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Preconcentration of Copper(II) and Iron(III) from natural waters using a C18-silica packed mini-column and their determination by FAAS

Cennet Karadaş*[1]

ABSTRACT

In the present study, a new solid phase extraction method was developed for simultaneous preconcentration of copper(II) and iron(III) ions from natural waters. The analytes were first complexed with 4-aminoantipyrine at pH 8.0 and then passed through the column packed with C18-silica. The retained analytes on the C18-silica were eluted with 1.0 mL of 0.5 M nitric acid in 10% ethanol and determined using flame atomic absorption spectrometer. The influence of several variables such as sample pH, ligand amount, eluent type, sample and eluent flow rates, and sample volume on the retention/or elution of the analytes were examined and optimized. The effects of some interfering ions on the retentions of analytes on C18-silica were also enquired. The detection limits were 0.89 µg/L for Cu and 1.41 µg/L for Fe with a preconcentration factor of 20. The calibration graphs were linear in the concentration range of 5.0-125 µg/L of the analytes. The calibration equations were $A=2.36x10^{-3}$ C + $4.55x10^{-4}$ for Cu and $A=1.45x10^{-3}$ C + $8.88x10^{-4}$ for Fe. The accuracy of the proposed method was verified by the analysis of SPS-SW2 Batch 127 certified reference water. The method was applied to river water and seawater samples with recoveries in the range of 95-99%.

Anahtar Kelimeler: copper, iron, preconcentration, solid phase extraction

C18-silika dolgulu mini kolon kullanılarak doğal sulardan Bakır(II) ve Demir(III) iyonlarının önderiştirilmesi ve alevli AAS ile tayini

ÖZ

Bu çalışmada, doğal su örneklerinden bakır(II) ve demir(III) iyonlarının aynı anda önderiştirilmesi için yeni bir katı faz ekstraksiyon yöntemi geliştirilmiştir. Analitler 4-aminoantipirin ile pH 8.0'de kompleksleştirilmiş ve C18-silika ile paketlenmiş mini kolondan geçirilmiştir. Kolonda alıkonunan analitler %10 etanolde hazırlanmış 1 mL 0,5 M nitrik asit çözeltisi ile elüe edilmiş ve alevli atomik absorpsiyon spektrometresi ile tayin edilmiştir. Örnek pH'sı, ligand miktarı, elüent türü, örnek ve elüent akış hızları ve örnek hacmi gibi çeşitli değişkenlerin analitlerin alıkonması veya elüsyonu üzerine etkisi incelenmiş ve optimize edilmiştir. Ayrıca analitlerin C18-silika kolonunda alıkonmasına bazı yabancı iyonların etkileri incelenmiştir. Gözlenebilme sınırları 20 kat önderiştirme faktörü ile Cu için 0,89 µg/L ve Fe için 1,41 µg/L olarak belirlenmiştir. Kalibrasyon grafikleri 5,0-125 µg/L bakır(II) ve demir(III) derişimi aralığında doğrusaldır. Kalibrasyon eşitlikleri Cu için $A=2,36x10^{-3}$ C + $4,55x10^{-4}$ ve Fe için $A=1,45x10^{-3}$ C + $8,88x10^{-4}$ olarak belirlenmiştir. Önerilen yöntemin doğruluğu sertifikalı referans su örneğinin (SPS-SW2 Batch 127) analizi ile doğrulanmıştır. Geliştirilen yöntem nehir suyu ve deniz suyu örneklerine % 95-99 arasındaki geri kazanım değerleri ile başarılı bir şekilde uygulanmıştır.

