ISSN : 0974-7419 Volume 11 Issue 6

Trade Science Inc.

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ, 11(6) 2012 [214-219]

Iron determination with micelle assisted liquid phase microextraction method

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Received: 5th February, 2012 ; Accepted: 5th March, 2012

ABSTRACT

A simple and sensitive method based on direct solvent microextraction was introduced for determination of iron in water samples. In this method iron (II) reacts to 1,10-phenantroline and then extracted into organic solvent following micelle formation with sodium dodecyl sulfonate (SDS). The parameters influencing the extraction process were studied and optimum conditions were obtained as below: solvent type: 1-octanol, sample volume: 12 mL, 1-octanol volume, 100 μL; pH = 7; temperature: 30 ºC; stirring rate of solution: 1000 rpm; ion-pairing concentration 30 mg L^{-1}; time: 30 min; amount of 1,10-phenantroline: 2.5 mg and without addition of salt. The calibration graph was linear for iron in the range of 10-2000 μg L^{-1} and 3-10000 μg L^{-1} for spectrophotometric and high performance liquid chromatography (HPLC) determination, respectively and limit of detection (LOD) based on $3S_{bl}$ was 3 and 1 μg L^{-1} by spectrophotometric and HPLC determination, respectively. This technique is found to be simple, sensitive, reproducible inexpensive, accurate and successfully applied for determination of iron in water samples.

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KEYWORDS

Ion-pairing solvent microextraction;
1,10-phenantroline;
Iron;
HPLC.

INTRODUCTION

Iron is essential for a wide spectrum of biologic functions, including oxygen transport, mitochondrial electron transfer, and DNA synthesis. Iron may also be present in drinking-water as a result of iron coagulants (ferric chloride) used during raw water treatment to remove colloidal or suspended particles or to eliminate organic matter[1]. At the outlet of these units, maximum tolerable level of this cation has been fixed to 200 μg L^{-1} by European Legislation[2]. Nowadays water can be considered the most precious natural asset and attention has been given to assure its quality for human consumption, and also to obtain its mitigation after industrial uses[3] but it is potentially toxic in excess concentrations because of its pro-oxidant activity. The extremely low concentration of dissolved iron in water is one of the important aspects that characterise the quality of drinking and clinical water. Iron is present in nature in form of its oxides, or in combination with silicon or sulfur. The soluble iron content of surface waters rarely exceeds 1 mg L^{-1}, while ground waters often contain

higher concentrations. The safety of drinking water is a very important health issue. The United States and World Health Organization have established well defined standards for drinking water purity. For example, U.S. Federal regulations limit the amount of iron to less than 0.3 mg L^{-1} in municipal drinking water, as iron concentrations in excess of 0.3 mg L^{-1} impart a foul taste and cause staining[4]. High concentrations in surface waters can indicate the presence of industrial effluents or runoff. Thus, it is necessary that an accurate, fast and a cheap method for the determination of iron in water samples should be developed to improve its detection limit and selectivity of determination.

Several methods for the analysis of iron in water samples have been reported, including volumetric analysis[5], flame atomic absorption spectrometry[6] high performance liquid chromatography[7] and spectrophotometry[8,9]. As compared with the other techniques, spectrophotometry not only is very simple, rapid and less expensive for determination of elements in a variety of samples[10] but also, based on complexing reagent is specific for ferrous iron.

Traditional sample preparation is still a challenge for analytical chemists because the steps involved often employ large volumes of hazardous organic solvents, are time consuming and/or expensive. Currently, liquid-phase microextraction (LPME), as a minimized-solvent based pretreatment method and a simple and cost-efficient technique, has been developed. The solvent microextraction technique effectively overcomes these difficulties by reducing the amount of organic solvent and by allowing sample extraction/clean up and preconcentration to be done in a single step[11,12]. Hydrophobic analytes are easily extracted into organic solvents from aqueous sample solutions, but polar and ionic (hydrophilic) analytes have low solubility in water immiscible organic solvents and it is necessary to be hydrophobic for extraction into organic solvents. Ion-pair extraction is a method for partitioning of ionic compounds with the aid of counter ions of opposite charge between water and a water immiscible organic solvent[13-15].

