



Mixed Micellar Cloud Point Extraction and Spectrophotometric Determination of Iron(II) Using 1,10-Phenanthroline: Effect of Sodium Nitroprusside on Extraction Efficiency

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A new cloud point extraction (CPE) procedure with spectrophotometry for the pre-concentration and determination of iron(II) has been developed. In this method, Fe^{2+} was complexed with 1,10-phenanthroline at a pH of 4.2. Fe^{2+} -1,10-phenanthroline complex was then extracted into mixed micelles of Triton X-114 (TX-114) and docusate sodium salt (DOSS). Various parameters such as pH, concentration of 1,10-phenanthroline, concentrations of the surfactants (TX-114 and DOSS), concentration of salt (Na_2SO_4), equilibration temperature and equilibration time were optimized. Under optimum conditions the linear range of Fe^{2+} was found to be $0.14\text{--}2.23 \mu\text{g mL}^{-1}$. The corresponding detection limit was found to be 5.1 ng mL^{-1} . The proposed method has been successfully applied to the determination of Fe^{2+} in tap water and sea water samples. The recoveries were found to be in the range of 80-95 % and the effect of sodium nitroprusside on the recovery was studied.

Keywords: Cloud point extraction, Spectrophotometry, 1,10-Phenanthroline, Mixed micelles, Sodium nitroprusside.

INTRODUCTION

In biological systems iron is the most important metal as it is the main constituent element in haemoglobin, myoglobin and some enzyme co-factors [1]. The deficiency of iron may lead to the anaemia [2]; whereas, the high levels of iron may cause sickle celled disease and thalassemia, which is an abnormal form of haemoglobin [3,4]. Hence, it is essential to monitor the accurate levels of iron in natural waters, due to its importance in biological systems.

Direct determination of iron in natural waters with the aid of sophisticated instruments is a complicated process, due to its low concentrations and the considerable unwanted high matrix effects. Hence, minimizing the matrix effects is a prerequisite task for their determination. In this context, to minimize the matrix effects, some preconcentration techniques have been adopted, such as dispersive liquid-liquid micro extraction, solid phase extraction, co-precipitation and cloud point extraction (CPE), etc. Amongst these preconcentration schemes, CPE is an environmental friendly technique, as it is in good agreement with the green chemistry principles and requires only less toxic surfactants as extracting agents. In the cloud point extraction

techniques, clouding behaviour of surfactants plays a crucial role. The surfactants used are mostly of non-ionic type like Triton X-114, Triton X-100 and PONPE 7.5 [5,6]. One of the fundamental limitations of CPE when implemented with the non-ionic surfactants (e.g., TX-114) is of its lower extraction efficiencies of hydrophilic inorganic species and polar organic compounds. In order to circumvent these limitations, an ionic surfactant can be added to the non-ionic surfactants, which forms a mixed micellar system [7,8]. As a result, a substantial increase in the extraction efficiency of polar compounds may be noticed. These mixed surfactants have both hydrophobic and electrostatic interactions and that facilitates the extraction of compounds with different charges and the cloud point of the mixed micellar system has been decreased by salting out effect [9,10].

Previously, CPE has been successfully applied to the extraction of inorganic analytes, where the metals form complexes with ligands such as APDC (ammonium pyrrolidinedithiocarbamate) [11,12], 5-Br-PADAP (2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol) [13], ECR (eriochrome cyanine R) [3], TAN (1-(2-thiazolylazo)-2-naphthol) [14,15], PHBI (2-phenyl-1H-benzo[d]imidazole) [16] and NR (neutral red) [4]. In the

present work 1,10-phenanthroline has been used for the extraction of Fe^{2+} . The analyte Fe^{2+} gave intense coloured complex with 1,10-phenanthroline at 505 nm in visible region.

In the previous works, sophisticated instruments like flame atomic absorption spectrometry (FAAS) [1,3,11,12] and capillary electrophoresis have been reported for the determination of Fe^{2+} in different samples followed by cloud point extraction.

The present work reports the spectrophotometric determination of Fe^{2+} , while it forms complexation with 1,10-phenanthroline (O-phen) ligand, wherein preconcentration has been performed into the mixed micelles of TX-114 and docusate sodium salt (DOSS). The co-extractant sodium nitroprusside (SNP) affects the recovery of analyte into the mixed micelles. As per the best of our knowledge, there are no previous reports available on the preconcentration of Fe^{2+} with 1,10-phenanthroline into the mixed micelles of TX-114 and DOSS and effect of sodium nitroprusside on the extraction of Fe^{2+} . The factors affecting the mixed micellar cloud point extraction were optimized, further subsequently the optimized system has been used to the determination of Fe^{2+} in different water samples.

