VERSITA

Cent. Eur. J. Chem. • 6(3) • 2008 • 488-496
DOI: 10.2478/s11532-008-0049-9

Central European Journal of **Chemistry**

Combination of cloud point extraction and flame atomic absorption spectrometry for preconcentration and determination of trace iron in environmental and biological samples

Research Article

Mehrorang Ghaedi[1], Ardeshir Shokrollahi[1*], Raziyeh Mehrnoosh[1], Omid Hossaini[1], Mustafa Soylak[2]

[1] *Chemistry Department, Yasouj University, Yasouj, Iran*

[2] *Chemistry Department, University of Erciyes, 38039 Kayseri, Turkey*

Received 10 February 2008; Accepted 26 March 2008

Abstract: In the presented work, the conditions for cloud point extraction of iron from aqueous solutions using 7-iodo-8-hydroxyquinolin-5-sulphonic acid (Ferron) was investigated and optimized. The procedure is based on the separation of its ferron complex into the micellar media by adding the surfactant Triton X-114. After phase separation, the surfactant-rich phase was dissolved with 1.0 M HNO_3 in methanol. Iron was determined by flame atomic absorption spectrometry. Optimization of the pH, ligand and surfactant quantities, incubation time, temperature, viscosity, sample volume, and interfering ions were investigated. The effects of the matrix ions were also examined. The detection limits for three times the standard deviations of the blank for iron was 0.4 ng m L^{-1}, enrichment factor of 19.6 and preconcentration factor of 30 could be achieved. The validity of cloud point extraction was checked by employing real samples including soil, blood, spinach, milk, meat, liver and orange juice samples using the standard addition method, which gave satisfactory results.

Keywords: *7-iodo-8-hydroxyquinolin-5-sulphonic acid (Ferron) • Iron • Cloud point extraction • Triton X-114 • Flame atomic absorption spectrometry*

© Versita Warsaw and Springer-Verlag Berlin Heidelberg.

Abbreviation

TAN and Phen - tannins and other phenolic compound,
PMBP - 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone,
GF-AAS - graphite furnace atomic absorption spectrometry,
FAAS - flame atomic absorption spectrometry.

1. Introduction

It is widely accepted that the presence of Fe(III), alone or in combination has beneficial or deleterious effects on the properties of many substances and the nature of various biological systems. It provides a fundamental structure of hemoglobin, myoglobin, hem-enzymes and many co-factors involved in enzyme activities. Trace amounts of Fe(III) in various substances may be vital and can promote rancidity. It plays a central role in the biosphere and serves as the active center of proteins responsible for O_2 transport and electron transfer mechanisms and of metallo-enzymes such as oxidases, reductases, and dehydrases [1]. Fe(III) may control the mobility and toxicity of other metals, whilst Fe(III) may also be a limited nutrient for phytoplankton growth in the open ocean [2,3], Fe(II) is probably the preferred nutrient [4-6].

The concentration of Fe^{3+}. ions in biological fluids is usually found at trace level, requiring sensitive instrumental techniques. Frequently a pre-concentration step is required when a complex matrix has to be analyzed. Flame atomic absorption spectrometry (FAAS)

* *E-mail: ashokrollahi@mail.yu.ac.ir*

Brought to you by | Erciyes Üniversitesi
Authenticated
Download Date | 2/26/20 4:56 PM

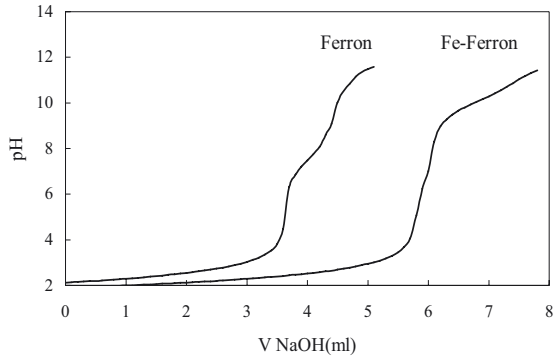


Figure 1. Potentiometric titration curves for ferron in the absence and presence of Fe(III) ion (Fe to ferron ratio of 1:3) with KOH of 0.098 M at 25.0°C and μ= 0.1 M of KNO_3.

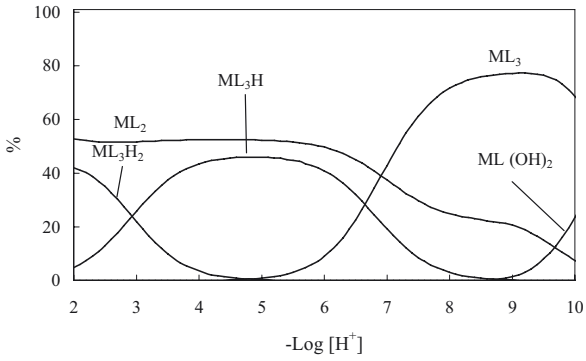


Figure 2. Distribution curve of Fe(III) - Ferron system.

has been widely used for the determination of trace metal ions, a relatively simple and precise technique. However, direct determination of metal ions at trace levels by FAAS is limited not only due to insufficient sensitivity, but also by matrix interference. For this reason, preliminary separation and preconcentration of trace elements from the matrix is frequently necessary to improve the detection limit and the selectivity.

