 μg L^{-1}	[8]
FAAS	LLE	up to 5 μg mL^{-1}	0.999	2.1	93–107	20 (phase ratio)	0.24 μg L^{-1}	[9]
ICP-MS	Co-precipitation	0.5–18 μg L^{-1}	–	1.3–14	–	10	0.09 nM (≈5.03 ng L^{-1})	[13]
HPLC (with Vis. detection)	LLE	10 ng mL^{-1}–10 μg mL^{-1}	0.999	–	99.2 ± 0.9	–	7 μg L^{-1}	[17]
FAAS	LLE	25–150 μg L^{-1}	0.9988	7	90	–	9 μg L^{-1}	[28]
Spectrophotometry	DLLME	0.025–1.0 μg mL^{-1}	0.998	1.2	90–108	5	7.5 μg L^{-1}	This work

The relative standard deviation (RSD) obtained for the repetitive determination of 0.2 μg mL^{-1} of Fe was 1.2% (n = 5). The limit of detection (LOD), calculated as three times the standard deviation of the measurement of blanks divided by the slope of the calibration curve, was found to be 7.5 μg L^{-1}. The obtained LOD was comparable with some of sensitive methods based on extraction and preconcentration systems presented in Table 2. In comparison with other reported methods, DLLME has short extraction procedure and time (less than 5 min), low sample consumption (7.0 mL), wider linear dynamic range and lower RSD. These characteristics can be of key interest for routine laboratories in trace metal ion analysis.

3.10. The validation and application of the method

Proposed method was applied to the determination of Fe(II) and Fe(III) in tap water and total Fe in bottled mineral water and parenteral solutions and the results are listed in Tables 3 and 4. In order to validate the applicability of proposed method, aliquots of 5.0 mL of different samples were spiked with known concentrations of Fe(II) or Fe(III) and recovery experiments were conducted as well for these samples. The results summarized in Tables 3 and 4 showed that satisfactory recoveries in the range of 90–108% were achieved for these real samples. Also, these results indicated that no significant matrix effect was observed in the proposed procedure.

Accuracy of the proposed method was further proved by analyzing for Fe in tap water with proposed method and an independent LLE–FAAS method [30] and the results were found to be 93.5 ± 1.22 (n = 3) and 97.2 ± 2.15 (n = 3) μg L^{-1}. A comparison using t-test at 95% confidence interval demonstrates that there is not significant difference among the achieved results using the proposed method and reported method.

Table 3
Analytical results (mean ± s, n = 3) for determination of Fe(II) and Fe(III) in tap water.

Sample	Measured (μg L^{-1})		Added (μg L^{-1})		Found (μg L^{-1})		Recovery (%)	
	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
Tap water	nd[a]	93.5 ± 1.22	–	–	–	–	–	–
			200	0	216 ± 2.72	–	108	–
			400	0	420 ± 5.42	–	105	–
			0	200	–	190 ± 2.45	–	95
			0	400	–	400 ± 4.92	–	100

[a] nd = not detected.

Table 4
Analytical results (mean ± *s*, *n* = 3) for determination of Fe as Fe(II + III) in different samples.

Sample	Measured ($\mu g\,L^{-1}$) Fe(II + III)	Added ($\mu g\,L^{-1}$) Fe(III)	Found ($\mu g\,L^{-1}$) Fe(III)	Recovery (%) Fe(III)
Mineral water 1	30.5 ± 0.38	–	–	–
		200	214 ± 2.71	107
Mineral water 2	28.2 ± 0.34	–	–	–
		200	210 ± 2.65	105
Mineral water 3	nd[a]	200	204 ± 2.42	102
NaCl physiological solution	nd[a]	200	192 ± 2.32	96
Ringer physiological solution	nd[a]	200	180 ± 2.19	90

[a] nd = not detected.

4. Conclusions

An alternative DLLME method has been developed for the rapid extraction of Fe and its speciation determination in different water samples. The proposed DLLME method has lower extraction time, approximately 3 min, since the extraction equilibrium is attained very quickly. Whereas, the extraction times for other extraction and preconcentration systems listed in Table 1, such as LLE, SPE, SPME and cloud point extraction (CPE), may range from 12 to 30 min. The precision, expressed as RSD (1.2%), is lower than these methods. This low RSD is probably because of rapid attainment of equilibrium. As well as, DLLME has a wider linear range and lower solvent consumption. In addition to these advantages, DLLME is rapid, easy to use, inexpensive, and environmentally friendly.

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