Keywords: bakır, demir, önderiştirme, katı faz ekstraksiyonu

* Corresponding Author
[1] Balıkesir Üniversitesi, Fen-Edebiyat Fakültesi, Kimya Anabilim Dalı, 10145, Balıkesir, Türkiye, karadas@balikesir.edu.tr

1. INTRODUCTION

Heavy metals can easily enter water, plants, soil and food through a number of pathways such as mining and smelting operations, industrial production and use, and agricultural and domestic use of metals and metal-containing compounds [1]. Some of these metals, such as iron, copper, manganese, and zinc, etc. are necessary at low concentrations for many biological systems, whereas they are harmful at high concentrations [1,2]. Copper plays a crucial role in the metabolism of carbohydrate and lipid [3]. Its deficiency in the body can lead to different health problems such as anaemia, kinky hair and arteriosclerosis. However, its excessive intake causes accumulation of the metal in liver cells and hemolytic crisis, jaundice, and neurological disturbances [4-6]. Iron is a cofactor in many enzymes and vital for many living bodies owing to its role in transfer of oxygen and electron, and synthesis of DNA [7]. On the other hand, exposure to excess iron causes tissue damage because of the generation of free radicals [8]. Therefore, improvement of accurate methods for the determination of Cu and Fe in environmental samples is important.

Flame atomic absorption spectrometry (FAAS) is one of the most popular spectroscopic techniques because of its low cost, short analysis time, ease of use and good selectivity [9]. However, since it has relatively poor sensitivity, direct determination of metals using FAAS is restricted if they are present at very low concentrations. Matrix effects may also be problematic [2,9]. A separation and preconcentration step is therefore frequently required. Solid phase extraction (SPE) is a commonly utilized preconcentration method due to its various benefits such as low cost, high preconcentration factor, simple operation, reusability of sorbents, environmentally friendliness and low organic solvent consumption [10]. This extraction method is based on transferring analytes from the aqueous phase to the solid phase. Different solid phases have been used as sorbent for the separation and preconcentration of copper or iron, including multi-walled carbon nanotubes [11], hybrid amine-functionalized titania/silica nanoparticles [12], C18 cartridge [13], polyurethane foam [14], Schiff base-modified duolite XAD 761 [15], Dowex Optipore L-493 resin [16], Schiff base-modified Amberlite XAD-4 [17], etc.

In this work, a new SPE method was developed for the preconcentration of Fe(III) and Cu(II) using a mini-column packed with C18-silica. 4-aminoantipyrine was used as complexing agent. The effects of several analytical parameters were enquired in detail. The suggested method was used to the determination of Cu and Fe in natural waters. The accuracy of the method was verified by analyzing SPS-SW2 Batch 127.

2. MATERIALS AND METHODS

2.1. Chemicals and Solutions

4-aminoantipyrine and silica gel 100 C_{18}-reversed phase were purchased from Fluka (Gillingham, Dorset, UK). Nitric acid, sodium acetate, sodium dihydrogen phosphate, acetic acid, boric acid, sodium tetraborate, ammonium acetate, methanol, and ethanol were obtained from Sigma-Aldrich (St. Louis, MO, USA). All the aqueous solutions were prepared using deionized water obtained from AquaTurk Reverse Osmosis System (HSC ARITIM, Istanbul, Turkey). Stock standard solutions of Cu and Fe (1000 mg/L) were obtained from VHG Labs. To adjust the sample pH, sodium dihydrogen phosphate/phosphoric acid (pH 3), sodium acetate/acetic acid (pH 4-5), ammonium acetate/acetic acid (pH 6-7) and sodium tetraborate/boric acid (pH 8-9) buffer solutions were used. The SPS-SW2 level 2 Batch 127 certified surface water was obtained from Spectrapure Standards AS (Oslo, Norway).

2.2. Apparatus

A PerkinElmer AAnalyst 200 FAAS (Shelton, CT, USA) furnished with deuterium background correction, multi-element (Fe, Cu, Mn, Ni, Co) hollow cathode lamp and an air-acetylene burner was used in this work. The acetylene and air flow rates were 2.3 mL/min and 10 mL/min, respectively. The working wavelengths were 324.75 nm for Cu and 248.33 nm for Fe. The pH measurements were performed using a Hanna Instruments pH-meter (Cluj-Napoca, Romania). A Watson Marlow model 323 SD peristaltic pump (Falmouth, UK) and a glass mini-column of 5 cm length and 3 mm diameter (Omnifit, Cambridge, UK) were used for the SPE experiments.

