



## An Eco-Friendly Cloud Point Extraction for Preconcentration of Iron(III) in Water Samples prior to Spectrophotometric Determination

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### Abstract

A simple, low cost, fast and environmentally safe cloud point extraction procedure (CPE) for separation and preconcentration of iron (Fe(III)) in different environmental water samples prior to its spectrophotometric determination has been developed. The CPE method is based on the reaction of iron(III) with N,N'-bis(salicylidene)ethylenediamine (Salen) as a reagent yielding a complex at pH 4.0, respectively which extracted in a mixed micelle system consists of Triton X-114 (non-ionic surfactant) and cethyltrimethyl ammonium bromide (CTAB) at  $\lambda_{\max}$  612 nm. The main parameters affecting the CPE efficiency, such as the pH of the solution, Salen concentration, surfactant concentration, incubation time and temperature were investigated and optimized. Under the optimum conditions, the calibration curve was linear in the range of 5.0-400  $\mu\text{g L}^{-1}$  with  $R^2 \leq 0.9996$ . The detection limit was 1.5  $\mu\text{g L}^{-1}$  with preconcentration factor was 50. The intra-day and inter-day precision (as the relative standard deviation, RSD%) was 1.75 and 2.0%, respectively. The interference of various cations and anions has been studied. The proposed CPE procedure was successfully applied for the determination of trace amount of Fe(III) in various water samples with high efficiency and satisfactory results.

Keywords: Cloud point extraction; Spectrophotometry; Iron; Mixed micelle system; Water samples.

### 1. Introduction

Iron (Fe(III)) is the most important transition element involved in living systems, being vital to both plants and animals. It plays an important role in environmental and biological systems. Its versatility is unique. It is at the active center of molecules responsible for oxygen transport and electron transport and is found in such diverse metalloenzyme as nitrogenase, various oxidases, hydrogenases, reductases, dehydrogenases, deoxygenases and dehydrases. Iron involved in an enormous range of function and the whole gamut of life forms, from bacteria to man. Its deficiency leads to anemia and other diseases [1]. Iron has two readily inter converted oxidation states (Fe(II) and Fe(III)) [2]. The excess concentration of Fe is potentially toxic to human due to its pro-oxidant activity. The detection of Fe in aquatic system is very important for environmental and biological studies because of the influence of the chemical forms on the bioavailability of Fe and

physicochemical and toxicological properties of other trace elements and organic substrates [3].

Determination of trace metal ions in water, food and environmental samples is interesting and important for analytical chemistry [4]. The most widely methods used for determination of Fe(III) are atomic spectrometry techniques—mainly flame atomic absorption spectrometry (FAAS) [5], electrothermal atomic absorption spectrometry (ETAAS) [6], inductively coupled plasma spectrometry (ICP-AES) [7] are extensively employed, but their sensitivity and selectivity is usually insufficient for direct determination of iron at a very low concentration level in complex matrix environmental samples. Therefore, a sample separation/preconcentration techniques prior to analysis are usually necessary. Several studies for spectrophotometric determination of Fe in different oxidation states in water, food and environmental samples has been reported [8-25]. The sensitivity expressed as molar absorptivity of the proposed method is compared in Table 1 with those of published spectrophotometric methods.

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Table 1: Comparison of selected reagents for the spectrophotometric determination of iron.

Reagent	LOD ng mL <sup>-1</sup>	$\lambda_{\max}$ (nm)	$\epsilon/10^4$ L mol <sup>-1</sup> cm <sup>-1</sup>	Linear range (ng mL <sup>-1</sup> )	Ref.
Chlortetracycline	100	435	-	500-20000	[8]
Methylthymol blue - cetyltrimethylammonium (CTAB) and Triton X-100 bromide	60	514		250-2500	[9]
Di-2-pyridyl ketone salicyloylhydrazone	0.09 $\mu$ M	375	4.21	-	[10]
Ferrozine-Tetrabutylammonium bromide	34	562	2.8	up to 1000	[11]
Sodium oxalate-KI	40	352	-	100-5000	[12]
1-nitroso-2-naphthol- Triton-X100	60	420	2.57	50-6000	[13]
Squaric Acid	300	515	0.395	10-10000	[14]
Morin	0.5	415	6.85	650-6450	[15]
Gallic acid- CTAB	70	565	-	200-15000	[16]
1, 10-phenanthroline/neocuproine	-	510	-	100- 8000	[17]
2-(2,3-dihydroxy-4-oxocyclobut-2- enylidene) hydrozinecarbothiamide	80	465	1.95 x 10 <sup>3</sup>	0.27-33.50	[18]
Ferron- Dodecyltrimethylammonium bromide	3.5	510	0.38	50-2600	[19]
Diphenylamine-4-sulfonic acid sodium salt	1.5	410	-	5.0- 200	[20]
Thiocyanate and cetyltrimethyl ammonium bromide	-	474	3.2	0.0-6.0	[21]
N-ethyl-2-methyl-3-hydroxypyridin- 4-on	2.5 x 10 <sup>-6</sup> M	456		2.5 x 10 <sup>-6</sup> - 1.0 x 10 <sup>-4</sup> mol L <sup>-1</sup>	[22]
Azid - tetrahydrofuran		396	1.53	670-2800	[23]
1-(5-Bromo-2-pyridylazo)-2-naphthol-6- sulphoric acid -SPS	2.1	765	47.7	0-25000	[24]
2,3-dichloro-6-(3-carboxy-2-hydroxy-1- naphthylazo) quinoxaline	300	743	286	1000- 20000	[25]

