Enrichment and Separation of Fe(III), Mn(II), Ni(II), and Zn(II) as Their Congo Red Chelates on Multiwalled Carbon Nanotube (MWCNT) Disk in Food and Water Samples

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INTRODUCTION

Heavy metals are major environmental pollutants and one of the most serious environmental problems. The treatment of metals at trace levels is of special concern due to their recalcitrance and persistence in the environment (1,2). Because of their long-term effects on health, the detection of elements at trace levels in environmental samples is of special concern (3).

Flame atomic absorption spectrometry (FAAS) is a widely used instrumental technique for trace metal determination. However, levels of the analyte elements that are lower than the limit of detection of FAAS and interferences from co-existing ions are the limitations of this technique (4,5). To solve these limitations (6), solid phase extraction (SPE) is the enrichment-separation method that effectively enhances the sensitivity and selectivity of FAAS in saline samples. The advantages of using SPE include its ability for quantitative recoveries, offering high enrichment factors, easy application, and use of green technique (7).

Carbon nanotubes (8,9) have attracted much attention as solid phase extractants. They offer easy preconcentration and separation of metal ions such as lead (10,11), cadmium (12), chromium (13,14), copper (15), and nickel (16) from water and food samples. Congo Red

ABSTRACT

In this study, a novel method of using multiwalled carbon nanotube disk-solid phase extraction (MWCNT disk-SPE) of iron, manganese, nickel, and zinc in food and water samples is described. Congo Red (CR) was used as the chelating agent. The analytical parameters of the MWCNT disk-SPE system, including pH, amount of CR, sample volume, type of eluent, and sample flow rates, were investigated. Detection limits of 4.2, 1.2, 2.1, and 1.8 ng/mL for iron, manganese, nickel, and zinc, respectively, were obtained and a preconcentration factor of 25 was achieved. The SPE technique was applied to the determination of analyte elements in certified reference materials, water and food samples with satisfactory results.

(CR) is an important reagent for metal complexation and can be used in SPE studies (Figure 1). According to our literature survey, no work has been published using the combination of Congo Red and a multiwalled carbon nanotube disk.

In the present work, a solid phase extraction procedure for the separation and enrichment of trace amounts of iron(III), manganese(II), nickel(II), and zinc(II) as their Congo Red chelates in environmental samples on a MWCNT disk has been established. The analytical parameters for the quantitative recoveries of the analytes were investigated and optimized.

EXPERIMENTAL

Instrumentation

A Model AAnalyst™ 800 atomic absorption spectrometer (PerkinElmer, Inc., Shelton, CT, USA), equipped with an air-acetylene burner (17/2.1 L/min), was used. PerkinElmer hollow cathode lamps were used as light sources, using a 0.2 nm slit width. Deuterium lamp background correction was employed. The operating parameters for the instrument were set as recommended by the manufacturer and are listed in Table I. A Model Ethos Plus microwave labstation with computer-controlled easy-wave software (Milestone, CT, USA) was used to digest the solid samples. The pH was measured using an Accumet 15 pH meter (Fisher Scientific, USA).

Fig. 1. Congo Red.

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Reagents and Solutions

High purity chemicals were used in this study (E. Merck, Darmstadt, Germany) without additional purification. All solutions were prepared with reverse osmosis deionized water (Barnstead, Dobuque, IA, USA, 18.2 MΩ cm). For preparation of the standard stock solutions with an analyte concentration of 1000 mg/L, nitrate salts of the investigated analyte ions were used in 1 L calibrated flasks with 1% of HNO₃. The sample solutions were obtained by dilution of the stock standard solutions daily. The chelating reagent, 0.2% (w/v) CR, was prepared daily by dissolving the appropriate amounts of CR (B.D.H., Poole, England) in deionized water. For pH adjustment, a buffer solution was prepared using 100 mL of 0.025 M Na₂B₄O₇·10H₂O (borax) (Fluka) and 9.2 mL of 0.1 M HCl (Merck). In the elution step, HNO₃ (Merck) and acetone (Merck) were used.

Certified reference material (CRM) NCS ZC 73012 Cabbage from the China National Analysis Center for Iron and Steel (Beijing, P.R. China) and SPS SW1 Surface water from SpectraPure® Standards (Holger Teknologi AS, Norway) were used for method validation. Multi-walled carbon nanotubes (MWCNT) (No. 636614) were purchased from Aldrich, Milwaukee, WI, USA.