EXPERIMENTAL

All reagents used were of analytical grade. The non-ionic surfactant Triton X-114 (polyethylene glycol *tert*-octylphenyl ether) was obtained from Sigma-Aldrich (USA) and anionic surfactant DOSS (docusate sodium salt) was obtained from Fluka (USA). The stock solution of 10 % w/v Triton X-114 was prepared in doubly distilled water and stock solution of 10 % w/v DOSS was prepared in methanol. Stock standard solution of Fe^{2+} was prepared by dissolving appropriate amount of ammonium ferrous sulphate. Working standard solutions were prepared by diluting stock standard solutions with doubly distilled water. The chelating agent 1,10-phenanthroline (O-phen) obtained from Qualigens, India. 1,10-phenanthroline solution was prepared by dissolving appropriate amount of the compound in water in which 0.1 mol L^{-1} HCl was maintained. The stock solutions of 30 % w/v Na_2SO_4 (Merck, India) and 1 % w/v sodium nitroprusside (SNP, Merck, India) were prepared in doubly distilled water.

All absorbance values and spectra were measured with a double beam UV-visible spectrophotometer (UV-1800, Shimadzu, Japan). All pH measurements were carried out with Systronics digital pH meter 335. A Remi R-24 was used for centrifugation of samples.

Cloud point extraction procedure: In a 15 mL vial, acetate buffer at pH 4.2 and standards of the corresponding concentrations of Fe^{2+} from 0.14 to 2.23 $\mu\text{g mL}^{-1}$ was added. To that 0.8 mL of 2.5×10^{-2} mol L^{-1} 1,10-phenanthroline, 0.7 mL of 10 % w/v DOSS, 1.6 mL of 10 % w/v TX-114, 1.0 mL of 30 % w/v Na_2SO_4 and 0.8 mL of 1 % w/v sodium nitroprusside were added and made up to 10 mL with double distilled water and heated at 60 °C for 25 min, which resulted into two phases. Subsequently, complete phase separation is obtained through the centrifugation and cooling the system for 10 min in an ice bath, then the supernatant aqueous phase was decanted. The surfactant rich phase was dissolved in 20 % methanol to decrease the viscosity and the homogenized surfactant rich phase was analyzed by using UV-1800 Spectrophotometer at 505 nm.

RESULTS AND DISCUSSION

The ligand, 1,10-phenanthroline forms coloured complex with the analyte Fe^{2+} at a pH of 4.2. This complex was extracted into mixed micelles of TX-114 and DOSS in the presence of sodium sulphate. For obtaining maximum extraction efficiency, the parameters affecting the cloud point extraction were optimized. The optimum conditions are discussed below.

Optimization of pH: Formation of the complex between analytes and ligand as well as extraction of complex into surfactant rich phase depends on the pH. For optimization, buffers in the pH range from 2 to 8 were used. To maintain pH in the range from 2 to 8, KCl/HCl, $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ and $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ buffers were used. The better recoveries were observed for acetate buffer ($\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$) at a pH of 4.2 (Fig. 1). Therefore, pH 4.2 was chosen for the determination of Fe^{2+} concentration in subsequent experiments.

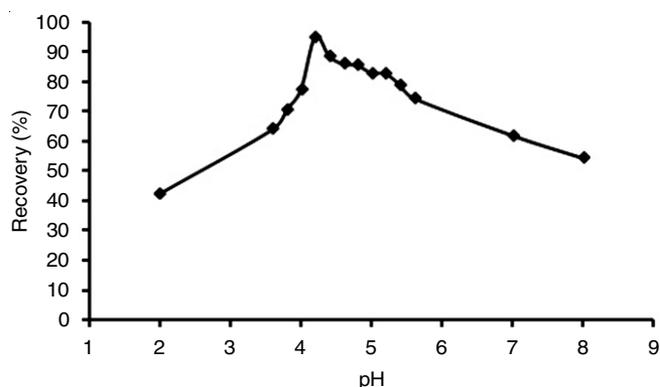


Fig. 1. Optimization of pH on the recovery of Fe^{2+} (Experimental conditions: 2.0×10^{-3} mol L^{-1} of 1,10-phenanthroline; 1.6 % w/v of TX-114; 0.7 % w/v of DOSS; 3.0 % w/v of Na_2SO_4 ; 0.08 % w/v of sodium nitroprusside; Equilibration temperature 60 °C; Equilibration time 25 min)