The purpose of this study is to develop a new extraction and preconcentration method for determination of low concentration of iron (II) in water samples based on ion-pairing liquid phase microextraction (IP-LPME) following iron-1,10-phenatroline-chelate formation. This technique is faster, more inexpensive, sensitive, greener, and simpler than conventional methods and uses simple equipment.

EXPERIMENTAL

Reagents and solutions

$FeSO_4.7H_2O$, sodium acetate, 1,10-phenantroline, NaCl, methanol, ethanol, 1-octanol, undecanol, dodecane sodium dodecyl sulfonate sodium salt (SDS), ascorbic acid and hydrochloric acid were obtained from Merck (Darmstadt, Germany). 20% (w/v) of sodium acetate, 20% (w/v) of ascorbic acid and 0.1% (w/v) of SDS were prepared in doubly distilled water and 0.25% (w/v) of 1,10 phenantroline prepared in ethanol. Stock standard solutions (1000 ppm) of Fe (II) were prepared in doubly distilled water. A fresh working sample was prepared by spiking doubly distilled water with Fe (II) at known concentrations daily.

Apparatus

The analytical chromatographic system consisted of an Agilent 1200 series vacuum degasser, an automatic sample injector, a quaternary pump, a variable wavelength detector (VWD), and a C18 with guard column, 5 μm, 150 mm × 4.6 mm i.d. (Waters Corporation, Ireland) and controlled by a computer running Chem Station software (Agilent Technologies). Mobile phases were filtered through a Millipore 0.22-μm membrane filter before use. Analytical chromatography was performed with a flow rate of 1.0 mL min^{-1} at 25 ± 1 °C. The column was stabilized at 25 ± 1°C (room temperature) for 1 h before chromatography. An aliquot (20 μL) of the octanol solution was injected into HPLC system and eluted with the mobile phase consisting of methanol and the detection wavelength was 510 nm. A single wavelength Unicam 5625 UV/VIS spectrometer (USA) equipped with a 1.5 mL semi-micro 10.0 mm path length (Labware Kartel Co., Milan, Italia) was used in all experiments. A pH meter Metrohm carried out with a glass-calomel electrode was employed for setting pH. A 100 μL Hamilton model 1701 syringe (Hamilton, Bonaduz, Switzerland), with a bevel needle tip (length: 5.1 cm, ID: 0.013 cm, bevel 22°) was employed for extraction procedures. A cylindrical sample cell (80 mm × 20 mm i.d.) with a screw cap was used and a heater/magnetic stirrer

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(IKA-Yelloewline) and a PTFE coated stirring bar (15 mm × 3 mm o.d.) were used to stir the solutions and controlled the temperature of the samples.

Procedure

12 mL of the aqueous solution of Fe (II) at known concentration (500 μg L^{-1} except otherwise stated) was transferred into a 15 mL vial and 1 mL of ascorbic acid was added. Known volume of 1, 10-phenanthroline (1 mL, except otherwise stated) was added into sample solution at appropriate pH (pH = 7, except otherwise stated) at desired temperature (t = 30 ºC, except otherwise stated), then 0.3 mL of SDS was added to ample solution (except otherwise stated). The stirrer was turned on (rpm = 600, except otherwise stated) and a few microliter volume of extracting solvent (100 μL, except otherwise stated) placed on the surface of solution using a microliter syringe and the cap of the vial was sealed and. After a prescribed extraction time (25 min, except otherwise stated) extracting solvent was transferred into the conical vial. For spectrophotometric determination, methanol was added into vial to final volume of 500 μL (except otherwise stated) and absorption read at 510 nm and for HPLC determination 20 μL of the octanol was injected to instrument (Figure 1).

