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ÖZCAN YALÇINKAYA

ORHAN MURAT KALFA

ALİ REHBER TÜRKER

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Chelating agent free solid phase extraction (CAF-SPE) method for separation and/or preconcentration of iron(III) ions

Özcan YALÇINKAYA, Orhan Murat KALFA, Ali Rehber TÜRKER*

Faculty of Science and Arts, Gazi University, 06500, Ankara-TURKEY

e-mail: aturker@gazi.edu.tr

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This paper presents a chelating agent free solid phase extraction (CAF-SPE) method for the separation and/or preconcentration of trace iron(III) ions. This method is based on the sorption of Fe(III) ions without using any chelating agent onto Amberlyst 36 resin. A good relative standard deviation (3%), high recovery (>95%), high enrichment factor (100), and low detection limit ($0.32 \mu\text{g L}^{-1}$) were obtained. The adsorption capacity of resin was 117 mg g^{-1} for iron(III). The method was applied for the determination of iron various in water and commercial tea bag samples. The accuracy of the method was confirmed by analyzing Certified Reference Material (GBW 07605).

Key Words: Iron determination; solid phase extraction; preconcentration; water analysis; flame atomic absorption spectrometry; separation.

Introduction

Metal quantification at low concentration levels ($\leq \mu\text{g L}^{-1}$) comprises one of the most important targets in analytical chemistry. The general trend in modern analytical chemistry for the determination of trace components is pretreatment of sample and developing ecologically safe, sensitive, and selective methods.¹ This interest is demonstrated in different areas such as medicine, the environment, and the food industry.²⁻⁴ Atomic spectrometry techniques are extensively employed for the quantification of metallic species in various samples. Among these techniques, flame atomic absorption spectrometry presents desirable characteristics, such as low costs, operational facilities, high analytical frequency, and good selectivity.⁵ However, the direct

*Corresponding author

determination of trace metals by this technique is generally difficult because of matrix interference problems and low concentrations of metals in samples. These problems can be overcome by applying sample pretreatment procedures such as separation and/or preconcentration, before the detection procedure. Solid-phase extraction (SPE)⁶⁻⁸ is a widely used sample pretreatment method that is highly effective and ecologically safe compared to the other techniques such as liquid-liquid extraction,⁹ cloud-point extraction,¹⁰⁻¹² and liquid membrane.¹³

Among the metals, iron in small amounts is essential for most life on earth, including humans and animals. It is well known that iron deficiency is the most common cause of anemia. On the other hand, too much iron can cause several health problems. High levels of iron are associated with an increased risk for cancer, heart disease, and other illnesses such as endocrine problems, arthritis, diabetes, and liver disease.¹⁴ A sanitary security limit for iron was restricted to 2 mg L⁻¹ by the World Health Organization.¹⁵ European legislation has established a maximum contaminant level of water as 200 µg L⁻¹ for iron.¹⁶

Mahmoud *et al.* applied a preconcentration procedure to the determination of iron in environmental waters using a silica gel-chemically immobilized purpurogallin (SGBP).¹⁷ Elçi *et al.* described a flame atomic absorption spectrometry method for the determination of trace amounts of iron, lead, and chromium ions after adsorption onto XAD-2000 and elution with 10.0 mL of 0.5 mol L⁻¹ HNO₃.¹⁸ Kendüzler and Türker proposed a method for the determination of iron, manganese, and zinc in water samples by flame atomic absorption spectrometry after preconcentration onto Ambersorb 572.¹⁹

In many preconcentration procedures, such as those described above, either a chelating agent is added to the solution to form the metal chelate or a microorganism is immobilized on a support of column prior to the enrichment procedure.²⁰⁻²⁴ In the proposed study, no agent was used as a chelating material or immobilized material to increase the enrichment factor and the recovery of Fe(III) ions, because Fe(III) ions were retained sufficiently on the Amberlyst 36 resin without using any chelating agent in the solution or on the sorbent. This resin has been used before, as a catalyst in the reactions of some organic components.²⁵⁻²⁷ We first reported the use of this resin as a solid phase extractor for preconcentration of some Mn(II), Cr(III), Ni(II), and Cu(II) ions in various media.²⁸⁻³¹ In those studies, chelating agent free solid phase extraction, which reduces the usage of additional chemicals, was also applied.

