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Solid Phase Extraction and Flame Atomic Absorption Spectroscopic Determination of Trace Amounts of Iron(III) Using Octadecyl Silica Membrane Disks Modified with 2-Mercaptopyridine-1-oxide

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A simple and selective method for rapid extraction and determination of trace amounts of iron(III) using octadecyl-bonded silica membrane disks modified with 2-mercaptopyridine-1-oxide and flame atomic absorption spectroscopy is presented. The factors influencing extraction efficiency were evaluated, including the nature of the counter anion, pH of the sample solution, amount of ligand, flow rate of the sample and type of stripping solution. The maximum capacity of the membrane disk, modified by 10 mg of the ligand, was found to be 926 ± 6 μg of iron(III). The breakthrough volume was greater than 2500 ml. Iron(III) was completely recovered (>99%) from water with a preconcentration factor of more than 166. The limit of detection of the proposed method was 0.63 ng ml^{-1}. The various cationic interferences had no effect on the recovery of iron(III) from the binary mixtures. The proposed method was applied to the determination of iron(III) from three different water samples.

Keywords: Solid phase extraction, 2-Mercaptopyridine-1-oxide, Flame atomic absorption spectrophotometry

INTRODUCTION

The determination of trace amounts of iron from different types of matrices is of great importance. Iron is an essential element used by the body for the production of hemoglobin, which absorbs oxygen and distributes it to the tissues. Non-heme iron is stored in the body by the protein ferritin and transported by the protein transferrin, neither of which are normally saturated with iron(III). However, in cases of iron overload the natural storage and transport proteins are overwhelmed and the iron spills over into other tissues and organs, such as the muscle, spleen and liver [1], proving to be toxic [2]. Numerous techniques, such as spectrophotometric [3-6], potentiometric titration [7], flame [8] and electrothermal atomic absorption spectrophotometry [9], flow-injection [10-14] and photoacoustic [15] methods, have been used for the determination of iron species. However, due to the low levels of iron in environmental samples, its separation from other coexisting elements is essential, and usually necessitates a preconcentration step prior to iron determination.

Liquid-liquid extraction of iron(III) in the presence of various ligands [16-18] has attracted considerable attention. However, the uses of classical extraction methods for this purpose are usually time-consuming, labor-intensive and require large amounts of high purity solvents for extraction. Nevertheless, several other techniques for the pre-concentration and separation of iron have been proposed using an adsorbent, such as *Aspergillus niger* [19] or ammonium tetraphenylborate-naphthalene [20] followed by solid-phase extraction (SPE) [21-30].

Solid-phase extraction is an attractive technique that reduces the consumption of and exposure to solvent, disposal

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*Corresponding author. E-mail: gkhayatian@yahoo.com costs and extraction time [31,32]. Recently, SPE disks were successfully utilized for the extraction and analysis of many different organic and environmental matrices [33-35]. Moreover, the SPE disks modified by suitable ligands are successfully used for the separation and sensitive determination of metal ions [36,37].

In this paper, a rapid, efficient and selective method for the solid phase extraction, concentration and determination of iron(III) in aqueous media using octadecyl silica membrane disks modified by 2-mercaptopyridine-1-oxide, hereafter referred to as thione (Fig. 1), and flame atomic absorption spectrometry (FAAS) is reported.

EXPERIMENTAL

Instrumentation

The determinations of iron(III) and other cations were performed on a Shimadzu AA-670 atomic absorption spectrophotometer (Kyoto, Japan) under the recommended conditions for each metal ion. The wavelength used to detect iron(III) was 248.3 nm and the bandwidth 0.2 nm. The determination of Hg^{2+} was made by cold vapor AAS on a Varian-220, VGA-77, under the recommended conditions. A Metrohm E-691 digital pH meter equipped with a combined glass calomel electrode was used for the pH adjustments.