Cloud point extraction (CPE) is a promising separation and extraction technique which is based on the use of surfactants, as an alternative to organic solvents. Cloud point is the temperature above which an aqueous solution of a water-soluble surfactant becomes turbid. When heating a surfactant solution over the critical temperature, the solution is easily separated into two distinct phases: a surfactant-rich phase (SRP) of small volume and a diluted aqueous phase (AQ), in which the surfactant concentration is close to the critical micellar concentration. The hydrophobic compounds, initially present in the solution and bound to the micelles, are extracted to the SRP.

Among the separation techniques used for the preconcentration step, CPE has attracted considerable attention in the last decade, mainly because it complies with the "green chemistry" principles [26-28]. The

CPE method is solvent-free and non-polluting. Now, it has been applied to the separation of environmental and biological samples with a complicated matrix.. To date, several methods for the determination of iron based on CPE procedures have been described [29-53] (Table 2).

The present work aims to develop novel, sensitive, simple, economical, green and valide CPE procedure combined with spectrophotometry for preconcentration and determination of trace amount of Fe(III) in various water samples. N,N'-bis(salicylidene)ethylenediamine (Salen) as new complexing agent. A mixed surfactant system of a nonionic surfactant (Triton X-114) and cetyltrimethylammonium bromide (CTAB) that have relatively low-cost and less toxic. The experimental parameters affecting the CPE efficiency were investigated and optimized.

Table 2: Comparison CPE methods for determination of Fe.

Reagent	Micellar system	Detection system	LOD ng mL <sup>-1</sup>	PF	RSD%	Samples	Ref
PAN	Triton X-114	FAAS	3.0	9.6	2.54	Produced water from the petroleum industry	[29]
ECR	T X-114	FAAS	0.33	141	1.9	Water and food	[30]
DOPHHBA	T X-114	UV-Vis	1.2	100	NA	Water and food	[31]
APDC	Triton X-100: Triton X-45 (6:4)	FAAS	20	NA	2.4	Wine	[32]
Neutral Red	T X-114	FAAS	0.7	98	2.1	Spice	[33]
5-Br-PADAP	T X-114	UV-Vis	0.8	20	2.0-2.6	Beer	[34]
5-Br-PADAP	T X-114	UV-Vis	4.0	NA	6.5	Fortified wheat and maize flours	[35]
ECR	CTAB/ T X-114		30	100	NA	Titanium concentrates	[36]
Ferron	T X-114	FAAS	0.4	30	2.4	Environmental and biological	[37]
IYPMI	T X-114	FAAS	2.8	30	2.0	Water, soil, blood, orange juice and lotus tree leaves	[38]
DPT/Neutral Red	T X-114	FAAS	25	20	≤ 3.8	Drinking water	[39]
DPPAHS	T X-114	UV-Vis	1.20	40	1.52	Water, food and environmental	[40]
Ferron	T X-114	FI-FAAS	1.7	75	2.1	Water and milk	[41]
Zincon	T X-114/CTAB	UV-Vis	3.1	50	2.5	Water and blood	[42]
APDC	C16MeImCl/ T X-114	UV-Vis	10 μg mL <sup>-1</sup>	20.4	3.9	Synthetic and water	[43]
PHBI	T X-114	FAAS	2.8	38	3.6	Biological and environmental	[44]
APDC	Triton X-100: Triton X-45 (6:4)	UV-Vis	7.0	50	2.6	Water	[49]
BIYPYBI	T X-114	FAAS	2.2	30	≤ 1.4	Blood, orange juice and lotus tree	[45]
2,6-diamino-4-phenyl-1,3,5-triazine	T X-114	FAAS	1.85	25	2.06	Water and Canned Food	[46]
TAN	T X-114	FAAS	6.45	70.2	1.30-1.95	Serume and urine	[47]
MPTAN	Triton X-100	UV-Vis	16	NA	0.08	Meat, vegetable, soil, water, and fruit	[48]
Benzidine	T X-114	UV-Vis	0.25	NA	3.07	Urine	[49]
1,10-phenanthroline	T X-114/ DOSS	UV-Vis	5.1	NA	NA	Water	[50]
5-Br-PADAP/ TPB	T X-114	FAAS	0.78	29.9	1.67	Mineral water	[51]
ETB	T X-114	UV-Vis	1.50	50	2.60	Water, biological and food	[52]
TAN	T X-114	UV-Vis	1.0	30	NA	Plant materials	[53]
Salen	Triton X-114/CTAB	UV-Vis	1.50	50	1.75-2.0	Water samples	This work