Cloud point extraction (CPE) [7-9] is probably the most versatile and simple method for the preconcentration and extraction of hydrophobic species from water. The mechanism by which this separation occurs is attributed to the rapid increase in the aggregation number of the surfactant's micelles as the temperature is increased [10]. The cloud point phenomenon is reversible and when the temperature falls below the CPT, a single phase appears again. This phenomenon which is especially observed with polyoxyethylene surfactants can be attributed to the ethyl oxide segment in the micelle that repel each other at low temperature and attract each other at high temperature. The cloud-point phenomenon is related to the phase separation which occurs in aqueous solutions of nonionic surfactants that become turbid when heated to a temperature known as the cloud point [9,10].

As a result, a micellar phase of nonionic surfactant composed of coarse hydrated micelles with small volume and an aqueous micellar solution of the same surfactant with the concentration close to critical micelle concentration will be formed. The micellar phase is used for the preconcentration of micro-components. The solubility of nonionic surfactants in water is due to the formation of hydrogen bonds between the oxygen atoms of the surfactant polyoxyethylene chain and water molecules [11-13]. Any analytes solubilized in the hydrophobic core of the micelles will separate and become concentrated in the small volume of the surfactant- rich phase [13].

In CPE with a simple single-step extraction procedure analysis of many samples enable researchers to perform the overall procedure easily on-line [14-27].

The small volume of the surfactant-rich phase obtained with this methodology permits the design of extraction schemes that are simple, cheap, highly efficient, fast, and of lower toxicity to the environment than extractions that use organic solvents. CPE also provides results comparable to those obtained with other separation techniques. Accordingly, any species that interacts with the micellar system, either directly (generally hydrophobic organic compounds) or after a prerequisite derivatization reaction (e.g. metal ions after reaction with a suitable hydrophobic ligand) may be extracted from the initial solution and also be preconcentrated.

Ferron has been used as complexing agent due to its capacity for extracting several transition metal ions. Alkaline and alkaline earth elements do not react with this agent. This reagent has sufficient hydrophobicity to be used as a complexing agent in cloud point extraction. According to these characteristics, ferron was employed as a complexing agent for Fe(III) extraction.

Therefore, in the present work using ferron a simple, selective and sensitive CPE method for preconcentration and determination of Fe(III) ions in various real samples has been established.

2. Experimental Procedures

2.1. Reagents

All solutions were prepared with deionized water. Analytical-grade methanol, acids, and other chemicals used in this study were obtained from Merck Company. A 1.0% (w/v) Triton X-114 from E. Merck (Darmstadt, Germany) was prepared by dissolving 1.0 g of Triton X-114 in 100 mL volumetric flask with stirring. All chemical such as nitrate of Fe(III) and other cations were the analytical grade purchased from Merck Company. The ligand 7-iodo-8-hydroxyquinolin 5-sulphonic acid was purchased from Merck Company.

Brought to you by | Erciyes Üniversitesi
Authenticated
Download Date | 2/26/20 4:56 PM

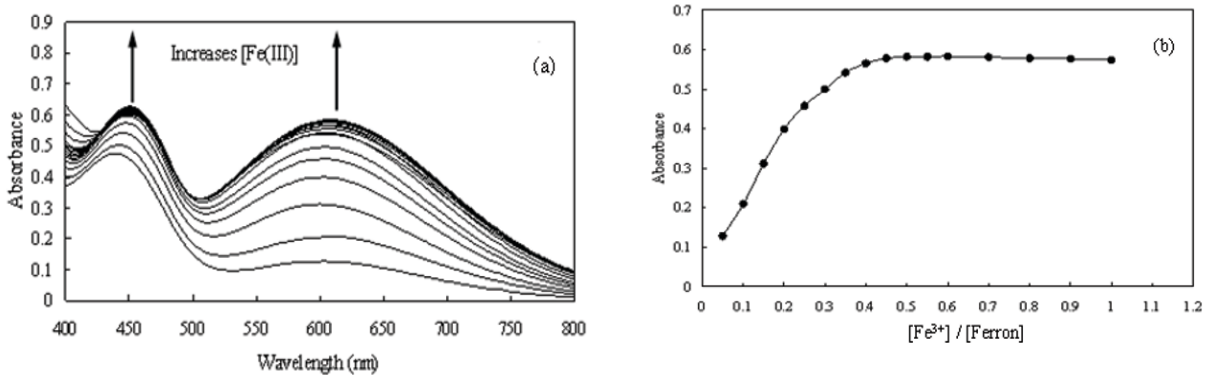


Figure 3. a) UV-visible spectra for titration of ferron (1.0×10^{-2} M) with Fe(III) (1.0×10^{-2} M) in water (T = 25°C and I = 0.05 M), b) the Corresponding molar ratio plot.