Reagents

Extra pure methanol, acetonitrile, nitric acid, hydrochloric acid, picric acid (all from Merck) and 2-mercaptopyridine-1-oxide (Fluka, Buchs, Switzerland) were used as received. Nitrate, perchlorate, chloride and sulfate salts of the cations (all from Merck) were of highest purity available and used without any further purification except for vacuum drying over P_2O_5. The anions, such as sodium perchlorate, sodium chloride, sodium fluoride, sodium thiosulfate, sodium acetate and sodium citrate (all from Merck) were used as received. Doubly distilled deionized water was used throughout.

The standard stock solution of iron(III) (1000 mg l^{-1}) was prepared by dissolving an appropriate amount of $Fe(NO_3)_3 \cdot 6H_2O$ in the presence of a few milliliters of concentrated HNO_3 solution and standardized by titration with EDTA [38]. Working standard solutions were prepared daily by diluting the stock standard solution with doubly distilled water and adjusting the pH to 3 by the drop wise addition of 0.5 M HNO_3.

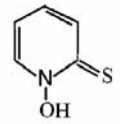

Fig. 1. Structure of ligand 2-mercaptopyridine-1-oxide (thione).

General Extraction Procedure

Extractions were performed using Empore™ membrane disks (3 M Co., St. Paul, MN, USA): 47 mm diameter, 0.5 mm thickness with 90% octadecyl-bonded silica (8 µm particle, 60 Å pore size) and 10% PTFE fiber. The disks were used in conjunction with a standard Millipore 47 mm filtration apparatus connected to a water aspirator [35,36].

In order to remove potential interferences and to ensure optimal extraction of the analyte of interest, the recommended disk cleaning and conditioning was performed before use. After placing the membrane disk in the filtration apparatus, 10 ml methanol was poured onto the disk and immediately was drawn through the disk by applying a slight vacuum. After all of the solvent had passed through the disk, it was dried by passing air through it for few minutes. The disk conditioning was then begun by pouring 10 ml methanol onto the disk. Immediately, a low vacuum was applied and the solvent was drawn through the disk until solvent surface almost reached the surface of the disk, without allowing the disk to soak without vacuum, nor allowing air to contact with the surface of the disk. Then, a thione solution (10 mg in 5 ml acetonitrile) was introduced onto the disk and drawn slowly through the disk using a slow vacuum. The passed solution was collected in a test tube. Then, 2 ml water was added to the test tube and the resulting colloidal solution was again introduced to the reservoir and slowly passed through the disk. The filtration step was repeated until the passed solution became completely clear. Finally the disk was washed with 25 ml water and dried by passing air through it.

The general procedure for the extraction of iron(III) on the membrane disk was as follows. The modified disk was first washed with 0.5 ml methanol followed by 25 ml water with the same pH as the sample solution. This step wets the surface of the disk prior to the extraction of iron(III) from water and ensures good contact between the analyte and the ligand. The appropriate volume of iron(III) sample solution (adjusted to pH 3 using HNO_3) and 1.0×10^{-3} M picric acid was passed through the membrane (flow rate 5-10 ml min^{-1}). After the extraction, the disk was dried completely by passing air through it for a few minutes. The extracted iron was stripped from the membrane disk using 15 ml of 0.5 M nitric acid. The eluted solution was collected in a test tube and then transferred into a 25 ml calibrated flask. The eluted solution was finally diluted to 25 ml with 0.1 M nitric acid.

Procedure for Certified Reference Material

To test the proposed method against a known sample, we applied it to a standard aluminum alloy (NBS.SRM-85 B) with percentages of various of metals (Cu 3.99, Mg, 1.49, Mn, 0.61, Cr 0.211, Si 0.18, Ni 0.084, Zn 0.03, Ti 0.022, Pb 0.021, Ga 0.019, V 0.006), and a certified value of iron at 0.24%. A 0.5 g sample was dissolved in hydrochloric acid (1:1), aided by heat, and the solution was diluted to 1000 ml with hydrochloric acid (1:1). A 50 ml aliquot of this solution (after adjusting the pH to 3 with NaOH) was transferred onto the separating disk. The general determination procedure was then applied.

