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Optimization of a cloud point extraction procedure with response surface methodology for the quantification of iron by means of flame atomic absorption spectrometry

HOSSEIN ABDOLMOHAMMAD-ZADEH[1]*, ABDOLHOSSEIN NASERI[2]
and GOLAMHOSSEIN SADEGHI[1]

[1]*Department of Chemistry, Faculty of Sciences, Azarbaijan University of Tarbiat Moallem, 35 Km Tabriz-Marageh Road, P. O. Box 53714-161, Tabriz, Iran and* [2]*Department of Analytical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran*

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Abstract: A simple micelle-mediated phase separation method has been developed for the pre-concentration of trace levels of iron as a prior step to its determination by flame atomic absorption spectrometry (FAAS). The method is based on the cloud point extraction (CPE) of iron using the non-ionic surfactant poly(ethyleneglycol–mono-*p*-nonylphenylether) (PONPE 7.5) without the addition of any chelating agent. Several variables affecting the extraction efficiency were studied and optimized utilizing a central composite design (CCD) and a three-level full factorial design. Under the optimum conditions, the limit of detection (*LOD*), limit of quantification (*LOQ*) and pre-concentration factor were 1.5 μg L^{-1}, 5.0 μg L^{-1} and 100, respectively. The relative standard deviation (*RSD*) for six replicate determinations at 50 μg L^{-1} Fe(III) level was 1.97 %. The calibration graph was linear in the range of 5–100 μg L^{-1}, with a correlation coefficient of 0.9921. The developed method was validated by the analysis of two certified reference materials and applied successfully to the determination of trace amounts of Fe(III) in water and rice samples.

Keywords: iron; ligand-less cloud point extraction; central composite design; full factorial design; flame atomic absorption spectrometry; rice samples.

INTRODUCTION

Iron is the fourth most abundant element in the earth's crust. There is an increasing interest in its determination due to its vital importance for living organisms and the consequent role in global carbon cycling. Iron deficiency in food may cause diseases, such as anemia. Many researchers and the World Health Organization (WHO) are therefore recommending fortification of food, mainly of

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* Corresponding author. E-mail: h.abdol@azaruniv.edu

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grain products, with iron as one of the best options to combat its deficiency.[1] However, too much Fe is harmful and can be toxic when exposures exceed the physiological requirements. In drinking waters, a sanitary security limit for iron was restricted to 2 mg L^{-1} by the WHO.[2] Therefore, it is essential to establish simple, rapid, and efficient methods for the monitoring of iron at trace levels in environmental, biological and food samples.

Various methods have been developed for the trace determination of iron, including flame atomic absorption spectrometry (FAAS),[3–5] electrothermal atomic absorption spectrometry (ET–AAS),[6–9] inductively coupled plasma optical emission spectroscopy (ICP–OES),[10] inductively coupled plasma mass spectrometry (ICP–MS),[11,12] X-ray fluorescence,[13] spectrophotometry,[14,15] and electroanalytical techniques.[16–18] However, each of these methods have advantages/limitations regarding cost, interferences and especially limits of detection. In comparison with other instrumental analytical techniques, FAAS is less expensive, faster and widely available. However, it has a limited sensitivity regarding metal ions determination in complex matrices, such as biological and food samples. Therefore, a preliminary separation and pre-concentration step prior to its determination is often required.

Several techniques have been developed for the separation and pre-concentration of trace amounts of iron, including co-precipitation, ion-exchange separation, liquid–liquid extraction (LLE), solid phase extraction (SPE), and cloud point extraction (CPE). CPE is a separation and pre-concentration procedure that has been applied for trace metal determination in several different matrices.[19–22] Its major advantages are simple experimental procedures, low cost, high pre-concentration factors and environmental safety.[23] These aspects include it in a set of analytical methods in agreement with "green chemistry" principles. When a micellar solution of a nonionic or weakly polar surfactant is heated up, the polarity of the surfactant is decreased. Above a certain temperature, called the cloud point, the polarity is almost displaced and, hence, the surfactant molecules separate out from the aqueous phase. As a result, the clear solution becomes turbid and phase separation occurs. At the cloud point, the homogenous surfactant solution separates into two phases, one of which, called the surfactant-rich phase, contains most of the surfactant, while the other phase, called the aqueous phase, contains mostly water and surfactant monomers at a concentration near the critical micelle concentration (CMC). The hydrophobic compounds initially present in the solution and bound to the micelles will be extracted to the surfactant-rich phase, which leaves only a very small portion in the aqueous phase.[23]