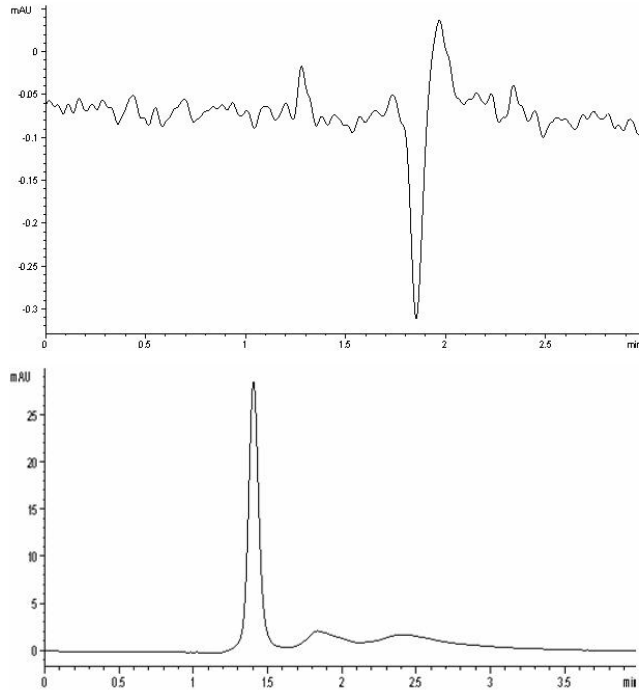

Figure 1 : $Fe(phe)_3^{2+}[CH_3(CH_2)_{11}SO_4^-]_n$-LPME-HPLC chromatograms of aqueous sample: Blank (lower), and spiked sample at 500 μg L^{-1}(higher).

RESULTS AND DISCUSSION

Iron (II) and 1,10-phenanthroline form a complex where three phenanthroline molecules surround the iron(II) ion forming a orange-colored complex. To form a complex, the iron must be first reduced to its ferrous state. This is done by reacting the iron with hydroxylamine hydrochloride or ascorbic acid, Fe^{2+} so that it can bind to the phenanthroline. Since the iron present in the water predominantly exists as Fe^{3+}, it is necessary to first reduce Fe^{3+} to Fe^{2+}. This is accomplished by the addition of the reducing agent (ascorbic acid). The sodium acetate buffer acts to maintain the pH. SDS react to iron-1,10-phenatroline-chelate to form neutral this complex (as below), otherwise iron can't extract to organic solvent:

$$Fe(phe)_3^{2+} + nCH_3(CH_2)_{11}SO_4^- \leftrightarrow Fe(phe)_3^{2+}[CH_3(CH_2)_{11}SO_4^-]_n \quad (1)$$

$$(Fe(phe)_3^{2+}[CH_3(CH_2)_{11}SO_4^-]_n)_{aq} \leftrightarrow (Fe(phe)_3^{2+}[CH_3(CH_2)_{11}SO_4^-]_n)_{org} \quad (2)$$

Selection of organic solvent

The selection of an appropriate extraction solvent is of great importance for the optimization of the LPME process. The extraction solvent must to have some properties: low volatility and low water solubility, to extract analytes well. Because of positive charge of iron-1,10-phenatroline chelate, the primary experiment show that immiscible polar solvent and non polar solvent can not extract $Fe(phe)_3^{2+}$. Thus sodium dodecyl sulfonate (SDS) as an ion pairing agent and micelle medium was added to neutralize $Fe(phe)_3^{2+}$. Based on these considerations, three organic solvents were investigated at similar condition: 1-octanol, 1-undecanol and n-dodecane. The results show than dodecane can not extract complex and 1-octanol has more extracting efficiency than 1-undecanol (1-undecanol extraction efficiency is about 65% of 1-octanol). 1-octanol was found to provide higher extraction efficiency. This may be attributed to greater polarity of 1-octanol than the others, which leads to the higher solubility of the ion-pair complex and hence higher extraction efficiency. Thus 1-octanol was selected as extracting solvent.

Effect of pH effect and ionic strength

The effect of pH was investigated in the range of 2-

8. Fe^{2+} is quantitatively complexed by 1,10-phenanthroline in the pH range from 3 to 8. For pH>8, the Fe^{2+} was oxidized to Fe^{3+} and precipitate; and for pH<5, H^+ was competed with Fe^{2+} for the basic 1,10-phenanthroline. Either way, you won't get complete complexation. Also pH affects ion pair formation between 1, 10-phenanthroline-iron chelate and SDS. As you can see, extraction efficiency increases up to pH = 7.0 and then slightly decreases (Figure 2).