PF: preconcentration factor; LOD: limit of detection; RSD%: relative standard deviation; NA; not available.

FAAS; Flame atomic absorption spectrometry; FI-FAAS; Flow injection flame atomic absorption spectrometry; UV-Vis: UV-Visible spectrophotometry

PAN: 1-(2-pyridylazo)2-naphthol; DOPHHBA: 4-(2-(2,4-dioxopentan-3-ylidene)hydrazinyl)-2-hydroxybenzoic acid; APDC: ammonium pyrrolidine dithiocarbamate; 5-Br-PADAP: 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol; ECR: eriochrome cyanine R; CTAB: cetyltrimethylammonium bromide; IYPMI: 3-((indolin-3-yl)(phenyl) methyl)indoline; DPT: 2,4-diamino-6-phenyl-1,3,5-triazine; DPPAHS: 7-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylazo)-8-hydroxyquinoline-5-sulphonic acid; Neutral Red: 3-amino-7-dimethylamino-2-methylphenazine; PHBI: 2-phenyl-1H-benzo[d]imidazole; BIYPYBI : 2-(6-(1H-benzo[d]imidazol-2-yl)pyridin-2-yl)-1Hbenzo[d]Imidazole; TAN: 1-(2-thiazolylazo)-2-naphthol; MPTAN: methyl phenyl thiazolyl azo]-3-methyl-4-methoxy-2-naphthol; TX-114: Triton X-114; DOSS: docusate sodium salt; 5-Br-PADAP: 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol; TPB: tetraphenylborate; ETB: 2-(3-ethylthioureido)benzoic acid

## 2. Experimental

### 2.1. Apparatus

All absorption spectra were made using Varian UV-Vis spectrophotometer (Cary 100 Conc., Australia) equipped with a 5.0 mm quartz cell was used for absorbance measurements. This spectrophotometer has a wavelength accuracy of  $\pm 0.2$  nm with a scanning speed of  $200 \text{ nm min}^{-1}$  and a bandwidth of 2.0 nm in the wavelength range of 200-900 nm. Hanna pH-meter instrument equipped with a combined glass-calomel electrode (Portugal) (HI: 9321) was used for checking the pH of prepared buffer solutions. A centrifuge with 25 ml calibrated centrifuge tubes (Isolab, Germany) were used to accelerate the phase separation process. A thermostated water bath with good temperature control was used for the CPE experiments. In order to characterize Salen, the IR spectra were recorded KBr discs using Matson FTIR spectrophotometer in the  $4000\text{-}200 \text{ cm}^{-1}$  range.

### 2.2. Materials and reagents

Doubly distilled water and analytical-reagent grade chemicals were used throughout, unless stated otherwise.

#### Iron(III) standard stock solution

A stock of standard solution ( $1000 \text{ mg L}^{-1}$ ) of Fe(III) was prepared by dissolving the proper amount of ammonium ferric sulfate dodecahydrate ( $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ) (Merck, Darmstadt, Germany) in 100 ml bidistilled water acidified with  $\text{H}_2\text{SO}_4$ . The working standard solutions were prepared freshly by dilution with water. The solution was freshly prepared every day.

Buffer solutions were prepared to adjust the solution pH values. Sodium dihydrogen phosphate/phosphoric acid buffer was used to adjust solutions to pH 2.0. Acetate buffer was prepared by mixing different amounts of  $1.0 \text{ mol L}^{-1}$  sodium acetate and  $1.0 \text{ mol L}^{-1}$  acetic acid to maintain the pH range from 4.0-6.0. A di-sodium hydrogen phosphate/sodium dihydrogen phosphate buffer solution was used to adjust solutions to pH 7.0. Ammonical buffer solutions were prepared by adding an appropriate amount of Ammonia/ammonium chloride ( $0.1 \text{ mol L}^{-1}$ ) solutions to result in solutions of pH from 8.0-10 [54].