Optimization of concentration of 1,10-phenanthroline:

The chelating agent 1,10-phenanthroline was chosen for complex formation with analyte Fe^{2+} . The recoveries of the analyte was studied in the concentration range from 0.5×10^{-3} mol L^{-1} to 5×10^{-3} mol L^{-1} . As the concentration of 1,10-phenanthroline increases, the recoveries also increase up to 2.0×10^{-3} mol L^{-1} and then decreases (Fig. 2). Therefore, 2.0×10^{-3} mol L^{-1} of 1,10-phenanthroline has been chosen for the subsequent experiments.

Optimization of concentration of TX-114: The non-ionic surfactant TX-114 was chosen because of its low cloud point temperature, commercial availability and significantly low cost. The recovery of Fe^{2+} was studied in the concentration range of TX-114 from 0.2 to 3 % w/v. At lower concentrations, the extraction efficiency was low, as the formations of micelles were low and they were insufficient to trap the complex of analyte. The recovery of Fe^{2+} increase up to 1.6 % w/v of TX-114 and then decreases (Fig. 3). Thus, the optimum concentration of TX-114 chosen for the subsequent experiments was found to be 1.6 % w/v.

Optimization of concentration of DOSS: The positively charged analyte Fe^{2+} react with the chelating agent 1,10-phenanthroline and form positive complex. Therefore, for complete extraction of this analyte, it should be neutralized first with

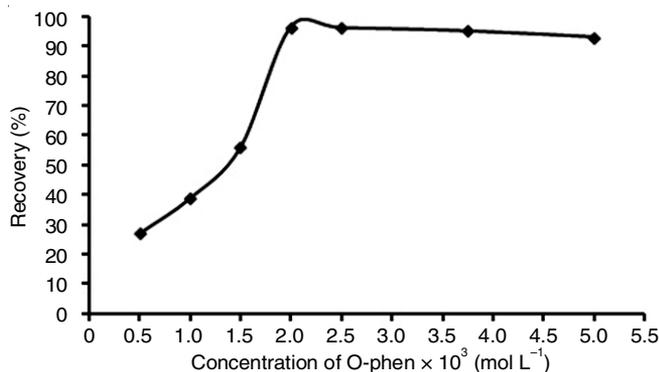


Fig. 2. Optimization of concentration of 1,10-phenanthroline on the recovery of Fe^{2+} (Experimental conditions: pH 4.2; 1.6 % w/v of TX-114; 0.7 % w/v of DOSS; 3.0 % w/v of Na_2SO_4 ; 0.08 % w/v of sodium nitroprusside; Equilibration temperature 60 °C; Equilibration time 25 min)

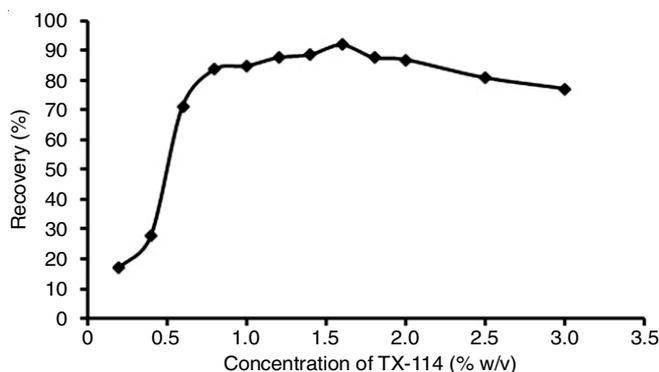


Fig. 3. Optimization of TX-114 concentration on the recovery of Fe^{2+} (Experimental conditions: pH 4.2; $2.0 \times 10^{-3} \text{ mol L}^{-1}$ of 1,10-phenanthroline; 0.7 % w/v of DOSS; 3.0 % w/v of Na_2SO_4 ; 0.08 % w/v of sodium nitroprusside; Equilibration temperature 60 °C; Equilibration time 25 min)

the negative species. Hence, an anionic surfactant DOSS was used along with TX-114. The neutral complex has been extracted into the surfactant rich phase. The concentration of DOSS was optimized in the range from 0 to 2.5 % w/v. As the concentration increases the recovery also increases up to 0.7 % w/v of DOSS and then decreases (Fig. 4). Thus, the optimum concentration of DOSS chosen for the subsequent experiments was found to be 0.7 % w/v.