In this study Amberlyst 36 was examined again as a solid phase extractor for the separation and/or preconcentration of Fe(III) from aqueous solution. Amberlyst 36, which has good physical and chemical properties such as porosity, durability, and purity and is resistant in concentrated mineral acids, bases, and organic solvents for a long time for the preconcentration of iron and determination of it by FAAS, was designed as a chelating agent free solid-phase extractor (CAF-SPE). The analytical parameters in order to obtain quantitative recovery for iron were studied systematically. This procedure was successfully applied to the determination of iron in water and tea samples. The main advantages of the method over many other solid-phase preconcentration methods are the ability to study in an acidic medium and not requiring any chelating agent.

Experimental

Instrumentation

A Varian 240 FS model flame atomic absorption spectrophotometer, equipped with an iron hollow-cathode lamp, a deuterium lamp for background corrector, and an air-acetylene flame as the atomizer, was used for the determination of iron. The apparatus was run under the conditions suggested by the manufacturer, i.e; lamp current, 9.0 mA; wavelength, 248.3 nm; bandwidth of the slit, 0.5 nm; acetylene flow rate, 1.0 L min⁻¹. A Jenway 3010 Model pH meter was used to measure the pH of solutions.

Reagents and solutions

All reagents were of analytical grade and all solutions were prepared using triple distilled water. The laboratory glassware was kept overnight in a 5% nitric acid solution. Afterwards, it was rinsed thoroughly with water and dried. A stock aqueous solution of iron(III) (1000 mg L⁻¹) was prepared by dissolving 0.4838 g of FeCl₃.6H₂O (Merck) in 100 mL of 1 mol L⁻¹ HCl solution. A working aqueous solution of Fe(III) (10 mg L⁻¹) was also prepared from iron stock solution of 1000 mg L⁻¹. Nitric acid (65%), hydrofluoric acid (48%), and hydrochloric acid (37%) acid were from Merck. Amberlyst 36 (Aldrich) was used after washing with methanol, 1 mol L⁻¹ HCl solution, and water, consecutively, and dried for 4 h at 60 °C.

Collection and preparation of samples

A tap water sample was collected from our laboratory, and commercial mineral water and tea bags were obtained from a local market in Ankara, Turkey. Mineral water samples were diluted with triple distilled water prior to analysis to decrease interfering effects. For this purpose 200 mL of mineral water was diluted to 500 mL. Dam water was collected from Atatürk Dam. The water samples were filtered through a Millipore cellulose nitrate membrane of pore size 0.45 μm. The samples were stored in polythene bottles and then acidified with 1.0 mL of concentrated hydrochloric acid per liter of sample. The following mineralization procedure was applied to tea samples (tea bag sample and certified reference tea leaves GBW 07605, China): A 100 mg of tea sample was taken in a 250 mL PTFE beaker. For dissolution, a minimal volume of 0.05 mol L⁻¹ nitric acid was added to moisten the sample thoroughly, followed by 10 mL of concentrated nitric acid. The beaker was heated on a hot plate for about 3 h. After cooling to room temperature the contents of the beaker were heated to near dryness. This procedure was repeated twice by using 5 mL of concentrated nitric acid. The resulting solution was transferred into a 25 mL volumetric flask by washing the interior surface of the beaker with small portions of 0.05 mol L⁻¹ nitric acid and diluted to the mark with water. Then 5 mL of each of these sample solutions was diluted to 100 mL to decrease the iron concentration at the working range of the atomic absorption spectrometric method. In addition, H₂O₂ was added to real sample solutions to oxidize the iron ions to Fe(III). Finally, the preconcentration and determination procedure given below was applied.

Column preparation

The glass column, having a stopcock, was 15 cm in length and 0.8 cm in internal diameter. A small amount of glass wool was placed at one end of the column in order to hold a certain amount (500 mg) of resin. Then another small glass wool plug was inserted onto the top of the resin. The bed height of the resin in the column was approximately 1.5 cm. It was washed successively with water, methanol, and 1 mol L⁻¹ hydrochloric acid. After each use, the resin in the column was washed with water and stored in water for the next experiment.