RESULTS AND DISCUSSION

Some preliminary experiments were undertaken in order to investigate the quantitative retention of iron(III) by the membrane disk in the absence and presence of thione after the recommended washing, wetting and conditioning procedures were carried out. The disks modified with 10 mg of the ligand were able to quantitatively retain 5 mg l^{-1} iron(III) from solutions containing 1.0×10^{-3} M picric acid, while the bare membrane disk could only retain about 17% of the cations.

Effect of Counter Anion

Recovery is often improved by the presence of a high selectivity counter ion. In order to investigate the effect of the presence of counter ions on the recovery of iron(III) by the modified disks, sodium acetate, sodium perchlorate, sodium chloride and picric acid were tested (Table 1). The obtained results indicated that, among the counter ions examined, only 1.0×10^{-3} M picric acid allowed for the quantitative extraction of iron(III) from sample solutions, most probably due to the high hydrophobicity of the picrate anion compared to the other anions [39]. On the other hand, these results revealed that thione behaves as a neutral ionophore at pH 3 [40,41]. Jones *et al.* [41] determined the pK_a to be 4.76 for thione; thus, the iron(III) ions are retained as ion-pair complexes on the membrane disks. The probable mechanism may be given as follows [42]:

Table 1. Effect of Counter Anions on Percent Recovery of Iron(III)[a]

Counter anions	Recovery (%)
$NaCH_3COO$	83
NaCl	81
$NaClO_4$	90
Picric acid	100

[a] Initial samples contained 0.25 mg iron(III) in 50 ml water and 1.0×10^{-3} M counter anion.

$$3C_5H_5NOS(I)_{(org)} + Fe^{3+}_{(aq)} + 3Picrate^{-}_{(aq)} \longrightarrow Fe(C_5H_5NOS)_3^{3+}(Picrate)^{-}_{3(org)}$$

Choice of Eluent

In order to choose a proper eluent for the retained iron(III), after the extraction of 0.25 mg iron(III) from 50 ml water by the disk modified with 10 mg of thione, the iron(III) was stripped with 15 ml of different reagents at varying concentrations. From the data given in Table 2, it is obvious that using 15 ml of 0.5 M HNO_3 can strip the retained iron(III) quantitatively.

Effect of pH

The influence of the pH of aqueous samples on the recovery of 0.25 mg of iron(III) from 50 ml solutions containing 1.0×10^{-3} M picric acid was studied in the pH range 0.0-7.5. The pH was adjusted using either 0.1 M nitric acid or sodium hydroxide. The results indicated that iron(III) is retained quantitatively by the modified membrane disk in the pH range of 2.5-3.5. The extraction efficiency of the modified

Table 2. Percent Recovery of Iron(III) from the Modified Disk Using Different Stripping Agents[a]

Stripping agent \ Concentration (M)	0.01	0.05	0.10	0.50	1.00
HNO_3	55.0	63.4	72.9	100.3	99.0
NaF	35.0	38.0	43.0	20.0	-
EDTA	50.5	67.5	65.0	-	-
Citrate	39.0	43.0	67.0	68.4	-
HCl	23.0	49.0	93.0	95.7	94.3

[a] Initial samples contained 0.25 mg iron(III) in 50 ml water and 1.0×10^{-3} M picric acid; 15 ml of stripping agent was used.

membrane sharply decreased in highly acidic media, which is most probably due to protonation of the ligand and picrate ion which decreased ion pair formation between $Fe(C_5H_5NOS)_3^{3+}$ and the picrate anion. Above pH 3.5, the decrease in extraction efficiency could be due to the formation of iron(III)-hydroxyl complexes in the sample solution [22]. Higher pH values (pH > 7.5) were not tested because of the possibility of hydrolysis of octadecyl silica in the disks.