2.3. Column Preparation

The glass mini-column was filled with silica gel 100 C_{18}-reversed phase. Before use, the mini-column was activated by washing with 10 mL of methanol and washed with 10 mL of deionized water. Then 10 mL of 2 M HNO_3 was passed through the C18-silica column to remove any metallic contaminants.

2.4. Procedure

An aliquot of the sample/or standard solution containing Fe(III) and Cu(II) ions was put into a 50 mL polyethylene tube. Then 1.0 mL of borate buffer (pH 8.0) and 0.5 mL of 1×10^{-2} M ligand solutions were added. The solution was diluted to 20 mL with deionized water. The activated mini-column was washed with deionized water for 60 s at a rate of 4.2 mL/min and then pre-conditioned by passing borate buffer solution (pH 8.0) for 20 s at the same flow rate. The sample solution was pumped through the column at a flow rate of 4.2 mL/min. Afterwards, the column was washed with 1×10^{-2} M borate buffer solution at a rate of 1.4 mL/min for 60 s and the retained metal complexes were eluted using 1.0 mL of 0.5 M nitric acid in 10% ethanol at a flow rate of 1.4 mL/min. The concentrations of analytes in the eluate solution were determined by FAAS. The FAAS instrument was used in continuous mode. A reading was taken every 5 s so that only approximately 0.5 mL of the sample was consumed per analyte.

2.5. Analysis of Real Water Samples

River water was taken from Büyük Bostancı River. Seawater was collected from the Edremit Coast (the Aegean Sea). The samples were filtered through a 0.45 µm membrane filter to remove suspended particulate matter; acidified with HNO_3 to pH 2 and stored in polyethylene containers. Before analysis, the pH of 20 mL of the water samples was adjusted to pH 8.0 using 10% (w/v) sodium hydroxide solution and borate buffer solution. Then, 0.5 mL of 1×10^{-2} M ligand solution was added to the samples and these samples were analysed according to the proposed method.

3. RESULTS AND DISCUSSION

3.1. Optimization of the experimental parameters

The experimental parameters (e.g. sample pH, type and concentration of eluent, amount of ligand, flow rates of sample and eluent, and sample volume) that affect the efficiency of the method were optimized. Standard solution (10 mL) containing 200 µg/L of Cu(II) and Fe(III) was used for these experiments.

Since the pH is an important parameter for determining the sorption efficiency of trace elements and for chelation reactions, the influence of pH on the retention of analytes on the C18-silica was investigated over the range of 3.0-9.0. The sample and eluent solutions were passed through the column at a flow rate of 1.4 mL/min to investigate the effect of pH on the performance of method. The elution of the analyte was achieved using 1.0 mL of 0.5 M HNO_3 in 50% ethanol. The effect of sample pH on the recovery of analytes is shown in Figure 1. The recoveries obtained were quantitative for both analytes over the pH range of 8.0–9.0. For subsequent experiments, pH 8.0 was selected as optimum sample pH.

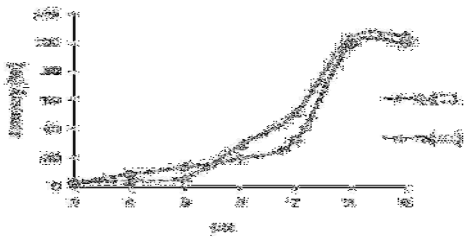

Figure 1. Effect of pH on the recovery of analytes

To elute the analyte ions from the C18-silica packed mini-column, 1 mL of different eluent agents such as 0.5 M HNO_3 solutions in 10 and 50% ethanol, and 2.0 M HNO_3 solution were tested at a flow rate of 1.4 mL/min. As seen in Table 1, the recoveries of analytes were quantitative (97.7-102.2%) for all of the eluents studied. However, the highest signals were acquired using 0.5 M HNO_3 in 10% ethanol. Therefore, this eluent was used in all further experiments.