2.2. Instrumentation

A Perkin-Elmer AA 300 and a Shimadzu AA-680 atomic absorption spectrometer equipped with deuterium background correction and iron hollow-cathode lamp as the radiation source was used for absorbance measurements at wavelength 243.8 nm with slit width of 0.2 nm. The instrumental parameters were adjusted according to the manufacturer's recommendations. A 30 E 148 Sheme fan or Hettich centrifuge was used to accelerate the phase separation process. A Metrohm 692 pH meter furnished with a combined glass-saturated calomel electrode was used for pH measurements.

2.3. Potentiometric pH titrations

All potentiometric pH measurements were made on solutions in a 75-mL double-walled glass vessel using a Model 691 Metrohm pH / Ion meter and Titroprocessor model T23680 equipped with a combined glass-calomel electrode and the temperature was controlled at 25.0 ± 0.1°C by circulating water through the jacket, from a constant-temperature bath (home made thermostat). The cell was equipped with a magnetic stirrer and a tightly fitting cap, through which the electrode system and a 20-mL capacity piston burette were inserted and sealed with clamps and O-rings. Atmospheric CO_2 was excluded from the titration cell with a purging steam of purified nitrogen gas. The concentrations of Ferron was about 3.75×10^{-3} M, for the potentiometric pH titrations of ferron in the absence and presence of Fe(III) ions (1.25×10^{-3} M). A standard carbonate-free KOH solution (0.098 M) was used in all titrations. The ionic strength was adjusted to 0.1 M with KNO_3. For measuring pH at each point, sufficient time was allowed for the achievement of equilibrium. Ferron's protonation constants and the respective stability constant of Fe(III) complexes were evaluated using the program BEST described by Martell and Motekaitis [28]. A value of $10^{-13.78}$ was used for $K_w = [H^+][OH^-]$ in the calculations [29].

2.4. Spectrophotometric titrations

Standard stock solutions of Ligand (1.0×10^{-2} M) and the Fe(III) ions (1.0×10^{-2} M) were prepared by dissolving appropriate and exactly weighed (with an accuracy of ±0.0001 g) amount of pure solid compounds in pre-calibrated 25.0 mL volumetric flasks and diluted to the mark with deionized water. Working solutions were prepared by appropriate dilution of the stock solutions. According to the spectra reported (Fig. 3), titration of the ligand solution (3.4×10^{-4} M, 2.6 ml) was carried out by the addition of micro-liter amounts of a concentrated standard solution of the metal ion (1.0×10^{-2} M) using a pre-calibrated micro-syringe, followed by absorbance intensity reading at 25°C.

2.5. Test Procedure

A typical cloud point experiment required the following steps: an aliquot of 15 ml of a solution containing Fe(III) 0.2 µg m L^{-1}, 0.1% (w/v) Triton X-114 and 1.0 mM of ferron was adjusted to pH 3.5 by addition of acetate buffer. The mixture was shaken for 1 min and left to stand in a thermo-stated bath at 50°C, for 20 min. Separation of the phases was achieved by centrifugation at 3500 rpm for 15 min. The whole system was cooled in an ice-bath so for 5 min that the surfactant rich phase would regain its viscosity. In this way, the bulk aqueous phase was easily decanted. The remaining micellar phase was dissolved in 0.5 mL of 1.0 M HNO_3 in methanol and the iron content was readily evaluated by FAAS.

2.6. Application of real samples

The real samples including water, soil, blood, liver, meat and spinach samples was treated according to previous publication [30-33]. Then the procedure given in Section 2.5 has been applied.

Brought to you by | Erciyes Üniversitesi
Authenticated
Download Date | 2/26/20 4:56 PM

Table 1. Overall stability constants for the interaction of H^+ and Fe(III) with ferron at 25°C and ionic strength of 0.1 M.

System	Fe (III)	H^+	L	Log β	Max %	pH
LH	0	1	1	7.63	99.1	5.1
LH_2	0	2	1	10.52	76.4	2.0
LH_3	0	3	1	11.74	13.1	2.0
ML_2	1	0	2	23.68	52.8	2.0
ML_3	1	0	3	30.47	77.4	9.1-9.2
ML_3H	1	1	3	36.72	45.9	4.6-5.1
ML_3H_2	1	2	3	39.36	42.0	2.0
$ML(OH)_2$	1	-2	1	1.63	99.3	11.9

3. Results and Discussion

Nowadays, using pH measurements and the Best program [34-36], a potentiometric investigation of complexation can determine the speciation of the different possible forms of complexes obtained between the ligand and analyte ions by evaluating the dissociation constants of ligands and the stability constants of the respective complexes.