Metal ions could be extracted into the surfactant-rich phase directly or after complex formation with a suitable ligand. Method development for ligand-less CPE requires the optimization of several experimental parameters, such as pH, concentration of surfactant, ionic strength, *etc*. In traditional strategies, only one variable is changed whilst all the others remain constant. This approach does not allow the study of changes in the response that may occur when two or more factors are modified simultaneously. Furthermore, the optimization of the influencing parameters using "one variable-at-a-time" optimization method requires many experiments. Experimental design is an alternative to this strategy because it allows a large number of factors to be screened simultaneously and provides less ambiguous data. Furthermore, experimental designs combined with a response surface methodology help to visualize relationships between the responses and factor levels, which allow researchers to locate the region of the highest response values.[24]

In the present work, a ligand-less CPE method was developed for the separation and pre-concentration of Fe(III) in drinking water and rice samples prior to its determination by FAAS. In this CPE system, poly(ethyleneglycol–mono-*p*-nonylphenylether) (PONPE 7.5) was used as both the chelating agent and extractant. In addition, since the cloud point temperature for the employed ethanolic solution of the micellar system is around 25 °C, the requirement of a heating system to reach the phase separation was unnecessary. All these mentioned features are very important contributions because the majority of the methodologies reported in the literature require a heating step and a chelating reagent to realize the cloud point extraction process.[25] As a considerable number of variables can affect the extraction efficiency in a ligand-less CPE procedure, optimization and assessing of the proposed method were performed with the aid of experimental design and a response surface methodology (RSM). A central composite design (CCD) and a three-level full factorial design were employed for the determination of optimized experimental conditions for the ligand-less CPE of Fe(III) ions from real samples.

EXPERIMENTAL

Apparatus

A Varian model SpectrAA 220 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer, equipped with a deuterium lamp background correction and an iron hollow cathode lamp (operated at 15 mA) as the radiation source at the wavelength of 248.3 nm with 1 nm spectral band pass, was used. All of the absorbance measurements were performed using an air/acetylene flame at flow rates of 3.5 and 1.5 L min^{-1}, respectively. A centrifuge (Beckman GS-6, USA) was used to accelerate the phase separation process. The pH values were measured with a Metrohm pH meter (model 827, Switzerland), equipped with a combined glass electrode. A thermostated water bath (Julabo) model GMBH D-77960 was obtained from Germany. An electronic analytical balance (Mettler Toledo, PB303, Switzerland) was used for weighing the solid materials.

Standard solutions and reagents

All employed chemicals were of analytical-reagent grade and all solutions were prepared with deionized water (Shahid Ghazi Co., Tabriz, Iran). Stock solutions of iron and those used for the interference study (1000 μg mL^{-1}) were prepared by dissolving appropriate amounts of their corresponding salts in deionized water. The working standard solutions were prepared daily by stepwise dilution of the stock standard solution with deionized water. Suprapur® HNO_3 (65 %), H_2SO_4 (95–98 %) and H_2O_2 (30 %), used for sample digestion, ethanol and sodium bicarbonate were purchased from Merck (Darmstadt, Germany).

As it is not possible to obtain a real aqueous solution of the surfactant PONPE 7.5 (Tokyo Kasei Industries, Chuo-Ku, Tokyo, Japan) since the cloud point of its micellar solution is markedly below room temperature, it was experimentally convenient to prepare a 3 % (v/v) working solution by mixing 1.5 mL surfactant PONPE 7.5 with 20.0 mL ethanol (Merck) in a 50.0 mL volumetric flask and diluting to 50.0 mL with deionized water.