Cethyltrimethylammonium bromide (CTAB) (Sigma-Aldrich, USA) as cationic surfactant and polyethylene glycol tert-octylphenyl ether (Triton X-114) (Fluka, Buches, Switzerland) as non-ionic surfactant was supplied from (Fluka, Buches, Switzerland) and used without further purification. Aqueous (1.0 %, v/v) of the Triton X-114 solution was prepared by dissolving 1.0 ml of Triton X-114 in 100 ml of bidistilled water in 100 ml volumetric flask with stirring. Aqueous  $1.0 \times 10^{-2} \text{ mol L}^{-1}$  of CTAB solution

was prepared by dissolving 0.36 g of CTAB surfactant in 100 ml of bidistilled water in 100 ml volumetric flask with stirring. Nitric acid solutions were prepared by direct dilution with deionized water from the concentrated solutions. Methanol, acetone, and ethanol (Merck) were used to decrease the viscosity of surfactant-rich phase. The solutions of various cations and anions used for the interference study were obtained from the respective high purity inorganic salts (Sigma-Aldrich, USA) by proper dilution in bidistilled water.

### 2.3. Synthesis of Salen reagent

The Schiff-base ligand (Salen) was synthesized by reporting methods [55]. Briefly, 5 mmol of 1,3-propanediamine (0.42 ml) was mixed with 10 mmol of 2-hydroxyacetophenone (1.20 ml) in 20 ml methanol. The resulting solution was refluxed for ca. 2 h, and allowed to cool. The purity of the resulting Schiff-base is also checked by measuring the melting point constancy. The chemical structure was detected by IR spectra (Fig. 1).

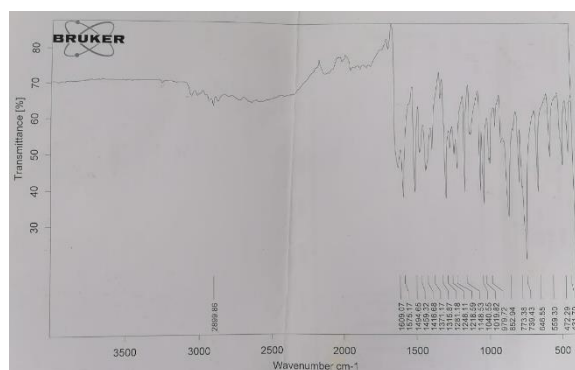


Fig. 1. FT-IR spectrum for the synthesized Salen reagent.

A  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  solution of the Salen reagent was prepared by dissolving an appropriate weight of reagent in (1.0 %, v/v) Triton X-114 and then completed to the mark in 100 ml calibrated flask with bidistilled water.

### 2.4. Preconcentration CPE procedure

An aliquots of Fe(III) ( $5.0\text{-}400 \text{ } \mu\text{g L}^{-1}$ ) standard solution was transferred to a 50 ml centrifuge tube, 5.0 ml of acetate buffer solution (pH 4.0) and 2.0 ml of the  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  Salen solution was added. After that, 1.0 ml of (1.0% v/v) Triton X-114 solution and 1.0 ml of ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) CTAB solution was added and completed to the mark with bidistilled water. The mixture was sonicated in an ultrasonic bath for 10 min at  $40^\circ\text{C}$  to reach the cloud point temperature. To separate the two phases, the mixture was centrifuged for 5.0 min at 4000 rpm. Then, the resultant turbid solution was cooled in an ice-bath for 5.0 min in order to increase the viscosity of the surfactant-rich phase. The surfactant-rich phase became a viscous phase,

which could then be separated by inverting the tubes to discard the aqueous phase. The remaining micellar phase was diluted with ethanol, until a final volume of 1.0 ml was reached. The absorbance was measured at 612 nm against a reagent blank prepared with bidistilled water. A blank solution containing all reagents except Fe(III) was prepared and treated in the same way as the sample. The calibration graph was performed and the concentration of Fe(III) was calculated.

### 2.5. Application for real water samples

The proposed method was applied to different water samples, including tap, well, river and bottled mineral water samples. The samples collected in polyethylene bottles from a natural pond within the city of Zagazig, Egypt and its neighborhood. The water samples were filtered through a cellulose membrane filter (Millipore) of 0.45  $\mu\text{m}$  pore size to remove any suspended particulate matter, then 100 ml of each filtered water sample was accurately transferred into a 250 ml round bottom flask, and 10 ml of a mixture consisting of  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  (1:9, v/v) were added. These samples were digested by heating under reflux for 2.0 h. The cooled samples were transferred into 100 ml volumetric flask and made up to the mark with deionized distilled water, mixed well, then the pH of the samples was adjusted to pH 4.0 buffer solution and stored in a refrigerator in the dark. Aliquots of water samples were subjected to the CPE methodology as described above in the general procedure.

## 3. Results and discussion

### 3.1. Absorption spectra

The absorption spectrum of the Fe(III)-Salen complex in surfactant-rich phase shows a maximum absorbance at 612 nm against reagent blank (Fig. 2).