Effect of Amount of Ligand

In order to investigate the optimum amount of thione on the quantitative extraction of iron(III) by the membrane disk, iron(III) was extracted from a 50 ml aqueous solution under the optimal experimental conditions using varying amounts of ligand, from 0 to 15 mg. It was found that extraction of iron(III) is quantitative in the range of 8-15 mg of thione. Hence, subsequent SPE experiments were carried out with 10 mg of the ligand.

Effect of Flow Rates of Sample and Stripping Solution

The effect of flow rates on the recovery was examined using optimum conditions. The sample solution was passed through the disk with the flow rates adjusted in the range of 1-20 ml min^{-1}. The optimum flow rate of the sample solution was found to be 8 ml min^{-1} (Fig. 2). On the other hand, quantitative stripping of iron(III) from the disk was achieved with 0.5 M HNO_3 solution at a flow rate of 1.5 ml min^{-1}.

Analytical Performance

Under optimal experimental conditions, when solutions of 100 µg iron(III) in 10, 50, 100, 500, 1000, 2000, and 2500 ml water were passed through the disk, iron(III) was quantitatively retained in all cases. Thus, the breakthrough volume for the method must be greater than 2500 ml, providing a concentration factor of >166 (in 15 ml). The limit of detection, the concentration corresponding to three times the standard deviation of the blank signal, was found to be 0.63 ng ml^{-1} for iron(III) using a synthetic blank solution. The capacity of the modified disks was determined by passing 50 ml portions of sample solutions containing 1000 µg of iron and 1.0×10^{-3} M picric acid at pH 3.0, followed by the determination of the retained metal ions in the eluting solution using FAAS. The maximum capacity of the disk obtained from three replicate measurements was 926 ± 6 µg of iron on the disk. The precision of the determination of iron(III) was evaluated under the optimum conditions mentioned above. For this purpose, ten successive retention and elution cycles were performed with 15 µg iron(III) in 50 ml of solution. It was

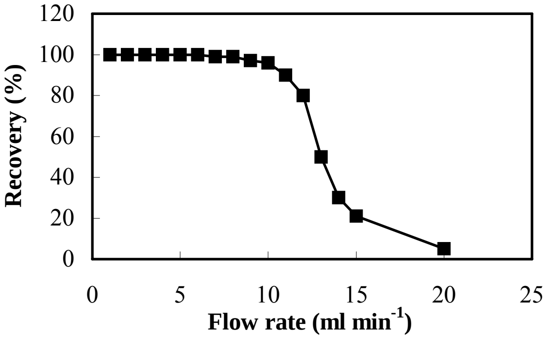

Fig. 2. Effect of flow rate of sample solution on percent recovery of iron(III).

found that the percent recovery of iron(III) was 100.0 ± 1.7. Thus, the precision of the method is good and the recovery of the analyte is quantitative.

In order to investigate the selective separation and determination of iron(III) from its binary mixtures with various metal ions consisting of an aliquot of aqueous solutions (250 ml) containing 35 μg iron(III) and milligram amounts of other cations was taken. The recommended procedure was followed and the results, summarized in Table 3, show that the iron recovery is almost quantitative in the presence of milligrams of diverse ions.

The proposed method was applied to the extraction and determination of iron(III) from 500 ml water samples from the Kamyaran River, Sanandaj Spring and drinking water, all from Kurdistan, Iran. The samples were fixed with concentrated HNO_3 (pH < 2) and analyzed as soon as possible after sampling (Table 4). As seen from Table 4, the concentration of iron(III) in river water, spring water and drinking water were 0.21, 0.17 and 0.l3 mg l^{-1}, respectively. Furthermore, added iron(III) is quantitatively recovered from the water samples. In addition, the disk is stable for up to 40 runs using 100 ml samples at pH 3.