A stock buffer solution (0.2 mol L^{-1}) was prepared by dissolving appropriate amounts of sodium bicarbonate in deionized water and adjusting to pH 6 by adding a dilute HNO_3 solution. A 2 mol L^{-1} $NaNO_3$ solution was used for the ionic strength study. Two standard reference materials, SRM 1549 (Non-Fat Milk Powder) and SRM 1566b (Oyster Tissue) (from the National Institute of Standards and Technology (NIST), Giathersburg, MD, USA) were used for validation of the presented method. The pipettes and vessels used for trace analysis were kept in 15 % (v/v) nitric acid at least overnight and subsequently washed three times with deionized water.

Sample preparation

Tap water was obtained from the drinking water system of Azarshahr, Iran. After sampling, a 50.0-mL aliquot of this sample was analyzed within 24 h of collection without previous treatment or filtration.

After milling in a glass mortar, an accurately measured amount (25 mg) of a powdered rice sample or a standard reference material (NIST SRM 1566b, Oyster Tissue) was heated to dryness on a hot plate at a fairly low temperature in the glass beaker containing a mixture of concentrated nitric acid 65 % (10 mL) and hydrogen peroxide 30 % (5 mL).[26] After cooling to room temperature, the residue was dissolved in a 1.0 mL of HNO_3 0.1 mol L^{-1}. After dilution with deionized water, the pH was adjusted to nearly 6 by the addition of a dilute NaOH solution. Then, the solution was transferred into a 50.0 mL volumetric flask and after dilution to the mark with the deionized water, the concentration of Fe(III) was determined as described in the section “General procedure”. The same procedure was applied in the case of 1.0 g certified material (NIST SRM 1549) using concentrated sulfuric acid (10 mL) and nitric acid (4 mL) in the digestion step.

General procedure

For the cloud point extraction experiments, a 50.0 mL aliquot of a solution containing Fe(III) in the range of 5–100 µg L^{-1}, buffer solution (2×10^{-3} mol L^{-1}, pH 6), 0.5 mol L^{-1} $NaNO_3$ and 0.2 % (v/v) PONPE 7.5 were placed in a screw-cap conical-bottom polypropylene centrifuge tube. The mixture was diluted to 50 mL with deionized water. The resulting solution immediately became turbid at room temperature without heating. Phase separation was accelerated by centrifuging the tubes at 4000 rpm for 10 min. Subsequently, the aqueous phase was separated completely using a 10 mL syringe centered in the tube without cooling in an ice bath. Then, the surfactant rich phase was heated in a water bath and the residue was made up to 500 µL by adding 0.1 mol L^{-1} HNO_3 in ethanol to decrease the viscosity. Finally, the resultant solution was introduced into the flame of an AAS by conventional aspiration.

Data analysis

MINITAB (Minitab Inc.), release 14.0, statistical package was used for the experimental design, ANOVA and regression analysis of the experimental data. The fit quality of the polynomial model equation was expressed by the regression coefficient R^2, and its statistical significance was checked by the Fisher F-test. The level of significance given as values of the probability (p) was less than 0.05.

RESULTS AND DISCUSSION

In this study, ligand-less CPE combined with FAAS was developed for the extraction and determination of Fe(III) ions in water and rice samples. The non-ionic surfactant PONPE 7.5 was used as both the extracting solvent and chelating agent. Based on previous studies, under appropriate conditions, PONPE 7.5 may form a complex with Fe(III) through its polyoxyethylene groups and thereby can be extracted into the surfactant-rich phase.[27] Complex formation between the ether linkages of PONPE 7.5 and some cations, such as Pb(II), Al(III) and Co(II), has also been reported by other researchers.[25,28,29]

Optimization of ligand-less CPE procedure

The aim of this study was to optimize the experimental conditions for high extraction efficiency of Fe(III) ions by employing the ligand-less CPE methodology. Different variables can affect the extraction efficiency in a ligand-less CPE procedure, *i.e.* surfactant concentration, pH, ionic strength, type of buffer and its concentration, equilibrium temperature, incubation time, and centrifugation time and speed, and in most cases they are optimized. Therefore, a multivariate approach is recommended for their optimization. However, some variables might not have a significant effect and thus can be neglected. Based on previous experience,[30] the equilibrium temperature and incubation time have no significant effect upon the extraction efficiency, and a centrifugation time of 10 min at 4000 rpm is sufficient for complete phase separation. Therefore, the influence of five factors on the extraction efficiency, namely surfactant concentration, pH, ionic strength, buffer type and its concentration were studied and optimized utilizing two optimization methods, *i.e.*, a central composite design (CCD) and a three-level full factorial experimental design. First, three factors (surfactant concentration, pH and ionic strength) were optimized using CCD, and in the second step, after obtaining the optimum pH value from CCD optimization technique, the buffer type and its concentration were studied and optimized utilizing a three-level full factorial design.