3.1. Potentiometric Investigation

In preliminary experiments, the fully protonated form of ferron was titrated with a standard KOH aqueous solution, in order to obtain some information about their protonation constants. The protonation constants ($K_n^H = [H_mL] / [H_{(m-n)}L][H^n]$, the charges are omitted for simplicity) were calculated by fitting the potentiometric pH-volume data to the BEST program. The results are summarized in Table 1. The titration curve of ferron and the corresponding species distribution diagram is shown in Figs. 1 and 2. The most likely species in the case of ferron alone are LH ($\log\beta_1 = 7.64$), LH_2 ($\log\beta_2 = 10.52$) and LH_3 ($\log\beta_3 = 11.74$). The most abundant of these species are present at pH 5.1, 2.0 and 2.0 respectively.

In order to investigate the stoichiometry and the stability constant of the desired complex of Fe(III) with ferron, known concentrations of ferron in the absence and presence of the Fe(III) ion in 1:3 mole ratio were titrated with a 0.098 M solution of KOH at a temperature of 25.0 ± 0.1°C and an ionic strength of 0.100 M maintained by KNO_3. From the divergence between the curves (Fig.1), it can be concluded that a strong interaction exists between Fe(III) ion and ferron in aqueous solution. The experimental curve was used to calculate the equilibrium constants for the reactions between the Fe(III) ion and ferron. The overall stability constants, $ß_{mlh}$; are defined by Equation (1) (charges are omitted for simplicity).

$$mM + lL + hH \rightarrow M_mL_lH_h$$
$$ß_{mlh} = [M_mL_lH_h] / [M]^m[L]^l[H]^h \quad (1)$$

Where M is Fe(III) ion, L is ferron and H is proton, and m, l and h are the respective stoichiometric coefficients. Since the ferron and complexes activity coefficients are unknown, the $ß_{mlh}$ values are defined in terms of concentrations. The errors are minimized by use of a high constant ionic strength of 0.1 M and low ferron concentrations of 3.75×10^{-3} M.

As can be seen from the results presented in Fig. 2 and Table 1, the dominant species with overall stability (logβ) constants for this system are: ML_2, ML_3, ML_3H, ML_3H_2 and $ML(OH)_2$, 23.68, 30.47, 36.72, 39.36 and 1.63, respectively.

3.2. Spectrophotometric Investigation

The spectra of ferron with addition of Fe(III) ion and corresponding mole ratio plot at wavelength of 604 nm have been depicted in Fig. 3. It seems that complexation occurs through binding of Fe(III) ion to nitrogen and through ion-dipole interaction with an oxygen atom leading to the ML_3 complex. Formation of a complex is pictured as the substitution of coordinated water molecules by the incoming ligand. The process is usually dissociative and the rate determining step is the rupture of the metal-water bond. Trivalent ions, may substitute as exemplified by Fe(III)-complexation associatively as well as dissociatively [37].

Due to the presence of a strong interaction between Fe(III) ion and ferron, the aim of this paper is to develop a simple, sensitive and available method for the preconcentration and determination of trace amount of Fe(III) in various real samples using flame atomic absorption spectrometry with CPE. In this regard, the influence of various effective parameters including, pH, surfactant and ferron concentrations, heating time and temperature, centrifuge time and rate and the effect of electrolyte on sensitivity and extraction efficiency were optimized.

Brought to you by | Erciyes Üniversitesi
Authenticated
Download Date | 2/26/20 4:56 PM

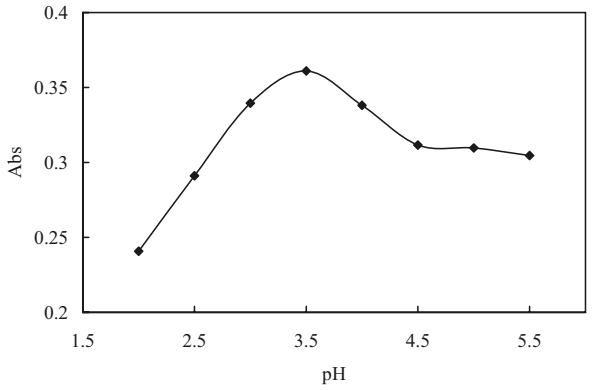


Figure 4. Effect of pH on absorbance of Fe(III), **conditions:** 0.2 μg mL^{-1} Fe(III), 0.1% (w/v) triton X-114, 1.0 mM ferron, 20 min heating at 50°C, 15 min centrifuge in 3500 rpm in various pH.

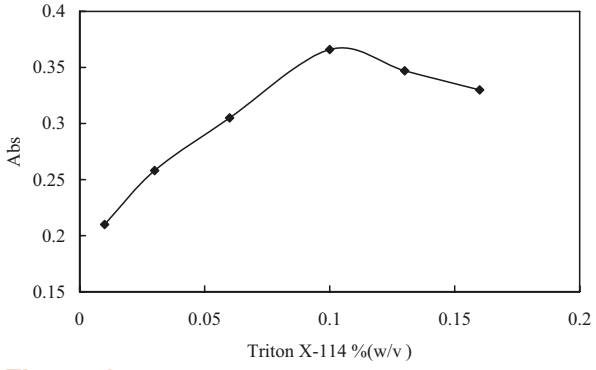


Figure 6. Effect of amount of triton X-114 on Fe(III) ions absorbance (N=3), **conditions:** 0.2 μg mL^{-1} Fe(III), 1.0 mM ferron, pH 3.5, 20 min heating at 50°C, 15 min centrifuge in 3500 rpm, at different triton X-114 concentration.