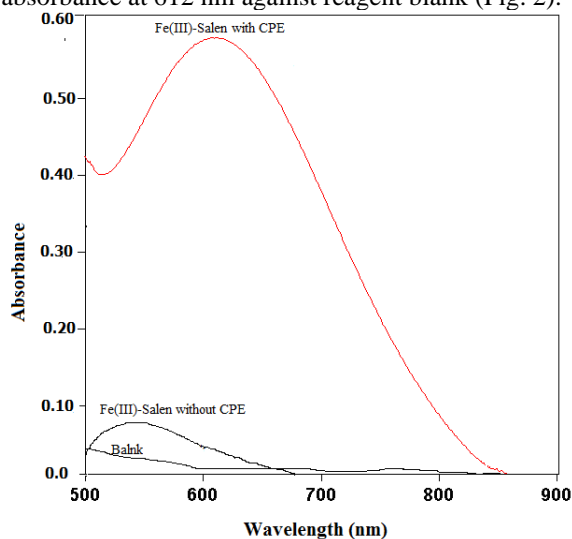


Fig. 2. Absorption spectra for 400 ng mL<sup>-1</sup> Fe(III) complexed with 1.0 x 10<sup>-3</sup> mol L<sup>-1</sup> Salen at pH 4.0,

(1.0%, v/v) Triton X-114 and (1.0x10<sup>-3</sup> mol L<sup>-1</sup>) CTAB with and without CPE against reagent blank.

### 3.2. Optimization of the cloud point extraction conditions

The analytical variables such as pH, reagent and surfactant concentrations, temperature and centrifugation times, were optimized by applying the CPE procedure described above.

#### 3.2.1. Effect of pH

The pH of the aqueous solution is an important factor in CPE of Fe(III) using Salen, because this parameter is directly related to the formation of metal-ligand species. Complexation was carried out in different types of buffer solutions. The acetate buffer solution was used to maintain the optimum one which gives highest absorbance value in addition to the stability of the color complex. The effect of pH on the CPE efficiency of Fe(III) was studied in the pH range 3.0–9.0, keeping the other conditions constant and the results are shown in Fig. 3. As can be seen, maximum absorbance was obtained at the pH 4.0. In addition, the influence of the buffer volume was assessed. The results have shown that if 5.0 ml of the acetate buffer solution was chosen as the optimum volume for maximum sensitivity.

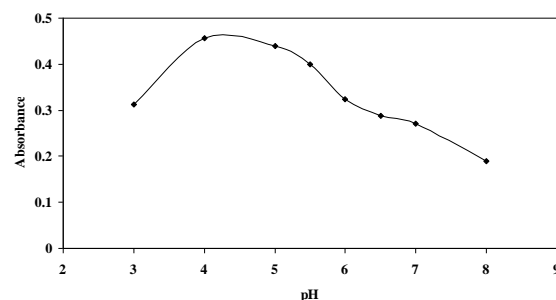


Fig. 3. Effect of pH on the CPE of 400 ng mL<sup>-1</sup> Fe(III). Extraction conditions: 1.0 x 10<sup>-3</sup> mol L<sup>-1</sup> Salen, (1.0%, v/v) Triton X-114 and (1.0x10<sup>-3</sup> mol L<sup>-1</sup>) CTAB.

#### 3.2.2. Effect of reagent concentration

The effect of salen concentration on the analytical performance was studied for Fe(III) solution and various concentrations of the reagent in the range of 2.0 x 10<sup>-5</sup>–2.0 x 10<sup>-4</sup> mol L<sup>-1</sup>. An increase of the reagent concentration resulted in an increase of the absorbance of the complex (against the reagent blank) and was observed to be constant in the range 0.8 x 10<sup>-4</sup>–1.5 x 10<sup>-4</sup> mol L<sup>-1</sup> (Fig. 4). The optimum absorbance of the complex coupled with minimum blank reading was found to be 1.0x10<sup>-4</sup> mol L<sup>-1</sup>. A higher concentration of the reagent was tried, and constant/or decreasing absorbance was obtained. In the subsequent studies, the optimum concentration of the reagent 1.0x10<sup>-4</sup> mol L<sup>-1</sup> was sufficient for



optimum results. This concentration ensures sufficient excess to compensate for any consumption of the reagent by other metals.

In order to study the influence of Salen concentration which is **complexes** with Fe(III) on the extraction and analytical response, different volumes of the ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) Salen chelating reagent ranging between 0.25–4.0 **ml** were used, and the general procedure was applied. The results in Fig. 4 showed that the absorbance is increased with increasing the volume of Salen ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) up to 2.0 **ml**, after that there is no significant change in the absorbance. Therefore, for all further investigations 2.0 **ml** of Salen ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) solution was selected as the optimum volume which give maximum complex formation yield.