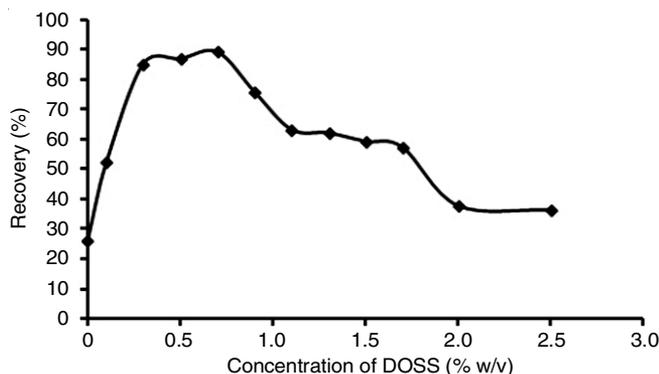


Fig. 4. Optimization of concentration of DOSS on the recovery of Fe^{2+} (Experimental conditions: pH 4.2; $2.0 \times 10^{-3} \text{ mol L}^{-1}$ of 1,10-phenanthroline; 1.6 % w/v of TX-114; 3.0 % w/v of Na_2SO_4 ; 0.08 % w/v of sodium nitroprusside; Equilibration temperature 60 °C; Equilibration time 25 min)

Optimization of concentration of Na_2SO_4 : The surfactants mixture (TX-114 and DOSS), that was used for the extraction of analyte has a cloud point temperature around 90-100 °C. To accelerate and to reduce the phase separation of mixed surfactants, a salting out agent was used. The recovery of analyte increased as a function Na_2SO_4 concentration until 3.0 % w/v and then the recoveries were almost stable. Thus, the optimum concentration of Na_2SO_4 was found to be 3.0 % w/v as shown in Fig. 5.

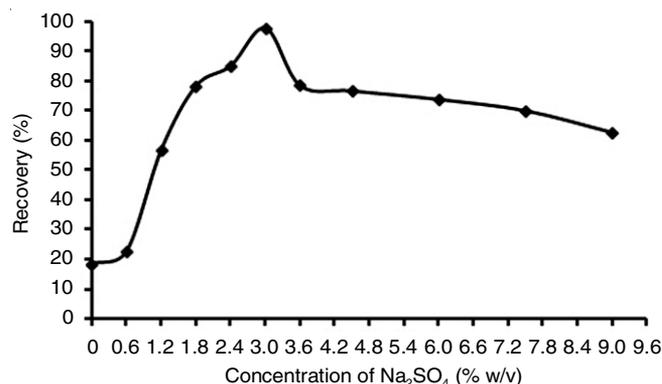


Fig. 5. Optimization of concentration of Na_2SO_4 on the recovery of Fe^{2+} (Experimental conditions: pH 4.2; $2.0 \times 10^{-3} \text{ mol L}^{-1}$ of 1,10-phenanthroline; 1.6 % w/v of TX-114; 0.7 % w/v of DOSS; 0.08 % w/v of sodium nitroprusside; Equilibration temperature 60 °C; Equilibration time 25 min)

Optimization of equilibration temperature and time: Equilibrium temperature and time are important for the formation of micelles, phase separation and complete extraction of analytes. To achieve good quantitative extraction, equilibrium temperature and time were studied in the range from 25-100 °C and 5-60 min, respectively. In this study below 40 °C temperature the recoveries were low and increased up to 60 °C and then decreased. In the study of time, the recoveries were increased up to 25 min and then decreases. Hence, the optimum equilibration temperature and time were found to be 60 °C and 25 min.

Effect of the concentration of sodium nitroprusside: The effect of the concentration of sodium nitroprusside (SNP) on the recovery of the analyte Fe^{2+} was studied from 0 to 0.30 % w/v. Without addition of sodium nitroprusside the recovery of the analyte was 70 % and then the recoveries were increased up to 96.5 % at 0.08 % w/v concentration of sodium nitroprusside and then decreases as shown in Fig. 6. Hence, 0.08 % w/v was chosen as the optimum concentration for further studies.