Certified Reference Material Analysis

The proposed method was successfully applied to the determination of iron in a standard aluminum alloy (NBS.SRM-85 B). Our method found the sample to be 0.234% (±0.002) iron, using an average of five determinations, *vs*. the certified value of 0.24%, showing good precision and accuracy.

Comparison of this Method with other Systems

As shown in Table 5, several methods have been reported in the literature for the preconcentration and determination of iron. The main advantages of this method are: (i) simple and fast preparation of the extraction system, (ii) very high preconcentration factor and (iii) very good detection limit.

CONCLUSIONS

The proposed method provides is a selective, simple, sensitive and accurate technique for the preconcentration and extraction of iron(III). Quantitative recovery of iron(III) is

Table 3. Effect of Interference by Various Metal Ions on the Percent Recovery of Iron(III) in Samples with Binary Mixtures[a]

Diverse ion	Amount taken (mg)	%Recovery of iron(III)
Na^+	130	101.4 (0.4)[b]
K^+	90	102.5 (0.5)
NH_4^+	130	100.43 (0.3)
Ag^+	54	102.4 (1.4)
Cu^{2+}	130	100.16 (0.7)
Pb^{2+}	56	102.25 (2.1)
Zn^{2+}	160	101.7 (0.8)
Ba^{2+}	68	97.9 (1.0)
Ni^{2+}	175	99.5 (1.3)
Cd^{2+}	96	100.7 (0.2)
Mn^{2+}	140	97.3 (2.1)
Sr^{2+}	84	99.6 (0.5)
Mg^{2+}	370	98.6 (0.7)
Hg^{2+}	12	96.5 (2.3)
Cr^{3+}	68	101.7 (1.1)
Al^{3+}	243	98.6 (2.0)
Bi^{3+}	82	99.2 (2.1)

[a] Initial samples contained 35 μg iron(III) and different amounts of diverse ions in 250 ml water (with 1.0×10^{-3} M picric acid). [b] Values in parentheses are RSDs based on three replicates.

Table 4. Determination of Existing and Added Iron(III) in Different Water Samples[a]

Sample	Iron(III) added (mg l^{-1})	Iron(III) determined (mg l^{-1})	RSD (%)[b]
River water	0.00	0.21	0.11
	0.40	0.60	0.50
Spring water	0.00	0.17	0.22
	0.40	0.54	0.070
Drinking water	0.00	0.13	0.31
	0.40	0.52	0.050

[a] Adjusted to pH 3 with HNO_3. [b] Based on three replicates.

Table 5. Comparison of the Present Method with other Systems[a]

Parameter	FAAS (present method)	FAAS [22]	FAAS [23]	FAAS [24]
Detection technique	SPE-FAAS	SPE-FAAS	SPE-FAAS	SPE-FAAS
Sorbent	Octadecyl silica modified with thione	Analcime zeolite modified with NPMPS	Pyrrolidine ditiocarbamate on a column (Chromosorb-102)	Cellulose loaded with 8-hydroxyquinoline
Eluent	HNO_3 (0.5 M)	EDTA (0.1 M)	Acetone	HCl (1 M)
Sample flow rate (ml min^{-1})	8	1	3.5	3
Elution flow rate (ml min^{-1})	1.5	1	-	2
Detection limit (ng ml^{-1})	0.63	0.084	11	3.3
Repeatability (%)	1.7	1.13	5	3.94
Preconcentration factor	>166	60	60	300
pH	2.5-3.5	3.5	4-6	>3
Recovery (%)	> 99	~99	>95	98

[a] FAAS: Flame atomic absorption spectroscopy; NPMPS: 5-(4-nitrophenylazo)-N-(2',4'-dimethoxy-phenyl)salicylaldimine.

achieved even when various metal ions are present at much higher concentrations using this method, which was found to be better than other existing methods. In addition, this method is very useful in the separation and determination of iron(III) in environmental and drinking water samples.

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