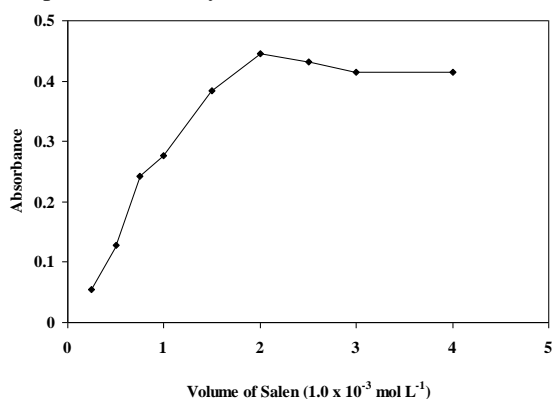


Fig. 4. Effect of Salen ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) volume on the CPE of  $400 \text{ ng mL}^{-1}$  Fe(III) complexation. Extraction conditions: pH 4.0, (1.0%, v/v) Triton X-114 and ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) CTAB.

### 3.2.3. Effect of surfactant concentration

The effect of cationic surfactant (CTAB) concentration on the CPE and determination of Fe(III) ions was studied in the volume ranges from 0.25–3.0 **ml** of ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) CTAB. The results were shown in Figure 5. By increasing CTAB volume to 1.0 **ml**, the absorbance was increased and then gradually decreased. The blank absorbance also increased by increasing CTAB concentration. This decrease can be due to increase in blank signal in absence of analytes. With the addition of CTAB of 1.0 **ml**, there is enough surfactant as ion-pairing reagent in the surfactant-rich phase and the solubilization **are** stronger, so the extraction efficiency is higher.

Triton X-114 is one of the non-ionic surfactant extensively used in CPE. This is due to its advantages such as commercial availability with high purity, relatively low cloud point temperature, low toxicity and cost and high density of the surfactant-rich phase which facilitates phase separation by centrifugation. The effect of non-ionic surfactant concentration within the Triton X-114 (1.0%, v/v) volume ranges from 0.25–3.0 **ml** on the CPE efficiency of Fe(III) ions. As shown in Figure 5, the absorbance of the complex was

increased by increasing the (1.0%, v/v) Triton X-114 volume up to 1.0 **ml** of both metal ions. A considerable decrease in the absorbance is observed with increasing the surfactant amount higher than (1.0%, v/v). This can be attributed to an increase in volume and viscosity of the micellar phase. At amounts below this value, the extraction efficiency of complexes was low because there are few molecules of the surfactant to entrap the metal-Salen complex quantitatively. Thus, 1.0 **ml** of Triton X-114 (1.0%, v/v) was selected for subsequent experiments.

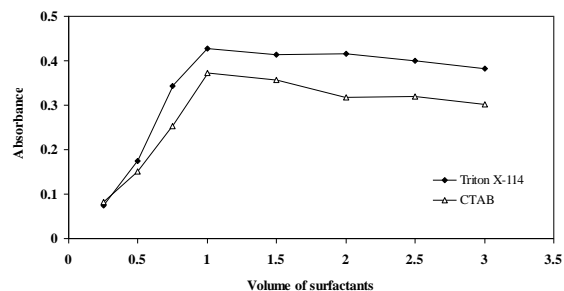


Fig. 5. Effect of Triton X-114 (1.0 %, v/v) and CTAB ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) volumes on the CPE of  $400 \text{ ng mL}^{-1}$  Fe(III) at pH 4 and Salen ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ).

### 3.2.4. Effect of ionic strength

Ionic strength has a negligible effect on micelle formation, but accelerated phase separation. Ionic strength was tested within the interval of 0.005–0.3  $\text{mol L}^{-1}$  NaCl concentration. It had no considerable effect upon the magnitude of extraction and sensitivity.

### 3.2.5. Effects of equilibration temperature and time

In order to achieve easy phase separation and efficient preconcentration in cloud point extraction processes, it is imperative to optimize the incubation time and temperature. It was desirable to employ the shortest incubation time and the lowest possible equilibration temperature, as a compromise between completion of extraction and efficient separation of phases. The influence of the incubation time and temperature was investigated in the ranges 5.0–20 min and at 30–60°C. The results demonstrate that at the incubation time of 10 min and the temperature of 40°C were chosen for further experiments. The extraction efficiency of the metal-Salen complex was constant. Therefore, an equilibrium temperature of 40°C was chosen for the separation process. Higher temperatures lead to the decomposition of Salen and the reduction of extraction yield. A centrifuge time period of 5.0 min at 4000 rpm was selected as optimum, as complete separation occurred within this time and no appreciable improvements were observed for longer periods.