Table 1. The effect of eluent types on the recovery of analytes

Eluent	Recovery	
	Cu(II)	Fe(III)
0.5 M HNO_3 in 50% ethanol	98.6 ± 2.7	97.7 ± 1.4
0.5 M HNO_3 in 10% ethanol	102.2 ± 0.6	100.5 ± 2.0
2.0 M HNO_3	99.8 ± 5.0	101.1 ± 0.8

To examine the influence of ligand amount on the recovery values of Fe(III) and Cu(II), amounts of 4-aminoantipyrine between 0.2 and 6.1 mg were used. For this purpose, different volumes (0.1-3.0 mL) of ligand solution of 1×10^{-2} M were added to 10 mL of standard solution containing the analyte ions at pH 8.0 and these solutions were passed through the C18-silica column. As seen in Figure 2, the recoveries were quantitative for both analytes over the ligand amount range of 0.6-6.1 mg. A ligand amount of 1.0 mg was selected to use for further experiments.

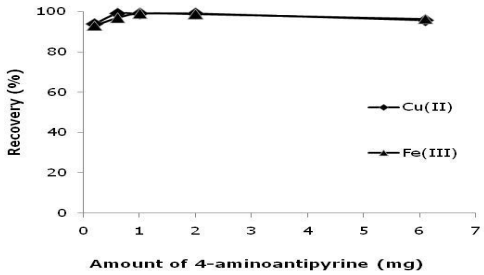

Figure 2. Effect of ligand amount on the recovery of analytes

The influence of flow rate of sample on the extraction efficiency of analytes was examined over the range 1.4-7.2 mL/min. The eluent flow rate was 1.4 mL/min in these experiments. According to Figure 3, sample flow rates over the range 1.4-4.2 mL/min had no considerable effect on the recoveries of analytes. At higher flow rates, the recoveries of analytes diminished slowly, but were still over 95%. For this reason, optimum experimental sample flow rate was set at 4.2 mL/min for all subsequent experiments.

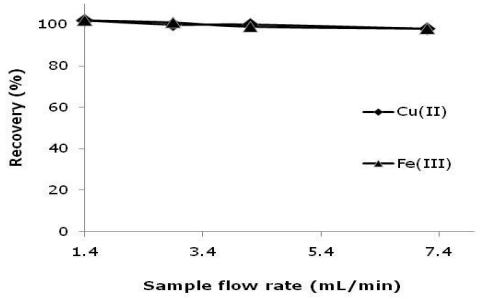

Figure 3. Effect of sample flow rate on the recovery of analytes

The effect of the eluent flow rate on the elution of adsorbed analytes was examined by varying it from 1.4 to 7.1 mL/min, as presented in Figure 4. The maximum recoveries of analytes were obtained at 1.4 mL/min, and hence an eluent flow rate of 1.4 mL/min was used for subsequent experiments.

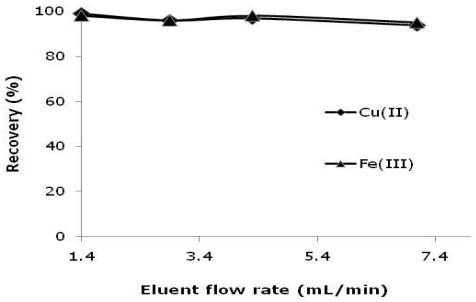

Figure 4. Effect of eluent flow rate on the recovery of analytes

The sample volume is an important parameter that affects the preconcentration factor. The effect of the sample volumes on the retention of analytes was investigated by passing 10-50 mL of the sample solutions through the C18-silica packed mini-column under the optimized experimental variables. Quantitative recoveries were obtained for the sample volumes studied (Table 2).