Preconcentration and determination procedure

The proposed preconcentration procedure was tested with model solutions prior to the determination of trace iron in samples. A 50 mL aliquot of a solution containing 10 µg of Fe(III) was placed in a beaker and adjusted to pH 2 using HCl solution. The column was preconditioned by passing the aqueous solution of pH 2 through the column and then the model solution was passed through the column at a flow rate of 5 mL min⁻¹. The adsorbed Fe(III) ions on the column were eluted into a 10 mL calibrated flask using 10 mL of 2 mol L⁻¹ hydrochloric acid solution. The eluent was analyzed for the determination of iron concentration by FAAS. The Amberlyst 36 column was used repeatedly after washing with 5 mL of 2 mol L⁻¹ hydrochloric acid solution and triply distilled water, consecutively. Using the procedure described above, the recovery of the iron was calculated from the ratio of the quantities of iron before and after the enrichment, respectively.³²

Results and discussion

In order to obtain the maximum recoveries and to determine the applicability of the method, many parameters such as pH of sample solution, amount of resin, the type and concentration of elution solution, sample volume, and flow rates of sample solution were optimized. Interfering effects and adsorption isotherms were also studied.

Effect of pH

The first variable optimized was the pH of the sample solution, because pH is one of the most important environmental factors influencing not only the site of resin but also the solution chemistry of heavy metals.

The recovery was determined by applying the general sorption procedure by changing the pH of the sample solution in the range of 1-8. The sample solutions were adjusted to the desired pH with diluted hydrochloric acid and/or a diluted ammonia solution and passed through the resin. The eluent was then analyzed by FAAS. The results for the recovery of Fe(III) are shown in Figure 1. Quantitative recoveries (>95%) were obtained at a wide range of pH values (1.5-8). In order to prevent the negative effects of basic solution such as precipitation, pH 2 was selected for subsequent studies. Lower pH values are generally preferred for analyzing real samples, because real samples (geological, biological, etc.) are dissolved generally with acids or stored in acidic medium, and the precipitation of metal ions, an unwanted situation, could be prevented at lower pH values. The suitability of a wide range of pH values reveals that controlling the pH does not play an important role in enhancement selectivity and sensitivity.

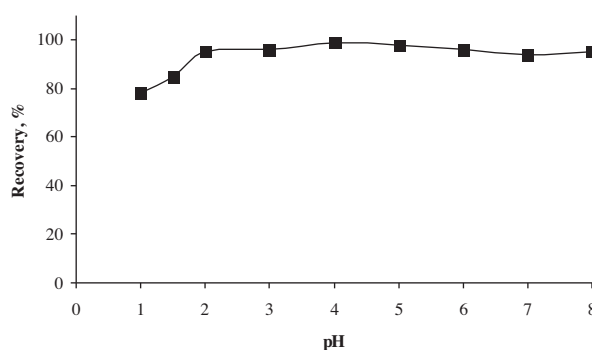


Figure 1. The effect of pH on the recovery of iron (sample volume, 50 mL; amount of iron, 10 μg ; eluent, 10 mL 2 mol L^{-1} HCl; flow rate of sample, 5 mL min^{-1}).

Effect of amount of resin

The amount of resin is another important parameter that affects the recovery. A quantitative retention is not obtained when the amount of resin is less. On the other hand, an excess amount of resin prevents the elution of the retained analyte by a small volume of eluent quantitatively. For this reason, the amounts of resin were optimized. For this purpose, different amounts of Amberlyst 36 (100-800 mg) were studied. Quantitative recoveries of the iron were obtained at above 300 mg of resin. Therefore, 500 mg of resin was used for subsequent experiments because of easy elution and for obtaining sufficient recovery in real samples containing various ions.

Effect of type and concentration of eluent

In order to choose a suitable eluent for desorption of the retained Fe(III) ions, to obtain a final concentration of iron of 1.0 $\mu\text{g mL}^{-1}$, the Fe(III) ions were stripped with varying concentrations of different inorganic acids as eluting agents. For this purpose, 5 and 10 mL of 1 and 2 mol L^{-1} HCl and HNO_3 were examined, respectively. The results showed that Fe(III) ions could be eluted efficiently (>95% recovery) with 10 mL of 2 mol L^{-1} HCl. Thus, in subsequent experiments, 10 mL of 2 mol L^{-1} HCl solution was chosen as the stripping agent to desorb the Fe(III) ions.