3.3. Effect of pH on Fe(III) ion CPE

The formation of the metal–chelate and its chemical stability are two important factors influence on CPE. The pH plays a unique role on metal–chelate formation and subsequent extraction and proved to be the main parameter for CPE. Extraction yield depends on the pH at which complex formation is carried out. In this view, a set of similar experiments in the pH range of 2.0-5.5 was conducted according to the described procedure in experimental section and respective results are illustrated in Fig. 4. The maximum sensitivity by CPE was obtained at a pH 3.5. In more acidic solutions, deterioration of the signal occurs due to protonation of ferron, while at a pH > 3.5, the signal decreases and the recovery was reduced due to precipitation of Fe(III) ions in the form of hydroxides. Consequently, pH = 3.5 was selected for the subsequent studies.

3.4. Effect of Ferron concentration on Fe(III) CPE

The 7-iodo-8-hydroxyquinolin-5-sulphonic acid (Ferron) behaves as a bi-dentate (N, O) univalent ligand to form chelates with several metal ions. The sensitivity

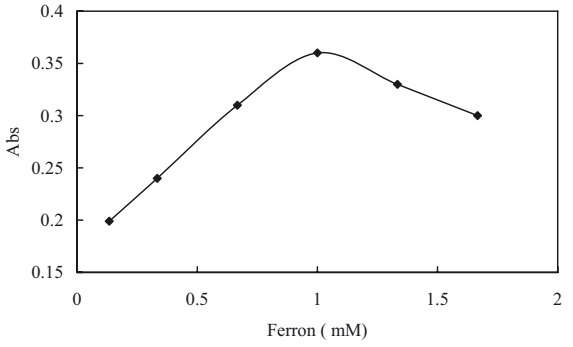


Figure 5. Effect of amount of ferron on Fe(III) ions absorbance (N=3), conditions: 0.2 μg mL^{-1} Fe(III), 0.1% (w/v) triton X-114, pH 3.5, 20 min heating at 50°C, 15 min centrifuge in 3500 rpm, at different ferron concentration.

of the method and extraction recovery as a function of the concentration of ferron is shown in Fig. 5. As can be seen increasing ferron concentration up to a 1.0 mM cause increases in sensitivity. Thus, a ferron concentration of 1.0 mM was chosen for optimization of other variables. A possible explanation for the decrease with higher concentrations may be attributed to the formation of charged complexes with excess ferron in the medium. Also, it is important to note that for liquid–liquid extractions, an uncharged chelate is preferentially extracted to the organic phase [38,39]. At the lower ferron concentrations (lower than 1.0 mM) insufficient ferron binding of iron was reflected in the low integrated absorbance.

3.5. Effect of Triton X-114 concentration

Due to Triton X-114's physicochemical characteristics, low CP temperature, commercial availability, relatively low price, as well as low toxicity, and its high density in the surfactant-rich phase, which facilitates phase separation by centrifugation, it has been chosen for this study as an efficient phase separating agent. The variation in sensitivity and extraction recovery of Fe(III) within the Triton X-114 concentration range of 0.01-0.16% was examined and the results are shown in Fig. 6. It can be seen that quantitative extraction was obtained with an optimum Triton X-114 concentration of 0.1% (w/v), where the highest sensitivity and greatest extraction efficiency for Fe(III) ions was achieved. For lower surfactant concentration (to 0.01% (w/v)) the preconcentration efficiency of the complex was very poor, since the assemblies at low concentration were probably inadequate to preconcentrate trace amounts of Fe(III) ions.

For higher Triton X-114 concentrations (0.16% w/v) detection was lower and may be attributed to the fact that in the presence of higher amounts of surfactant the viscosity of the surfactant-rich phase increases , which leads to a decrease in sensitivity [12,40].

Brought to you by | Erciyes Üniversitesi
Authenticated
Download Date | 2/26/20 4:56 PM

Table 2. Characteristic performance of present CPE of Fe(III) ion.