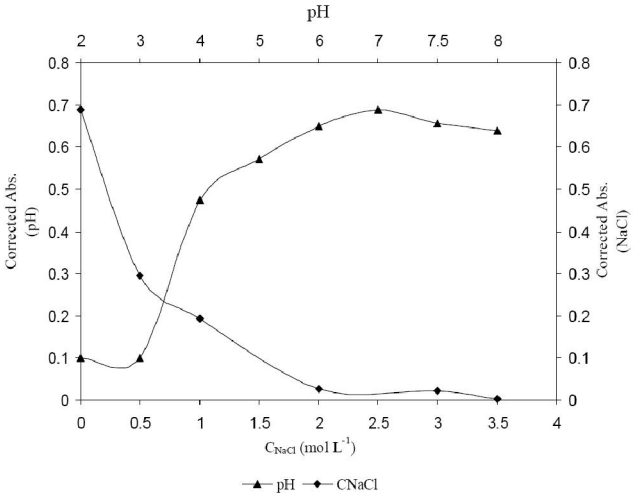

Figure 2 : Effect of pH of sample solution and the amount of NaCl on extraction efficiency of iron. Conditions: Sample volume: 12 mL (0.5 mg L^{-1}), the amount of 1,10-phenantroline:1.0 mL (0.25% w/v), concentration of SDS: 1.0 mL (0.1% w/v); stirring rate: 600 rpm; solution temperature: 30°C; pH = 7 (for effect of NaCl); solvent volume: 100 µL; extraction time: 25 min; without addition of NaCl (for effect of pH).

Ionic strength can affect complex formation between iron and 1,10 phenantroline and complex with ion-pairing agent. Thus extraction of iron to organic solvent depends on ionic strength of solution. For this purpose NaCl was added to sample solution in the range of 0-3.5 mol $L^{-1}$and iron was extracted to 1-octanol according to general procedure. The result show the recovery of extraction decreased as sodium chloride concentration increased (Figure 2). It can attribute to decrease ion pair formation with increasing ionic strength.

Organic solvent volume and amount of ion-pairing agent

The influence of extracting solvent was investigated in the range of 20-300 µL. It was found that the absorbance decreases with drop volume in the range of 20-300 µL (Figure 3). However, fraction of total analyte transferred to the organic phase or extraction efficiency increased with increasing volume of 1-octanol (Figure 3), and because for spectrophotometric determination, methanol was added into vial to final volume of 500 µL, we selected 100 µL of 1-octanol for further experiments. Ion-pair reagent concentration plays an important role in ion-pair extraction because it affects the distribution of counter ions, therefore influencing the extraction efficiency. Different concentrations (0–83 mg L^{-1}) of SDS as counter ion in the solution under the optimum condition described above were investigated. The results show that by increasing the concentration of SDS the absorbance increases up to 33 mg L^{-1} and after that approximately level off (Figure 3). It is to be noted that absorbance increase linearly respect to SDS concentration up to 33 mg L^{-1} and we can also determine SDS concentration in aqueous samples at optimum conditions.

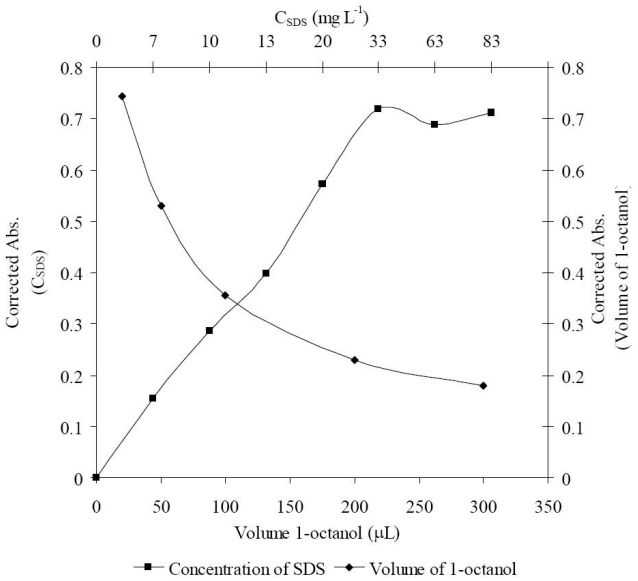

Figure 3 : Effect of organic solvent volume and amount of ion-pairing agent Conditions: Sample volume: 12 mL (0.5 mg L^{-1}), the amount of 1,10-phenantroline:1.0 mL (0.25% w/v), concentration of SDS: 1.0 mL (0.1% w/v) (for effect of 1-octanol volume); stirring rate: 600 rpm; solution temperature:30°C; pH = 7; solvent volume: 100 µL (for effect of SDS); extraction time: 25 min; without addition of NaCl.