Effect of flow rate of sample solution

The flow rate of the sample solution through the column is another important parameter, since it not only affects the recovery of analyte, but also controls the time of analysis. Because a large volume of sample solution is needed in the preconcentration, it is always expected that sample solutions can be passed through the column at a higher flow rate without reducing the recoveries. In order to evaluate the effect of flow rate, a set of solutions (50 mL) containing 10 μg Fe(III) was adjusted to the optimum pH value. They were then passed through the column at a flow rate that varied from 0.5 to 5 mL min^{-1} adjusted by gravity action. The analyte was desorbed with 10 mL of 2 mol L^{-1} HCl solution from the resin and determined as mentioned in the recommended procedure. According to the results, flow rates in the examined range had no significant effect on the recoveries of the iron. These results indicate that the Fe(III) sorption is very rapid. This fact is a useful

feature of the proposed method, because it permits a higher sample throughput. Therefore, the flow rate of 5 mL min^{-1} was found to be suitable for optimum loading of the analyte and was used for further studies. Because the eluent volume is very low the effect of eluent volume was not studied and 1 mL min^{-1} was selected as the eluent flow rate.

Effect of sample volume

The influence of sample volume on recoveries of iron was also examined in order to determine the maximum applicable sample volume or minimum analyte concentration. For this purpose, Fe(III) ions were preconcentrated from volumes of 50, 100, 250, 500, 750, and 1000 mL of sample solution containing $10 \mu\text{g Fe(III)}$, which corresponds to an iron concentration of 0.2, 0.1, 0.04, 0.02, 0.014, and $0.01 \mu\text{g mL}^{-1}$, respectively, were passed through the column at optimum experimental conditions by applying the general procedure mentioned above. The recovery of Fe(III) was quantitative ($>95\%$) for all of these sample volumes. The results show that iron was recovered quantitatively up to 1000 mL of sample solution. At higher sample volumes, the recoveries decreased gradually with increasing volume of sample solution. Since the original sample volume and final volume of solution (after preconcentration) are 1000 mL and 10 mL, respectively, an enrichment factor of 100 can be achieved for Fe(III). The enrichment factor could have been further improved by using a larger sample volume and/or a smaller eluent volume.

Influence of interfering species

The effects of potential interferences occurring in water samples on the determination of iron were investigated using the optimized preconcentration procedure. Metal ions were added individually to a solution as their nitrate or chloride salts, and the proposed preconcentration method was applied. The experimental results are given in Table 1. As can be seen, there was no interfering effect on the recovery of the iron up to 100 mg L^{-1} Na^+ , Mg^{2+} , K^+ , and Ca^{2+} ; 50 mg L^{-1} Zn^{2+} ; and 25 mg L^{-1} Ni^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+} , Mn^{2+} , and Cr^{3+} . The acceptable level of recovery is 95%-105%. These results indicate that the proposed method may not be applied for the determination of iron in high saline solutions such as sea water.

Adsorption isotherm and adsorption capacity

The adsorption capacity of the resin was determined by the batch technique. Therefore, the effect of contact (shaking) time on the adsorption of the iron was evaluated at room temperature ($25 \pm 1 \text{ }^\circ\text{C}$). For this purpose, 50 mL of the model solution (Fe(III) , $2 \mu\text{g mL}^{-1}$) and 100 mg of the resin were placed in a flask. The pH of the solution was adjusted to 2 and the flask was shaken at different time intervals at 200 rpm. The amount of residual Fe(III) in the supernatant was determined by FAAS after filtration. The data obtained from the adsorption of iron on the sorbent showed that a contact time of 50 min was sufficient to achieve equilibrium and the adsorption did not change with further increases in contact time.

The adsorption behavior of Amberlyst 36 was determined by studying the amount of adsorbed iron as a function of iron concentration. Therefore, 50 mL samples of solutions having iron concentrations in the range of 20 to 500 mg L^{-1} at pH 2 were shaken for 50 min with a constant weight (100 mg) of the resin. The profile of the adsorption isotherm of the resin for iron is shown in Figure 2, representing the amounts of adsorbed iron

Table 1. Effect of some ions on the recovery of iron.