Parameter	Value
Regression equation	Y = 1.158 C+ 0.117 (r^2 = 0.998)
Regression equation before preconcentration	Y = 0.060 C + 0.117
Linear range (μg mL^{-1})	0.01 - 0.40
Limit of detection ($3S_b$/m blank, ng mL^{-1}) (n = 5)	0.40
Reproducibility (R.S.D., %) (n = 5)	2.40
Preconcentration factor	30.0
Improvement factor	19.6

Table 3. Effects of the matrix ions on the recoveries of the examined metal ions (N = 3)

Interfering ion / Fe(III) ratio	Interfering Ions
Li^+, K^+, Na^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, CH_3COO^-, NO_3^-, Cl^-, Br	1000
Ni^{2+}, Mn^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Al^{3+}, Ag^+	500

3.6. Effect of NaCl concentration

Studies on the effects of some additives such as anionic and non-ionic surfactants and electrolytes, as NaCl, KNO_3 and $MgCl_2$ on the cloud point behavior of non-ionic surfactants have been reported [41-43]. It was observed that the electrolytes decrease the cloud point (salting-out effect) and increase extraction efficiency and sensitivity of the method, since dehydration of the poly (oxyethylene) chains in the presence of an electrolyte has been promoted [44]. The salting-out process occurs due to desorption of ions to the hydrophilic parts of the micelles (which increases the inter-attraction between micelles) and consequent precipitation of surfactant molecules. Based on this discussion, NaCl was investigated as an electrolyte in the concentration range of 7.0 - 400 mM giving the optimum Fe(III) ion recovery and sensitivity at 0.34 M NaCl. It is important to emphasize that different blank solutions were also evaluated and no significant signal was obtained.

3.7. Effect of methanol volume

The surfactant rich phase was diluted with a range of concentrations of methanolic nitric acid to introduce the surfactant rich phase to FAAS, where a solution of 0.5 ml of 1.0 M HNO_3 in methanol gave the greatest sensitivity.

Smaller volumes of methanol were not tested because in this case it was not possible to quantitatively transfer the surfactant rich phase from test tubes to the graduated tubes and it is not possible to measure the absorbance. Larger volumes of acidified methanol dilutions resulted in a gradual absorbance reduction. Therefore, a volume of 0.5 mL of 1.0 M methanolic nitric acid was used throughout the remaining experiments.

3.8. Effect of Temperature and equilibrium time on CPE

The greatest analyte preconcentration factor was achieved when the cloud point extraction procedure was performed at equilibration temperatures that were well above the cloud point temperature of the surfactant [45]. In order to achieve the shortest incubation time and the lowest possible equilibration temperature and to ensure the reaction is complete and the separation of phases is efficient, the effect of equilibration temperature and time were examined. Maximum signals were obtained at temperatures 50°C. At 20°C, which was below the cloud point temperature of Triton X-114, the two phases cannot be formed and the metal complex cannot be extracted. Therefore, 50°C was selected as the working equilibration temperature. The equilibration time was also selected for the best signal and efficient extraction in the time span of 5-60 min. It was found that an incubation time of 20 min was sufficient for quantitative extraction and obtaining high sensitivity.The results showed that there are no appreciable improvements for a time longer than 20 min.

3.9. Effect of centrifuge time and rates

It is often required to preconcentrate trace amounts of Fe(III) ion with high efficiency in a short time. Therefore, using the optimum conditions so far obtained, CPE was performed on a set of experiments made up of 15 mL samples at pH 3.5, 1.0 mM ferron, 0.2 µg mL^{-1} Fe(III) ion and 0.34 M ionic strength by heating at 50°C for 20 min to determine the best conditions for centrifugation and subsequent cooling. The results indicate that centrifugation for 15 min at 3500 rpm and cooling for 5 min in an ice-bath lead to the highest recovery and sensitivity for the Fe(III) ion.

3.10. Characteristics of the method

The figures of merits can be found in Table 2. The enrichment factor (19.6) was determined as the ratio between the slopes of the calibration curves with and without preconcentration. The highest enrichment factors obtained for Fe(III) ions can be explained using Pearson's theory: Ferron is a hard base and Fe(III) is a hard acid; therefore, the reaction between ferron and Fe(III) must be more favorable than the reaction between ferron and other cations.

The limits of detection (LOD) were calculated as the ratio between three times the standard deviation of ten blank readings and the slope of the calibration curve after preconcentration were found to be 0.4 ng mL^{-1}. The high sensitivity and low detection limits of the present CPE method suggests the method is efficient and sensitive for determination of very low concentrations of the Fe(III) ion in various complex samples.

Brought to you by | Erciyes Üniversitesi
Authenticated
Download Date | 2/26/20 4:56 PM

Table 4. Levels of Fe(III) ions in various real samples (N = 3).

Sample	Added ($\mu g\ g^{-1}$)	Found ($\mu g\ g^{-1}$)	RSD %	Recovery %
Blood sample[a]	0.0 0.2	0.350 0.556	1.3 1.0	--- 102.5
Soil sample[a]	0.0 0.2	0.253 0.459	1.4 1.1	--- 103.0
Spinach sample[a]	0.0 0.2	0.396 0.605	1.3 1.0	--- 104.5
Milk sample[a]	0.0 0.2	0.428 0.634	1.3 1.0	--- 103.0
Meat sample[b]	0.0 0.2	0.359 0.566	1.3 1.0	--- 103.5
Liver sample[b]	0.0 0.2	0.319 0.525	1.4 1.1	---- 103.0
Orange juice	0.0 0.2	0.568 0.773	1.2 0.9	--- 102.5

a) All values are in $\mu g\ mL^{-1}$, b) all value are in $\mu g\ g^{-1}$,
All values were carried out after suitable dilution of real samples.