Central composite design (CCD)

An optimization procedure was applied in order to determine the exact values of the most important factors to obtain high extraction efficiency. Systematic optimization procedures are performed by selecting an objective function, finding the most important factors and investigating the relationship between the responses and factors by the so-called response surface methodology (RSM). In this study, CCD or Box–Wilson,[31] one of the most commonly used response surface designs, was employed in order to determine the optimal conditions of the extraction process using a ligand-less CPE. Three independent variables, namely pH (X_1), the surfactant concentration (X_2), and ionic strength (X_3) were studied at five levels with four replicates at the central point. In the circumscribed CCD method, absolute upper and lower limits on certain factors are given, and these are specified as the star points. The coded levels of the variables and their real experimental values are given in Table I. The number of experiments in a CCD is defined by the expression: ($2f + 2f + C$), where f is the number of variables and C is the number of central points.[32] In this study, f and C were set at 3 and 4, respectively. Therefore, 18 experiments had to be performed for the CCD. In order to obtain a good estimate of experimental error (pure error), the 18 experiments were performed in duplicate. The thirty-six experiments were randomized in order to minimize the effect of uncontrolled variables, and divided into six blocks to remove the expected variation caused by some change during the course of the experiment. This design permitted the response to be modeled by fitting a second-order polynomial, which can be expressed as the following equation:

$$y = \beta_0+\beta_1X_1+\beta_2X_2+\beta_3X_3+\beta_{12}X_1X_2+\beta_{13}X_1X_3+ \\ +\beta_{23}X_2X_3+\beta_{11}X_1^2+\beta_{22}X_2^2+\beta_{33}X_3^2 \quad (1)$$

TABLE I. The variables and their coded values used in the central composite design (CCD)

Variable name	Abbreviation	Coded variables levels				
		–2	–1	0	+1	+2
pH	X_1	2	4	6	8	10
PONPE 7.5 concentration, % v/v	X_2	0.06	0.12	0.18	0.24	0.3
Ionic strength, mol L^{-1}	X_3	0.05	0.25	0.45	0.65	0.85