Interfering ions	Concentration, (mg L ⁻¹)	R ^a (%)	Interfering ions	Concentration, (mg L ⁻¹)	R ^a (%)
Na ⁺	1	96 ± 3	K ⁺	1	102 ± 1
	5	97 ± 2		5	96 ± 1
	25	95 ± 1		25	101 ± 2
	100	95 ± 1		100	97 ± 2
Mg ²⁺	1	96 ± 3	Ca ²⁺	1	98 ± 3
	5	97 ± 2		5	97 ± 4
	25	96 ± 3		25	99 ± 1
	100	99 ± 4		100	98 ± 2
Al ³⁺	1	102 ± 3	Co ²⁺	1	98 ± 3
	5	101 ± 3		5	100 ± 4
	25	95 ± 2		25	96 ± 2
Zn ²⁺	1	102 ± 4	Cd ²⁺	1	102 ± 3
	5	101 ± 1		5	98 ± 1
	50	97 ± 3		25	95 ± 3
Ni ²⁺	1	101 ± 1	Cu ²⁺	1	103 ± 2
	5	98 ± 3		5	96 ± 2
	25	99 ± 4		25	95 ± 3
Cr ³⁺	1	102 ± 2	Mn ²⁺	1	98 ± 3
	5	98 ± 3		5	102 ± 3
	25	100 ± 3		25	93 ± 4

^a Mean ± standard deviation for 3 determinations.

versus the iron concentration of the supernatant under equilibrium conditions. The analysis of the isotherm data is important in order to develop an equation that accurately represents the results. When the adsorption profile reaches a plateau, a monolayer adsorption is supposed to be established. The data of the isotherm reveal that the adsorption process conforms to the Langmuir model. In Figure 2, the graph shows an excellent fit to the data in the concentration interval studied in all cases for the Langmuir model. A modified Langmuir equation conformed to this kind of adsorption isotherm as represented below:

$$\frac{C_E}{Q_E} = \frac{C_E}{Q_0} + \frac{1}{Q_0 b}$$

where C_E is the concentration of Fe(III) in the solution at equilibrium (mg/L), Q_E is the amount of sorbed iron per gram of resin at equilibrium (mg/g), b is the “affinity” parameter or Langmuir constant (L/mg), and Q_0 is the “capacity” parameter (mg/g). Based on the linear form of the adsorption isotherm derived from plots of C_E/Q_E vs. C_E , the constant Q_0 values were calculated from the slope of the graph. The values of Q_0 (adsorption capacity) and b were found to be 117 mg/g and 0.122 L mg⁻¹, respectively. The adsorption capacity of Amberlyst 36 for iron is much higher than that of the sorbents already reported in the literature.^{33–35}

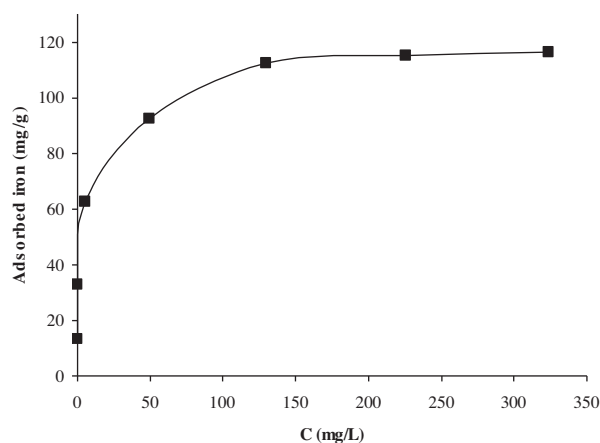


Figure 2. Adsorption isotherm of Amberlyst 36 for iron in batch procedure.

Analytical figures of merit

By using direct aspiration in FAAS without the preconcentration system the linear range for iron determination was between 0.1 and 5 $\mu\text{g mL}^{-1}$. The calibration equation was $A = 0.031 + 0.109 C$, where C is the iron concentration in $\mu\text{g mL}^{-1}$, and A is the absorbance. Calibration equation calculations are based on the average of triplicate readings for each standard solution.

The recovery of spiked iron and the precision of the procedure for 7 replicates determined as the percent relative standard deviation of recovery at the optimum conditions given above (amount of iron, 10 μg ; volume of solution, 50 mL; pH, 2; elution solution, 10 mL 2 mol L^{-1} HCl; flow rate, 5 mL min^{-1}) were in the range of 93%-102% (mean, $95 \pm 3\%$) and about 3%, respectively.