Table 5. Comparison of figures of merit of present method with previously reported.

Ligand	D.L[a]	Surfactant	Technique	L. R[b]	pH	E.F[c]	RSD %	PF[d]	Ref
Tan and Phen.	0.02 mg L^{-1}	TX-100 and TX-45	FAAS	Up to 0.35	3.0	---	----	20.0	14
8-quinolinolderivatives	----	Triton X-100	GF-AAS	0-0.064	1.70–5.44	95.9	2	102.2	15
PMBP	0.08	Triton X-100	GF-AAS	0-0.08	5-7	25	high	500.0	22

a) Detection limit ($ng\ mL^{-1}$), b) Linear range ($\mu g\ mL^{-1}$), c) Enrichment factor, d) Preconcentration factor.

Calibration with aqueous samples, submitted to the same pre-concentration procedure, showed itself to be sufficiently accurate to be applied to the various real samples. Correlation coefficients higher than 0.99 were obtained and only small deviations between sequential determinations were found. A preconcentration factor of 30 as the ratio of initial solution volume to the volume of surfactant rich phase was obtained. It should be mentioned that the preconcentration factor of our method can be improved by using larger volumes of initial solutions.

3.11. Interferences

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interferences studied were those related to the preconcentration step: cations that may react with ferron and anions that may form complexes with the Fe(III) ions and decrease extraction efficiency and sensitivity of method. The tolerance limit is defined as the ion concentration causing a relative error smaller than ± 5% related to the preconcentration and determination of analytes. The results are presented in Table 3. It can be seen that the major cations in real samples have no obvious influence on CPE of Fe(III) under the selected conditions. The high selectivity of the method may be attributed to the incorporation of an aromatic ring as a π donating compound and the oxygen atom as hard base in ligand structure, thus, leading to its high tendency for binding to Fe(III). On the other hand due to the low working pH range, most of cation could not compete appreciably with Fe(III) ion for complexation with ferron. Although aluminum has a known tendency toward ferron, the complexation between Al^{3+} ion and ferron takes place over a relatively long period of time (24 h) in at least three discrete stages which is significantly longer than the extraction time for Fe(III). Thus, the high content of aluminum can readily be tolerated.

3.12. Real Samples – Evaluation of method

We have explored the feasibility of the methodology using it for the determination of Fe(III) ion concentration in different matrices including, orange juice, meat, liver, spinach, soil and blood samples. To ensure that the method is valid and has reasonable accuracy and precision recovery of the Fe(III) ions in terms of method sensitivity in the various real samples were determined using this standard addition method and the results are shown in Table 4. The low relative standard deviations represent the high reproducibility in these measurements. Therefore, this proposed technique could be applied to the determination of ng ml^{-1} level of Fe(III) ion in different real samples.

Brought to you by | Erciyes Üniversitesi
Authenticated
Download Date | 2/26/20 4:56 PM

4. Conclusions

Cloud point extraction offers a simple, rapid, inexpensive and environmentally benign methodology for preconcentration and separation of trace iron in aqueous solutions. Triton X-114 was chosen for the formation of the surfactant-rich phase due to its excellent physicochemical characteristics. Ferron is a very stable and fairly selective complexing reagent. The proposed method gives very low LOD and good RSD, and can be applied to the determination of trace of Fe(III) ions in various real samples. In a full comparison of results presented in this paper with those previously reported (Table 5), the present method is superior in terms of linear range, detection limits and selectivity.