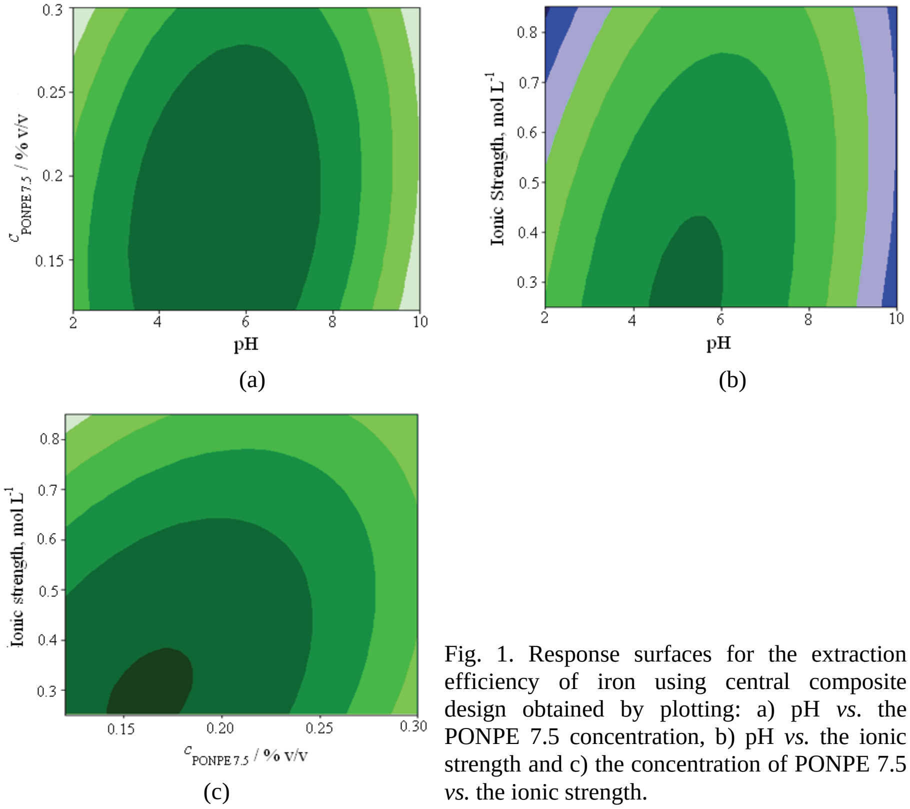
where y is the response function (recovery percentage), X_1, X_2 and X_3 are the three chemical variables, referring to the pH, concentration of PONPE 7.5 and ionic strength, respectively), β_0 is the intercept, β_1–β_3 are the linear parameters, β_{12}–β_{23} represent the interaction parameters and β_{11}–β_{33} are the quadratic parameters. After fitting the above equation by least-squares regression, ANOVA and regression analysis were employed to assess the significance of the variables. Estimates of the 10 parameters contained in Eq. (1) obtained by the least squares matrix are given in Table II. The determination coefficient obtained for this model was satisfactory (R^2 = 0.9518) and the lack of fit was not significant. These results show that the obtained model is reliable. The random distribution of the residual plot (residual *vs*. observed results) also confirmed this reliability (data not shown). The levels of significance of the results, given as values of the probability (p), are also listed in Table II. Values of p less than 0.05 were considered as significant. Accordingly, among linear parameters, β_2 and β_3 were not significant. However, their related quadratic and interaction parameters, *i.e.*,

β_{22}, β_{33} and β_{13}, were significant. Based on the obtained results, all of three variables were proved to have a significant effect on the extraction.

TABLE II. Regression results and analysis of variance of the central composite design (CCD)

Parameter	Parameter estimate	*p*-value
β_0	46.56	0.01
β_1	16.23	0.00
β_2	149.60	0.21
β_3	–45.914	0.25
β_{11}	–2.06	0.00
β_{22}	–947.78	0.00
β_{33}	–52.33	0.03
β_{12}	17.47	0.08
β_{13}	7.52	0.01
β_{23}	189.93	0.06

CCD was used to determine the variables that have a higher impact on extraction recovery and adjust them to yield the maximum probable recovery. The results may be used to give an insight on the robustness of the method close to the optimum conditions and show possible variable interactions. In this respect, the selection of the optimum conditions was enabled using the response surface plots *vs*. the affecting parameters. The obtained regression models were used to calculate the response surface for each variable separately. The response surface plots for the extraction efficiency as a function of each pair of independent variables are shown in Fig. 1. The response plots were generated with one variable kept at its central level, and varying the others within the experimental range. The response surfaces obtained for the pH and surfactant concentration, while keeping the $NaNO_3$ concentration constant at 0.45 mol L^{-1}, are shown in Fig. 1a. As can be seen, these factors nonlinearly affect the response. The response reaches the maximum value when pH and concentration of PONPE 7.5 are 6 and 0.2 % (v/v), respectively. From the contour plot and the obtained results listed in Table II, there is no significant interaction between the two previously mentioned variables. Fig. 1b shows the response surface function developed by the model considering pH and ionic strength, while keeping the PONPE 7.5 concentration constant at 0.18 % (v/v). The response reaches the maximum value when 6.0 for pH and 0.5 mol L^{-1} of $NaNO_3$ for ionic strength were taken, and from the contour plot and the obtained results listed in Table II, there is a significant interaction between these two variables. The response surface function developed by the model considering the concentration of PONPE 7.5 and ionic strength, while keeping the pH value constant at 6.0 is shown in Fig. 1c, from which it can be seen that these factors nonlinearly affect the response. The response reaches the maximum value when 0.2 % (v/v) for the concentration of PONPE 7.5 and 0.5 mol L^{-1} $NaNO_3$ for the ionic strength were taken and from the contour plot and the obtained results listed in Table II, there is no significant interaction between the two previously mentioned variables. The levels corresponding to the maximum response were selected as the optimum levels. Thus, the optimum conditions for ligand-less cloud point extraction were defined as: sample pH of 6.0, PONPE 7.5 concentration of 0.2 % (v/v) and ionic strength adjusted by 0.5 mol L^{-1} $NaNO_3$.