### 3.2.6. Effect of diluting agent

For the CPE method, the addition of a diluent into the surfactant-rich phase is often needed to obtain

a homogeneous solution compatible viscosity. Different solvent including methanol, ethanol, acetone and acetonitrile were tested as diluent solvents. The high viscosity of the surfactant-rich phase is drastically decreased using ethanol as diluting agents in order to have an appropriate amount of sample for transferring and measurement of the absorbance of the sample and also a suitable preconcentration factor. Hence the surfactant-rich phase was completed to 1.0 ml of ethanol. Therefore, a preconcentration factor was 50.

### 3.3. Analytical performance

The calibration graphs were linear in the range 5.0–400  $\mu\text{g L}^{-1}$  Fe(III) under the optimum conditions of the general procedure. The regression equations for Fe(III) determination were  $A = -6.0 \times 10^{-4} + 1.047C$  ( $R^2 = 0.9996$ ), where A is the absorbance and C is the metal concentration in solution ( $\mu\text{g L}^{-1}$ ). But spectrophotometric method without the preconcentration CPE procedure, the linear ranges were 0.3–6.0  $\mu\text{g mL}^{-1}$  with regression equations were  $A = 6.5 \times 10^{-3} + 0.0195C$  ( $R^2 = 0.9989$ ). The limit of detection, defined as  $C_L = 3S_B/m$  (where  $C_L$ ,  $S_B$  and  $m$  are limit of detection, standard deviation of the blank, and the slope of the calibration graph, respectively). The limits of detection and quantification limit were 1.50 and 5.0  $\mu\text{g L}^{-1}$ , respectively. The preconcentration factor, which is defined as the ratio of the initial sample volume (50 mL) to final measuring volume (1.0 mL) after CPE was 100. The enhancement factor was calculated as the ratio of the

slope of the calibration graph with preconcentration CPE procedure to the slope of the calibration graph without CPE was also approximately 53.69. The consumptive index is defined as the sample volume, in milliliters, consumed to reach a unit of enrichment factor (EF):  $CI = V_s(\text{ml})/EF$ , where  $V_s$  is the sample volume, CI was 25. The precision of the procedure was determined as the relative standard deviation (RSD) and relative error for six replicate measurements carried out in solutions containing 300  $\text{ng mL}^{-1}$  of Fe(III) at intra-day and inter-day repeatability (RSD%, 1.75 and 2.0) (Table 3). Alternatively, a significance test was applied to compare the accuracy and precision of the proposed method and reported methods [40]. The  $t$ - and  $F$ -values calculated were less than the theoretical values [56] in all instances (Table 3).

### 3.4. Effect of foreign ions

The effects of representative potential interfering species were tested. In these experiments, Synthetic solutions containing 400  $\mu\text{g L}^{-1}$  of Fe(III) and various amounts of other interfering ions were prepared and the proposed procedure for the determination of Fe(III) was followed. An error of  $\pm 5.0\%$  in the absorbance reading was considered to be tolerable. Solutions were prepared containing a 12000 molar excess of the foreign ions relative to Fe(III). For metal ions that were found to cause interference, a lower concentration of foreign ions was then prepared. The tolerance limits are given in Table 4.

Table 3: Analytical features of the proposed CPE method

Parameters	With CPE	Without CPE
$\lambda_{\text{max}}$ (nm)	612	550
Calibration range ( $\mu\text{g L}^{-1}$ )	5.0–400	300–6000
Molar absorptivity ( $\text{L mol}^{-1} \text{cm}^{-1}$ )	$3.46 \times 10^5$	$2.41 \times 10^3$
Sandell sensitivity ( $\text{ng cm}^{-2}$ )	0.162	25
Regression equation <sup>a</sup>		
Slope	1.047	0.0195
Intercept	$-6.0 \times 10^{-4}$	$6.5 \times 10^{-3}$
Correlation coefficient ( $r^2$ )	0.9996	0.9989
Preconcentration factor (PF)	50	-
Enrichment factor (EF)	53.69	-
Consumptive index (CI)	1.07	-
Intra-day precision (RSD%; $n=10$ ) <sup>b</sup>	1.75	2.94
Inter-day precision (RSD%; $n=10$ ) <sup>b</sup>	2.0	3.20
Limit of detection ( $\mu\text{g L}^{-1}$ )	1.5	81
Limit of quantification ( $\mu\text{g L}^{-1}$ )	5.0	270
Student $t$ -test/(2.57) <sup>c</sup>	1.15	1.90
$F$ -value/(5.05) <sup>c</sup>	2.40	3.70

<sup>a</sup>:  $A = a + bC$ , where C is the concentration of Fe(III) in  $\mu\text{g L}^{-1}$

<sup>b</sup> Theoretical values for  $t$ - and  $F$ -values at 95% confidence level for five degrees of freedom are 2.57 and 5.05, respectively.