Table 2. The effect of the sample volume on the recovery of analytes

Sample volume (mL)	Recovery	
	Cu(II)	Fe(III)
10	102.0 ± 1.1	100.7 ± 3.9
20	100.4 ± 0.8	98.8 ± 0.4
40	98.7 ± 2.0	103.0 ± 3.4
50	96.5 ± 1.3	100.5± 0.4

Table 3. Effect of interfering ions on the recovery of analytes

Interfering ion	Added as	Amount added (mg/L)	Recovery	
			Cu(II)	Fe(III)
Na^+	NaCl	10000	95.9 ± 1.6	103.3 ± 2.8
K^+	KNO_3	1000	100.7 ± 2.1	95.4 ± 2.8
Ca^{2+}	$CaCl_2$	1000	100.0 ± 1.1	102.0 ± 4.6
Mg^{2+}	$Mg(NO_3)_2$. $6H_2O$	1000	98.9 ± 0.5	103.3 ± 0.9
Ni^{2+}	$Ni(NO_3)_2$. $6H_2O$	10	103.4 ± 0.5	96.7 ± 2.7
Co^{2+}	$Co(NO_3)_2$. $6H_2O$	10	98.1 ± 2.6	100.7 ± 0.9
Cr^{3+}	$Cr(NO_3)_3$. $9H_2O$	10	98.1 ± 0.5	98.0 ± 0.9
Mn^{2+}	$Mn(NO_3)_2$. $4H_2O$	10	98.9 ± 0.5	98.0 ± 4.6
Pb^{2+}	$Pb(NO_3)_2$	10	99.3 ± 1.1	103.3 ± 2.8
Cd^{2+}	$Cd(NO_3)_2$. $4H_2O$	10	100.4 ± 1.6	105.9 ± 2.8
Zn^{2+}	$Zn(NO_3)_2$. $6H_2O$	10	96.6 ± 0.5	96.7 ± 0.9
Al^{3+}	$Al(NO_3)_3$. $9H_2O$	10	98.1 ± 1.6	100.0 ± 1.9

3.2. Interference studies

To examine the potential interference effects, various concentrations of foreign ions were added to 10 mL solutions containing 100 µg/L Cu(II) and Fe(III) ions. These solutions were treated according to the proposed SPE procedure. The experimental results are summarized in Table 3. The ions tested did not affect the recovery of Cu(II) and Fe(III). The results indicate that the developed method has a good selectivity.

3.3. Analytical features of the method

Calibration curves were prepared by applying the suggested method to 20 mL of standard solutions containing concentrations range from 5.0 to 125 µg/L Cu(II) and Fe(III). The calibration equations were $A=2.36x10^{-3}$ C+ $4.55x10^{-4}$ with a correlation coefficient (R^2) of 0.9998 for Cu and $A=1.45x10^{-3}$ C + $8.88x10^{-4}$ with a correlation coefficient (R^2) of 0.9988 for Fe, where C is the analyte concentration (µg/L) and A is absorbance. The limits of detection (LOD =$3S_b$/m) were found to be 0.89 µg/L for Cu(II) and 1.40 µg/L for Fe(III). Here, m is the slope of the calibration curve after preconcentration and S_b is standard deviation of ten replicate blank signals. The preconcentration factor was calculated to be 20 when the sample and eluent volumes were 20 mL and 1 mL, respectively.

3.4. Comparison with other methods in the literature

Table 4 summarizes the comparison of the developed method with some existing methods coupled with FAAS detection for the determination of Fe and Cu. The limits of detection of the analytes are superior than or comparable to those acquired with other reported methods [15, 20-24]. Although some of these methods have better detection limits or higher preconcentration factors, they need large sample volumes [15,16,18,19,21,22]. This often adds significantly to the time required for analysis and is clearly more problematic during the collection and transport of the samples. The proposed method requires a lower analysis time compared with the other methods described in Table 4.

3.5. Analytical application

To evaluate the accuracy of the proposed method, the method was applied to SPS-SW2 Batch 127 certified reference water. The results acquired by the proposed method and certified values are given in Table 5. The accuracy of the method was evaluated by Student's t-test. As seen in Table 5, the critical t value is bigger than experimental t values at a confidence level of 95%, confirming that the method is accurate.