Effect of stirring rate and sample solution temperature

Agitation of solution was used to facilitate the mass transfer process and thus improving the extraction efficiency. The stirring rate was optimized for extraction process. Figure 4 illustrates the effects of stirring rate

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on the enrichment factor that increased with increasing of the stirring rate up to 1000 rpm.

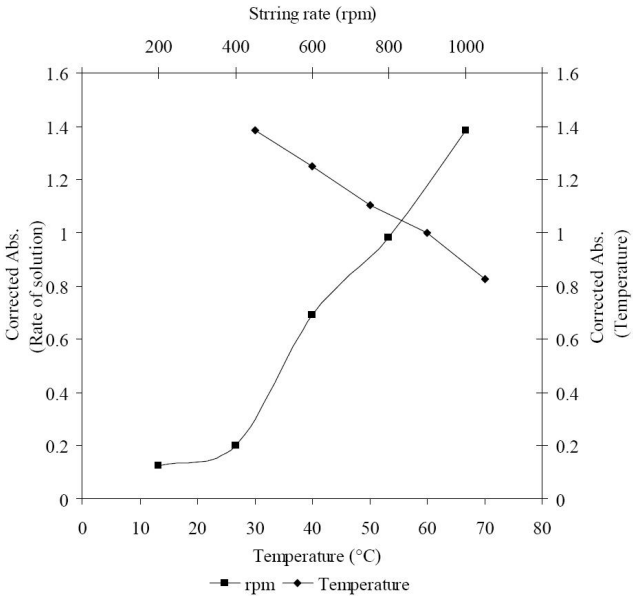

Figure 4 : Effect of stirring rate and sample solution temperature. Conditions: Sample volume: 12 mL (0.5 mg L^{-1}), the amount of 1,10-phenantroline:1.0 mL (0.25% w/v), concentration of SDS: 0.4 mL (0.1% w/v); stirring rate: 600 rpm (for effect of temperature); solution temperature: 30°C (for effect of stirring rate); pH = 7 ; solvent volume: 100 µL; extraction time: 25 min; without addition of NaCl.

Heating of the sample solution may affect ion-pair formation and the mass transfer of the analytes from the sample into the solvent. But, ion- pair formation is the rate determining step and with increasing temperature ion-pair formation decreased and the efficiency of the extraction decreased, or increasing the temperature will improve the dynamics, so the ion-pair formation rate will accelerate. On the other hand, the solubility of organic solvent in the sample solution will also increase (Figure 4).

Effect of ligand volume and extraction time

Three molecules of 1, 10-phenanthroline, chelate each atom of ferrous iron to form an orange-red complex. Thus it is to need investigate amount of 1, 10-phenanthroline for extraction efficiency. According to Loshatle–law it is necessary to use excess reagent in a equilibrium reaction. Figure 5 shows the absorbance of iron versus amount of 1, 10-phenanthroline. As you can see, the $Fe(phe)_3^{2+}$ absorbance increases with increasing 1, 10-phenanthroline up to 1000 µL (0.25 w/v) and then it was level of (maximum absorbance was obtained approximately in mole ratio of 100:1 1, for 10-phenanthroline to iron).

Extraction time is one of the most important factors in most of extraction procedures. The dependence of extraction efficiency upon extraction time was studied within a range of 0–50 min in the constant experimental conditions. Figure 5 shows the absorbance of iron versus extraction time. The results showed an increase of the $Fe(phe)_3^{2+}$ absorbance up to 25 min and leveling off at higher extraction time. Therefore 30 min was used as the optimum extraction time.