(a)

(b)

(c)

Fig. 1. Response surfaces for the extraction efficiency of iron using central composite design obtained by plotting: a) pH *vs.* the PONPE 7.5 concentration, b) pH *vs.* the ionic strength and c) the concentration of PONPE 7.5 *vs.* the ionic strength.

Full factorial design

Based on the obtained results from previous studies,[27,30,33] the type of buffer and its concentration are important variables that affect the extraction efficiency of ligand-less cloud point extraction of metal ions using the non-ionic surfactant PONPE 7.5. Hence, after obtaining the optimum value of the pH, it was necessary to find a suitable buffer and optimize its concentration. For this purpose, another kind of response surface methodology, three-level full factorial design (3^f), was used. Thus, two variables that could potentially affect the extraction efficiency were identified as the type of buffer and its concentration. Each variable was studied at three levels (*i.e.*, acetate, phosphate and bicarbonate buffer solutions, as three levels of the first variable and 0.002, 0.006 and 0.01 mol L^{-1} buffer concentrations, as three levels of the second variable). Therefore, nine (3^2) experiments had to be performed and in order to obtain a good estimation of the experimental error, the nine experiments were performed in duplicate. The coded levels of the variables, together with their real experimental values, are given in Table III. This design permitted the response to be modeled by fitting a second-order polynomial and the optimum values of variables determined. From the obtained model and response surfaces (not shown here), 2×10^{-3} mol L^{-1} bicarbonate buffer solution was selected for the subsequent experiments.

TABLE III. Variables and values used for the three-level full factorial design

Variable name	Abbreviation	Coded factor levels		
		–1	0	+1
Type of buffer	X_1	Acetate	Phosphate	Bicarbonate
Buffer concentration, mol L^{-1}	X_2	0.002	0.006	0.01

Sample volume and pre-concentration factor

The Fe(III) concentration in real samples, such as natural waters, is usually low. Thus, the sample volume is one of the most important parameters in development of a pre-concentration method, since it determines the sensitivity enhancement of the technique. Thus, the effect of sample volume was examined in a range of 10–65 mL for 50 μg L^{-1} Fe(III) under optimum conditions. It was observed that extraction efficiency of Fe(III) was quantitative between 10–50 mL and for the higher sample volumes, extraction efficiency decreased. Subsequently, a sample volume of 50 mL was selected for the further experiments. Thus, by analyzing 0.5 mL of the final solution after the pre-concentration of 50 mL of sample solution, the pre-concentration factor was found to be 100.

Analytical figures of merit

Under the optimum conditions, a series of experiments were designed to determine the linear range, precision, detection limit and enrichment factor. The calibration graph was linear in the range of 5–100 μg L^{-1}, with a correlation coefficient of 0.9921. The regression equation was $A = 0.007c_{\rm Fe} + 0.043$, where A is the absorbance and $c_{\rm Fe}$ is the Fe(III) concentration in μg L^{-1}. The limit of detection (*LOD*) and limit of quantification (*LOQ*) ($n = 6$), calculated as three times and ten times, respectively, the standard deviation of the blank signal divided by the slope of the calibration curve, were 1.5 and 5.0 μg L^{-1}, respectively. The relative standard deviation (*RSD*) resulting from the analysis of 6 replicates of 50 mL solution containing 50 μg L^{-1} Fe(III) was 1.97 %. As the amount of Fe(III) in the sample solution was measured with a final volume of 0.5 mL, the solution was concentrated by a factor of 100. Therefore, the enrichment factor, defined as the ratio of between the volume of the initial sample solution and the final volume of the surfactant-rich phase, was 100.