Table 4. The comparison between the proposed method and other methods for the determination of copper and iron by FAAS

Method[a]	Analyte	Detection limit (µg/L)	Preconcentration factor	Sample volume (mL)	Time of analysis (min)	Reference
SPE	Fe, Cu	0.89 (Cu) 1.41 (Fe)	20	20	8	This work
SPE	Fe, Cu, Zn	1.6 (Cu) 2.4 (Fe)	250	1500	750	(15)
SPE	Cu, Pb, Fe	0.64 (Cu) 0.82 (Fe)	62.5	250	51	(16)
SPE	Cu	0.2	400	2000	80	(18)
SPE	Fe, Mn	0.16	325	1300	164	(19)
USAE-SFODME	Cu, Fe	4.1 (Cu) 8.6 (Fe)	13.4	6.7	28	(20)
CPE	Co, Ni, Cu	1.5 (Cu)	25	50	40	(21)
CPE	Cd, Cu, Pb, Fe	0.48 (Cu) 1.85 (Fe)	25	50	30-35	(22)
DLLME-SFO	Cu	3.4	40	20	25	(23)
IL-DLLME	Fe	2.4	20	10	7	(24)

[a]SPE: Solid phase extraction, USAE-SFODME: Ultrasound-assisted emulsification solidified floating organic drop microextraction, CPE: Cloud point extraction, DLLME-SFO: Dispersive liquid-liquid microextraction-solidified floating organic drop, IL-DLLME: Ionic liquid based dispersive liquid-liquid microextraction.

Table 5. Results for the certified reference material

Certified reference material	Element	Certified value (µg/L)	Found value[a] (µg/L)	t[b]
SPS-SW2 Batch 127 surface water	Cu	100 ± 1	95.3 ± 3.3	2.5
	Fe	100 ± 1	102.8± 3.4	1.4

[a]Mean value ± standard deviation (N=3)

[b] $t = \frac{|\mu - \bar{x}|\sqrt{N}}{s}$, where t is statistical value (For 2 degrees of freedom, the critical value of t at the 95% confidence level is 4.30), µ is the certified value, x is the experimental mean value, N is number of independent determinations, and s is the standard deviation.

The developed method was also applied to river water and seawater samples. The applicability of the method was evaluated by spiking of these water samples with 15 µg/L of Fe(III) and Cu(II). As seen in Table 6, the average recoveries of the analytes obtained were between 94.7 and 98.7%. The results demonstrate the suitability and accuracy of the method for the determination of Cu and Fe in waters.

Table 6. Results of water samples and recovery of spiked analytes

Sample	Element	Added (µg/L)	Found[a](µg/L)	Recovery	RSD (%)
River water	Cu	-	4.3 ± 0.3	-	7.0
		15	19.1 ± 0.3	98.7	1.6
	Fe	-	90.4 ± 1.2	-	1.3
		15	105.0 ± 1.5	97.3	1.4
Seawater	Cu	-	5.4 ± 0.5	-	9.2
		15	19.6 ± 0.5	94.7	2.5
	Fe	-	140.4 ± 2.4	-	1.7
		15	155.2 ± 1.1	98.7	0.7

[a]Mean value ± standard deviation (N=3)

4. CONCLUSIONS

In this work, a new SPE method was developed for the simultaneous matrix separation and preconcentration of copper and iron in water samples. 4-aminoantipyrine was used as complexing agent and a C18-silica packed mini-column was the retention medium. The advantages of this method include the low cost, simplicity of operation and good accuracy. The method requires approximately 8 minutes of preparation time per sample and so is significantly quicker than many existing methods. In addition, the retained metal complexes are easily eluted using only 1 mL of 0.5 M HNO_3 in 10% ethanol. Since no chlorinated solvents are required, the method may be viewed as being environmentally friendly. The developed method can be used as a good alternative method for the determination of Cu and Fe in natural waters.

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