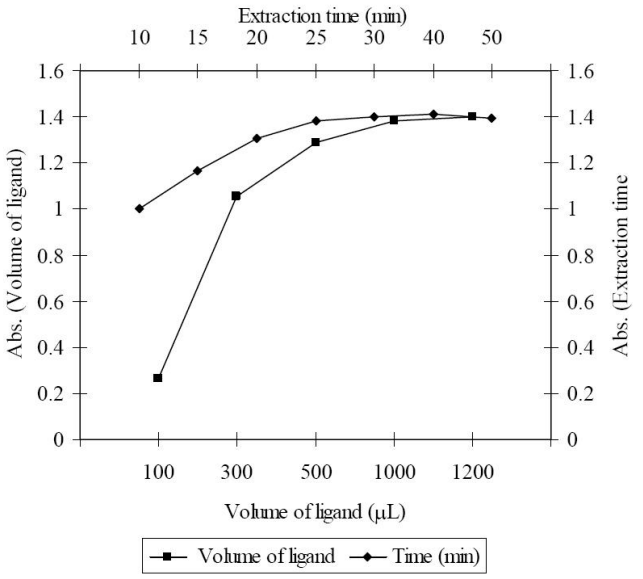

Figure 5 : Effect of extraction time and ligand volume. Conditions: Sample volume: 12 mL (0.5 mg L^{-1}), the amount of 1,10-phenantroline:1.0 mL (0.25% w/v) (for effect of extraction time); concentration of SDS: 0.4 mL (0.1% w/v); stirring rate: 600 rpm solution temperature: 30°C; pH = 7; solvent volume: 100 µL; extraction time: 25 min (for effect of ligand volume); without addition of NaCl.

Effect of interferences

The effect of various ions on the determination of iron was investigated. A given species was considered to interfere if it resulted in a ± 20% variation of the signal. The results obtained are presented in TABLE 1. As can be seen the effect of various ions are negligible and iron can be determined quantitatively in real samples without interference from matrix of the samples.

Analytical figure of merits and real sample analysis

Analytical characteristics of the optimized method for iron, including linear range (5 point) coefficient of

regression (r^2), limit of detection, repeatability and enhancement factor are 10-2000 μg L^{-1}, 0.9946, 3 μg L^{-1}, 7% and 60 for spectrophotometric detection and 3-10000 μg L^{-1}, 0.9996, 3 μg L^{-1}, 4% and 240 for HPLC detection, respectively. The detection limit was calculated as three times the standard deviation of the absorbance for five extractions of the blank, using the liquid phase microextraction procedure. The enhancement factor (EF) was obtained from the slope ratio of calibration graph after and before extraction (TABLE 2). Finally method used for determination of iron in water samples successfully (TABLE 3).

TABLE 1 : Effect of foreign ions on determination of iron at optimum conditions.

Foreign ions	Maximum tolerance ratio	% Recovery
Li^+	100	100 (± 3)
Na^+	100	100 (± 2)
K^+	100	100 (± 4)
Ba^{2+}	100	101 (± 6)
Ca^{2+}	100	95 (± 3)
Mg^{2+}	100	97 (± 6)
Sr^{2+}	100	99 (± 4)
Co^{2+}	100	100 (± 3)
Cr^{6+}	10	96 (± 5)
Cu^{2+}	4	95 (± 3)
Be^{2+}	100	100 (± 4)
Fe^{3+}	100	93 (± 2)
Mo^{6+}	100	100 (± 5)
Cd^{2+}	100	100 (± 3)
Mn^{6+}	10	97 (± 4)

TABLE 2 : Figure of merits for determination of iron with ion-pairing liquid phase microextraction at optimum condition.

Instrument	Equation	DLR[a] (μg L-1)	R^2	LOD (μg L^{-1})	Enhancement factor
Uv-Vis	Abs.= 0.4492C + 0.0059	10-2000	0.9946	3	100
HPLC	Area = 1642.9C + 138.7	3-10000	0.9996	1	220

[a]**DLR: Dynamic linear range.**

TABLE 3 : Determination of iron in various water samples at optimum conditions.

Sample type	Amount of Fe (μg L^{-1})		
	Amount added	Amount found	Extraction (±%RSD)[b]
Tap water (Tehran)	-	101	-
Tap water (Tehran)	100	198	97 (± 4)
Tap water (Tehran)	500	605	101(± 3)

CONCLUSION

This method is rapid, precise, sensitive, no expensive, environmental friendly and uses simple equipment which is found in most analytical laboratories for determination of Fe^{2+} in water samples. After the $Fe(phe)_3^{2+}$ was made hydrophobic and neutral by adding sodium lauryl sulfate, can extract to octanol. The SDS reagent provided excellent extraction efficiency for $Fe(phe)_3^{2+}$ through LPME. This method also is a rigorous quantitative speciation of ferrous and ferric in water and wastewater.

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