Analytical characteristics of the method: The analytical characteristics of the proposed method were evaluated under the optimized conditions. Calibration graph was drawn for Fe^{2+} under the optimum conditions, from which the observed linearity range for Fe^{2+} was 0.14-2.23 $\mu\text{g mL}^{-1}$. The calibration equation obtained was $A = 0.407168 [\text{Fe}^{2+}] + 0.064556$ with a correlation coefficient of 0.9914. The limits of detection for Fe^{2+} was 5.1 ng mL^{-1} . Comparison of the present method with other methods reported for the cloud point extraction of Fe^{2+} has been given in Table-1.

Applications: The proposed mixed micellar cloud point extraction method was successfully applied for the determi-

TABLE-1
COMPARISON OF THE PRESENT METHOD WITH OTHER METHODS FOR THE DETERMINATION OF Fe²⁺ AFTER CPE

Analytes	Ligand	Surfactants	LOD	Technique	Sample	Ref.
Fe, Cu	ECR	TX-114	0.33 and 0.57 ng mL ⁻¹ for Fe and Cu	FAAS	Food and water	[3]
Fe, Cu	Neutral red	TX-114	0.7 and 0.3 ng mL ⁻¹ for Fe and Cu	FIA-FAAS	Spice	[4]
Fe, Zn	TAN	TX-114	6.45 and 1.51 µg L ⁻¹ for Fe and Zn.	FAAS	Serum and urine	[14]
Fe	APDC	TX-100 and TX-45	0.02 mg L ⁻¹	FAAS	Wine	[11]
Fe	Ferron	TX-114	1.7 µg L ⁻¹	FI-FAAS	Water and milk	[17]
Fe	1,10-phenanthroline	TX-114 and DOSS	5.1 ng mL ⁻¹	Spectrophotometry	Tap and sea water	Present work

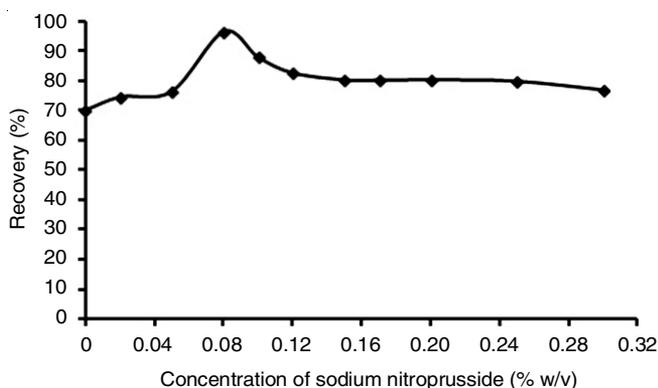


Fig. 6. Optimization of concentration of sodium nitroprusside on the recovery of Fe²⁺ (Experimental conditions: pH 4.2; 2.0 × 10⁻³ mol L⁻¹ of 1,10-phenanthroline; 1.6 % w/v of TX-114; 0.7 % w/v of DOSS; 3.0 % w/v of Na₂SO₄; Equilibration temperature 60 °C; Equilibration time 25 min)

nation of Fe²⁺ in tap and sea water samples. The spike recoveries were found to be in the range from 80-95 %. The results are given in Table-2.

TABLE-2
DETERMINATION OF Fe²⁺ IN REAL SAMPLES AND THEIR SPIKE RECOVERIES IN THE PRESENT DEVELOPED METHOD

Samples	Spiked (µg mL ⁻¹)	Detected (µg mL ⁻¹)	Recovery (%)
Tap water	–	Not detected	–
	0.558	0.448 ± 0.011	80.35 ± 1.97
	1.116	0.895 ± 0.013	80.28 ± 1.17
Sea water	–	Not detected	–
	0.558	0.529 ± 0.012	94.92 ± 2.08
	1.116	0.904 ± 0.022	81.00 ± 1.96

Conclusion

The mixed micellar cloud point extraction method for the preconcentration of Fe²⁺ and its determination with spectrophotometry in different water samples using mixed micelles of TX-114 and DOSS and 1,10-phenanthroline as a complexing agent was successfully employed. The proposed cloud point extraction method is sensitive, selective, low cost and accurate, which allows the determination of Fe²⁺ at ng mL⁻¹ level using spectrophotometry.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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