In order to determine the instrumental detection limit, 50 mL of a blank solution (triple water) was passed through the column and retained iron was eluted using 50 mL of the elution solution mentioned above. There was no preconcentration step. The instrumental detection limit based on 3 times the standard deviation of the blank ($\text{LOD}_i = 3\sigma/m$; where m is the slope of calibration curve) was found to be 32 $\mu\text{g/L}$ for iron ($N = 20$). The analytical or method detection limit (MDL) was calculated by dividing the instrumental detection limit by the enrichment factor (100 in the present work).^{36,37} The analytical detection limit (LOD_a) for iron was 0.32 $\mu\text{g L}^{-1}$. The limit of quantification (LOQ) was calculated as 0.96 $\mu\text{g L}^{-1}$ by considering 3 times the LOD value. As is well known, this iron concentration cannot be determined directly by flame AAS with sufficient accuracy and precision.

Validation of the proposed method

In order to evaluate the accuracy of the developed procedure, iron was also determined in certified reference material (tea leaves GBW 0760), and spiked water and tea samples. Iron concentration as the mean of 5 determinations at 95% confidence level was found as $251 \pm 8 \mu\text{g g}^{-1}$ with about 5% percent relative error. It was found that there was no significant difference between the result found by the proposed method and the certified value ($264 \pm 10 \mu\text{g g}^{-1}$) according to the t-test at 95% confidence level. Good agreement was obtained between the estimated content by the proposed method and the certified values for the analytes. The

relative errors obtained (below 5%) are acceptable for quantitative trace analysis. These results also indicate that the developed method is not affected by potential interferences from the major matrix elements of the analyzed reference material (tea leaves).

Analytical application

Since it was found that the proposed preconcentration method was useful for the preconcentration of trace iron in the presence of other metal ions and that there is good agreement between the estimated content and the certified values, the method was applied to the determination of iron in water and tea samples under optimal experimental conditions. The accuracy of the method was also checked by measuring the recovery of spiked samples (Table 2). Relative errors, below 5%, demonstrate the applicability of the method and indicate that the proposed method is essentially free from interferences when applied to the analysis of drinking water and tea samples.

Table 2. Determination of iron in various samples.

Sample	Added	Found ^a $\bar{x} \pm \frac{ts}{\sqrt{N}}$	Relative error (%)
Tap water	-	$39.2 \pm 0.3 \mu\text{g L}^{-1}$	-
	$40.0 \mu\text{g L}^{-1}$	$77.5 \pm 0.6 \mu\text{g L}^{-1}$	-2
Mineral water ^b	-	$28.0 \pm 0.2 \mu\text{g L}^{-1}$	-
	$30.0 \mu\text{g L}^{-1}$	$60.4 \pm 0.6 \mu\text{g L}^{-1}$	+4
Dam water	-	$38.9 \pm 0.4 \mu\text{g L}^{-1}$	-
	$40.0 \mu\text{g L}^{-1}$	$75.8 \pm 0.5 \mu\text{g L}^{-1}$	-4
Tea	-	$150 \pm 5 \mu\text{g g}^{-1}$	-
	$150 \mu\text{g g}^{-1}$	$292 \pm 9 \mu\text{g g}^{-1}$	-3

^a Mean of 7 determinations for tap water and mean of 5 determinations for other samples at 95% confidence level.

^b The composition of mineral water (values given on its label) (mg L^{-1}): Al: 0.0087, Ca: 235.5, Mg: 108.4, K: 63, Na: 265.2, SO_4^{2-} : 138.3, F^- : 0.46, Cl^- : 25.77, PO_4^{3-} : 1.87, HCO_3^- : 1865, $\text{NO}_3^- < 1$, $\text{NO}_2^- < 0.0005$

Conclusion

The proposed CAF-SPE procedure provides a simple, selective, accurate and precise method for the preconcentration and determination of iron in large volumes of various sample solution. The main advantages of the method over the many other solid-phase preconcentration methods are permitting study in a wide range of pH with no necessity for buffer to control the pH values precisely, the ability to study in an acidic medium, higher sample volume, and not requiring the chelating agent. Lower pH values are generally preferred for analyzing real samples, because real samples (geological, biological, etc.) are dissolved generally with acids and it is unlikely that sample components would precipitate. Amberlyst 36 does not show volume change in operating at wide pH ranges and therefore easy flow properties and constant flow rates can be maintained. 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. The present method is superior in terms of linear range, detection limits, and selectivity. The detection limit achieved was satisfactory for the samples studied, and can be improved by using more sensitive detectors such as ICP-AES and ICP-MS.

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