References

[1] F. Cotton, A.G. Wilkinson, Advanced inorganic chemistry, 3rd edition (Wiley, New York, 1998) 868-870
[2] J.H. Martin, S.E. Fitzwater, Nature, 331, 341 (1988)
[3] J.H, Martin, H. Gordon, R.M. Fitzwater, S.E. Broenkow, Vertex, Part A, 36, 649 (1989)
[4] R.J.M. Hudson., F.M.M. Morel, Abstracts of Papers, 198th National Meeting of the American Chemical Society, (Miami Beach, FL, 1989) 10-15
[5] M.H. Conklin, M.R. Hoffmann, Environ. Sci. Technol., 22, 899 (1988)
[6] V.A. Elrod, K.S. Johnson, K.H. Coale, Anal. Chem., 63, 893 (1991)
[7] M.J. Rosen, Surfactants and interfacial phenomena (Wiley, New York, 1987) 152
[8] M. Ghaedi, A. Shokrollahi, K. Niknam, M. Soylak, Sep. Sci. Tech., In press
[9] C.G. Pinto, J.L.P. Pavon, B.M. Cordero, Anal. Chem., 66, 874 (1994)
[10] D. Blankschtein, G. Thurston, G.B. Benedek, J Chem. Phys., 85, 7268 (1986)
[11] M. Corti, C. Minerov, V.J. Degiorgio, Phys. Chem., 88, 309 (1984)
[12] H. Tani, T. Kamidate, H.J. Watanabe, Chromatogr. A, 780, 229 (1997)
[13] A. Sanz-Medel, M.D.F. Campa, E.B. Gonzalez, M.L. Fernandez-Sanchez, Spectrochim. Acta B, 54, 251 (1999)
[14] E.K. Paleologos, D.L. Giokas, S.M. Tzouwara-Karayanni, M.I. Karayannis, Anal. Chim. Acta, 458, 241 (2002)
[15] A. Ohashi, H. Ito, C. Kanai, H. Imura, K .Ohashi, Talanta, 65, 525 (2005)
[16] K.A. Tony, S. Kartikeyan, B. Vijayalakshmy, T.P. Rao, C.S.P. Iyer, Analyst, 124, 191 (1999)
[17] X.P. Yan, M. Sperling, B. Welz, Anal. Chem., 71, 4353 (1999)
[18] D.L. Giokas, E.K. Paleologos, S.M. Tzouwara-Karayanni, M.I. Karayannis J. Anal. At. Spectrom., 16, 521 (2001)
[19] Q.F. Fang, M. Du, C.W. Huie, Anal. Chem., 73, 3502 (2001)
[20] D.L. Giokas, E.K. Paleologos, P.G. Veltsistas, M.I. Karayannis, Talanta, 56, 415 (2002)
[21] Y. Surme, I. Narin, M. Soylak, H. Yuruk, M. Dogan, Microchimica Acta, 157, 193 (2007)
[22] P. Liang, H.B. Sang, Z.M. Sun, J. Colloid Interface Sci., 304, 486 (2006)
[23] N. De Jong, M. Draye, A. Favre-Reguillon, G. LeBuzit, G. Cote, J. Foos, J. Colloid Interface Sci., 291, 303 (2005)
[24] A.R. Zarei, Anal. Biochem., 369, 161 (2007)
[25] A. Afkhami, M. Bahram, S. Gholami, Z. Zand, Anal. Biochem., 336, 295 (2005)
[26] C.D. Stalikas, Trends Anal. Chem., 21, 343 (2002)
[27] F.H. Quina, W.L. Hinze, Ind. Eng. Chem. Res., 38, 4150 (1999)
[28] A.E Martell, R.J. Motekaitis, Determination and use of stability constants, VCH Publishers, New York (1992)
[29] G .Schwarzenbach, H. Flaschka, Complexometric titrations, Methuen, London, (1969)
[30] M. Ghaedi, A. Shokrollahi,. A.H. Kianfar, A.S. Mirsadeghi, A. Pourfarokhi, M. Soylak, J. Hazar. Mat. In Press (2007)
[31] M.Ghaedi, F. Ahmadi, M. Soylak, J. Haz. Mat., 147, 226 (2007)
[32] M. Ghaedi, A. Shokrollahi, M.R. Fathi, S. Gharaghani, M. Soylak, Quim Nova, 31, 70 (2008)
[33] S.P. Fili, E. Oliveira, P.V. Oliveira, J. Braz. Chem. Soc., 14, 435 (2003)
[34] M. Ghaedi, A. Shokrollahi, F. Ahmadi, H.R. Rajabi, M. Soylak, J. Hazar. Mat., 150, 535 (2008)
[35] H. Karimi, M. Ghaedi, A. Shokrollahi, H. Rajabi, M. Soylak, J. Hazar. Mat., 151, 26 (2008)
[36] A. Shokrollahi, M. Ghaedi, M.S. Niband and H.R. Rajabi, J. Hazar. Mat., 151, 642 (2008)
[37] J.F. Rusling, C.N. Shi, T.F. Kumosink, Anal. Chem., 60, 1260 (1988)
[38] M.A.M. da Silva, V.L.A. Frescura, A.J. Curtius, Spectrochim. Acta, Part B, Atom. Spectrosc., 55, 803 (2000)
[39] J.R. Chen, K.C. Teo, Anal. Chim. Acta, 450, 215 (2001)
[40] C.G. Pinto, J.L.P. Pavon, B.M. Cordero, E.R. Beato,

Brought to you by | Erciyes Üniversitesi
Authenticated
Download Date | 2/26/20 4:56 PM

S.G .Sanchez, J. Anal. At. Spectrom., 11, 37 (1996)
[41] G.u TR, P.A. Galera-Gomez, Physicochem. A. Eng. Asp., 104, 365 (1999)
[42] C.C. Nascentes, M.A.Z. Arruda, Talanta, 61, 759 (2003)
[43] G. Komaromy-Hiller, N. Calkins, R. Wandruszka, Langmuir, 12, 916 (1996)
[44] J.K. Armstrong, B.Z. Chowdhry, M.J. Snowden, S.A. Leharne, Langmuir, 14, 2004 (1998)
[45] R.P. Frankewich, W.L. Hinze, Anal Chem., 66, 944 (1994)

Brought to you by | Erciyes Üniversitesi
Authenticated
Download Date | 2/26/20 4:56 PM