Interferences

The effects of foreign species on the determination of Fe(III) ion were investigated by measuring the absorbance of the solutions containing 50 μg L^{-1} of this ion in the presence of various amounts of other ions. The tolerance limit was taken as the amount of added ion causing less than ±5 % relative error ($p < 0.05$ at the 95 % confidence level) in the determination of Fe(III) ion. The maximum tolerances to the investigated cations and anions are summarized in Table IV. It can be seen that most of examined cations and anions did not interfere with the extraction and determination. Therefore, the proposed method is selective for the determination of Fe(III). As shown later, these results allowed the interference-free determination of Fe(III) in water and rice samples.

TABLE IV. Tolerance limits of interfering ions in the determination of 50 μg L^{-1} of iron by means of FAAS

Coexisting ions	Interferent to analyte ratio
Na^+, K^+, Cs^+,Ca^{2+}, Mg^{2+}, Sn^{2+}, Cl^-, Br^-, I^-, NO_3^-, CO_3^{2-}	1000:1
Ni^{2+}, Cr^{3+}, Bi^{3+}, Zn^{2+}, Ba^{2+}, Co^{2+}, Sr^{2+}	500:1
VO_3^-, Ag^+, Cu^{2+}	100:1
Cd^{2+}, PO_4^{3-}, Pb^{2+}	50:1

Application of the method

To test the reliability of the method, it was applied for the determination of Fe(III) ions in water and rice samples. In order to verify the accuracy of the established procedure, recovery experiments were also performed by spiking the samples with different amounts of Fe(III) before any pretreatment. The obtained results are given in Table V. As can be seen, recoveries between 96.7 and 104.2 % were obtained, which confirm the accuracy of the proposed method. Additionally, the accuracy of the proposed procedure was verified by applying the method to the determination of Fe(III) in two standard reference materials, NIST SRM 1566b (Oyster Tissue), and NIST SRM 1549 (Non-Fat Milk Powder) with certified Fe(III) contents of 205.8±6.8 and 1.78±0.1 μg g^{-1}, respectively. The obtained value of Fe(III) found in the former standard using the proposed procedure was 207.2±5.3 μg g^{-1} (mean ± standard deviation, $n = 3$), which is in good agreement with the certified concentration. However, in the case of the SRM 1549 standard, the found Fe(III) concentration was lower than detection limit of the presented method. It can be concluded that the proposed method is accurate and could be employed for the determination of Fe(III) in complex matrices, such as water and biological and food samples.

TABLE V. Determination of iron in water and rice samples (results of recoveries of spiked samples and certified reference materials)

Samples	Found Fe[a], μg g^{-1}	Added Fe, μg g^{-1}	Found Fe[a], μg g^{-1}	Recovery[b], %
Tap water[c]	24.6±2.2[d]	10.0[d]	34.5±2.1[d]	99. 0
Mineral water[e]	6.1±0.4[d]	10.0[d]	16.2±0.6 [d]	101.0
Rice$_{(1)}$[f]	104.0±4.8	40.0	143.2±5.3	98.0
Rice$_{(2)}$[g]	118.0±6.5	40.0	159.7±7.1	104.2
Rice$_{(3)}$[h]	146.0±5.9	40.0	184.7±7.6	96.7
SRM 1549	1.78±0.1[i]	Not detected		–
SRM 1566b	205.8±6.8[i]	207.2±5.3[j]		0.68[k]

[a]Mean ± standard deviation, n = 3; [b]recovery (%) = 100(found–base)/added; [c]from drinking water system of Azarshahr, Iran; [d]μg L^{-1}; [e]from ZamZam Co. Tabriz, Iran; [f, g and h]grown in Thailand, Iran (Bafekr Co.) and India (Sella Co.), respectively, and obtained from a local market (Azarshahr, Iran); [i]certified value; [j]assayed value; [k]relative error

Comparison of the presented method with other CPE/FAAS procedures

A comparison of the presented method with other CPE/FAAS procedures is given in Table VI. Apparently, the presented method has a low *LOD*, high preconcentration factor and these characteristics are comparable or even better than most of the other methods in Table VI. Besides the advantages of the multivariate optimization strategy, this methodology is a reproducible, simple and low cost method. Thus, the presented method could be used for Fe(III) determination in routine analytical laboratories.