Table 4: Effect of interfering ions on preconcentration and recoveries of 400  $\mu\text{g L}^{-1}$  Fe(III) (N=3).

Ions	Added as	Maximum tolerable amount ( $\mu\text{g mL}^{-1}$ )	Recovery (%) $\pm$ SD <sup>a</sup>
K <sup>+</sup>	KCl	10	96.0 $\pm$ 2.0
Na <sup>+</sup>	NaCl	10	97.0 $\pm$ 2.0
Al <sup>3+</sup>	Al(NO <sub>3</sub> ) <sub>3</sub>	2.0	95.0 $\pm$ 1.0
Cr <sup>3+</sup>	Cr(NO <sub>3</sub> ) <sub>3</sub>	1.0	99.0 $\pm$ 2.0
Ca <sup>2+</sup>	CaCl <sub>2</sub>	2.0	95.0 $\pm$ 3.0
Mg <sup>2+</sup>	MgCl <sub>2</sub>	1.0	98.0 $\pm$ 3.0
Zn <sup>2+</sup>	ZnSO <sub>4</sub>	2.0	97.0 $\pm$ 2.0
Pb <sup>2+</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	1.0	96.0 $\pm$ 2.0
Mn <sup>2+</sup>	Mn(NO <sub>3</sub> ) <sub>2</sub>	1.0	99.0 $\pm$ 3.0
Cd <sup>2+</sup>	Cd(NO <sub>3</sub> ) <sub>2</sub>	1.0	98.0 $\pm$ 2.0
Cu <sup>2+</sup>	CuSO <sub>4</sub>	0.5	97.0 $\pm$ 2.0
NO <sub>3</sub> <sup>-</sup>	KNO <sub>3</sub>	5.0	96.0 $\pm$ 3.0
SO <sub>4</sub> <sup>2-</sup>	Na <sub>2</sub> SO <sub>4</sub>	5.0	95.0 $\pm$ 2.0
Cl <sup>-</sup>	NaCl	10	97.0 $\pm$ 1.0
F <sup>-</sup>	NaF	10	96.0 $\pm$ 2.0

<sup>a</sup> Mean  $\pm$  standard deviation.

### 3.5. Analytical applications

In order to test the reliability of the proposed method, it was applied to the determination of Fe(III) from different water (tap, mineral, well, river and sea) samples. The results are described in Table 5. According this table, the added Fe(III) can be quantitatively recovered from the water samples by the proposed procedure. Recoveries (*R*) of spike additions (100 and 300  $\mu\text{g L}^{-1}$ ) to water samples were quantitative. The percentage recovery (*R*) was calculated by using the equation:

$$R \% = \{(C_m - C_0)/m\} \times 100.$$

Where  $C_m$  is a value of the metal in a spiked sample,  $C_0$  is a value of the metal in a sample and *m* is the amount of metal spiked. The results indicated that the recoveries were reasonable for trace analysis, in a range of 95.0–100.50% and confirm the validity and efficiency of the proposed method for Fe(III) determination in various water samples.

Table 5: Spiked recoveries of Fe(III) ions from various real water samples after being applied the proposed CPE method (N= 3).

Sample	Added ( $\mu\text{g L}^{-1}$ )	Found <sup>a</sup> ( $\mu\text{g L}^{-1}$ )	Recovery (%)	RSD (%)
Tap water	0	27.0	-	-
	100	122.0	96.0	1.38
	300	317.20	97.0	0.80
Mineral water	0	35.0	-	-
	100	130.0	96.0	1.54
	300	320.0	95.50	1.80
Well water	0	90.0	-	-
	100	185.0	97.20	0.90
	300	382.0	98.0	1.60
	0.0	85.0	-	-

River water	100	178.50	96.50	1.10
	300	366.0	95.0	1.37
Sea water	0.0	100.0	-	-
	100	194.0	97.0	0.75
	300	384.0	96.0	1.25

<sup>a</sup> Average of three determinations with 95% confidence level.

### 4. Conclusion

In this work, CPE system coupled to spectrophotometry was developed for the preconcentration and determination of trace amount of Fe(III) in various water samples. Salen is a very stable and fairly selective new complexing reagent. Triton X-114 and CTAB have relatively low-cost, low toxicity and are readily available in most laboratories. The CPE approach is a convenient, safe, sensitive, rapid, simple and economic, accurate, precise, has lower detection and quantification limits, better preconcentration factor and wider linear range. It also offers the advantage of isolating the analyte from the sample matrix, allowing for interference-free analysis. The proposed method can be applied to the analysis of trace amounts of Fe(III) in various water samples with good results.

### Conflict of interest

The authors confirm that this article content has no conflict of interest.

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