TABLE VI. Comparison of the presented method with other proposed CPE methods coupled with FAAS

Complexing agent	Sample matrix	Sample volume, mL	*PF*[a]	Linear range μg L^{-1}	Detection limit, μg L^{-1}	*RSD* / %	Ref.
APDC[b]	Water	10	50	<100	3.5	1.8	34
APDC	Wine	10	NA [c]	<350	20	2.4	35
APDC	Water	250	NA	10−100	NA	NA	36
Ferron[d]	Environmental, biological	15	30	10−400	0.4	2.4	19
Ferron	Water, Milk	20	75	10−250	1.7	2.1	20
IYPMI[e]	Environmental, biological	15	30	10−300	2.8	2.0	21
Neutral Red[f]	Spice	25	98	2.5−200	0.7	2.1	22
Ligand-less	Water, Rice	50	100	5−100	1.5	1.97	This work

CONCLUSIONS

In this research, an effective method was developed for the extraction and determination of trace amounts of Fe(III) using a relatively straightforward procedure. A multivariate optimization strategy was used to obtain the optimum conditions for the extraction of Fe(III) by ligand-less CPE. Optimization of the CPE variables was carried out using the central composite design (CCD) and three levels full factorial experimental design. The presented procedure does not require any chelating agent, long incubation time or cooling after centrifugation, and could be applied, as an inexpensive and wide spread technique for trace iron monitoring in routine analytical laboratories. Environmental pollution is limited to a very small amount of surfactant rich-phase. This fact is particularly attractive because the "green chemistry" concept can be employed here. Phase separation can be achieved at room temperature and the extraction efficiency is high, resulting in a low detection limit and high pre-concentration factor. The optimized ligand-less CPE coupled to FAAS enabled quantification of trace levels of Fe(III) in the different real samples with complicated matrices.

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ИЗВОД

ОПТИМИЗАЦИЈА ПРОЦЕДУРЕ ЕКСТРАКЦИЈЕ СА ТАЧКОМ ЗАМУЋЕЊА МЕТОДОЛОГИЈОМ ОДГОВОРА ПОВРШИНА ЗА КВАНТИФИКАЦИЈУ ГВОЖЂА ПРИМЕНОМ ПЛАМЕНЕ АТОМСЕ АПСОПЦИОНЕ СПЕКТРОМЕТРИЈЕ

HOSSEIN ABDOLMOHAMMAD-ZADEH[1], ABDOLHOSSEIN NASERI[2] и GOLAMHOSSEIN SADEGHI[1]

[1]*Department of Chemistry, Faculty of Sciences, Azarbaijan University of Tarbiat Moallem,35 Km Tabriz-Marageh Road, P. O. Box 53714-161, Tabriz, Iran* и [2]*Department of Analytical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran*

Развијена је једноставна сепарациона метода за преконцентрацију трагова гвожђа, преко мицеларне фазе, која претходи одређивању помоћу пламене атомске апсорпционе спектрометрије. Метода је базирана на екстракцији са тачком замућења, уз коришћење нејонског сурфактанта полиетиленгликолмоно-*para*-нонилфенил етра без додавања хелирајућег агенса. Испитивано је неколико променљивих које утичу на ефикасност екстаркције и оптимизовано коришћењем централног композитног дизајна и потпуног факторског дизајна на три нивоа. Под оптималним условима граница детекције, граница квантификације и преконцентрациони фактор износе: 1,5 μg L^{-1}, 5,0 μg L^{-1} и 100, редом. Релативна стандардна девијација за шест поновљених одређивања за концентрацију Fe(III) од 50 μg L^{-1} износи 1,97 %. Калибрациона крива је линеарна у опсегу 5–100 μg L^{-1} са коефицијентом корелације од 0,9921. Развијена метода је валидирана анализом два сертификована референтна материјала и успешно примењене за одређивање трагова гвожђа Fe(III) у води и пиринчу.

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