Preparation of MWCNT Disk

The suspension, containing 40 mg of MWCNTs in 50 mL of 5% (w/v) sodium dodecyl sulfate, was

filtered through a 47-mm diameter cellulose acetate membrane filter paper by using a vacuum pump to prepare a multiwalled carbon nanotube disk (Figure 2). Thus, the MWCNT adsorbents were distributed uniformly on the filter. The disk was washed with water and then allowed to dry at room temperature.

Procedure for FAAS Analysis

Treatment of the proposed method was performed for sample solutions prior to its application to real samples. A 25-mL amount of the sample solution containing 20 µg Fe(III) and Ni(II), 10 µg Mn(II) and Zn(II), 3 mL of pH 9 buffer solution, and 1 mL of CR chelating agent (0.2% w/v) was passed through the disk at a pump flow rate of 1.5 mL/min. After passage of the solution, the nanotube disk was washed with a related buffer solution. Then, the retained metal ions were desorbed from the disk with the aid of the 10 mL solution of 1M HNO₃ at a 3.0 mL/min flow rate. The glass filtration apparatus was washed with 2 M HNO₃ in acetone and then with deionized water before passing the next solution. The final solution was heated to evaporate the acetone, and the volume adjusted to 10 mL with 1 M HNO₃. The metal levels were determined by FAAS.

Samples and Sample Pretreatment

White bread, lettuce, zucchini, tomato, almonds and hazelnuts were purchased at local Ankara

markets. Samples of lettuce, zucchini, tomato, almond and hazelnuts were cleaned with tap and deionized water. The NCS ZC 73012 Cabbage CRM, vegetable and bread samples were dried at 105 °C for 24 hours, and then all samples (including the almonds and hazelnuts) were ground to a particle size of approximately 0.3 mm. Then, 200 mg of each sample, including the cabbage CRM, was digested in the Ethos Plus microwave oven with 3 mL of HNO₃ and 2 mL of H₂O₂. The steps for the digestion procedure were obtained from the literature (17). The digested solutions were left standing to cool, and each was then transferred into 250-mL volumetric flasks and diluted with deionized water. The digested cabbage CRM was diluted with 50 mL of distilled water. Then the FAAS procedure given above was applied to all of these solutions.

RESULTS AND DISCUSSION

Influences of pH on the Recovery of the Analytes

Since pH plays an important role in the quantitative extraction of metal ions in solid phase extraction (18-24), the influence of pH on the recovery of the analyte elements was examined ranging from 3.0-11.0. As shown in Figure 3, best quantitative recovery values were obtained at pH 9, which was chosen for subsequent experiments.

Influence of Congo Red Concentration

The concentration of ligand in the solid phase extraction studies is also a key factor for the quantitative recoveries of analyte elements (25-30). The influence of CR concentration on the recovery of the analyte elements was tested in the range of 0.005-0.4% (w/v). The SPE efficiency increased as the level of CR increased from 0.005 to 0.2% (w/v) and then almost remained constant at the concentration of 0.4% (w/v).

TABLE I
Instrument Settings

Elements	Wave-length (nm)	Slit Width (nm)	Lamp Current (mA)
Fe	248.3	0.2	35
Mn	279.5	0.2	20
Ni	232.0	0.2	25
Zn	213.9	0.7	15

Fig. 2. Photograph of the MWCNT disk.

TABLE II
Effects of Eluent Type on the Recovery Values

Eluent Type	Recovery (%)			
	Fe(III)	Mn(II)	Ni(II)	Zn(II)
1 M HNO ₃	88	89	97	89
2 M HNO ₃	92	91	96	89
3 M HNO ₃	94	94	95	90
3 M HCl	89	93	94	88
1 M HNO ₃ in acetone	99	97	101	98
1 M HCl in acetone	97	96	95	91

Fig. 3. Relationship between pH and analyte recovery ($n = 3$).

Fig. 4. The effects of sample volume on the recovery values ($n = 3$).

A CR concentration of 0.1% (w/v) was selected for further study.

Elution

The different concentrations of the solvents listed in Table II were tested, and high quantitative recoveries were obtained. However, the highest recovery values for all of the analyte ions were obtained with 1.0 M HNO₃ in acetone. So, 1.0 M HNO₃ in acetone was selected as the eluent for MWCNT disk-SPE. The optimum eluent volume was also tested, and quantitative recovery values were obtained both at 5 and 10 mL of eluent volume.

Sample and Eluent Flow Rates

The effect of sample flow rate on the recovery of the elements was studied with sample solutions ranging from 0.5–3.0 mL/min. The recovery values decreased slightly with an increase in sample flow rate above 1.5 mL/min because of incomplete retention of the metal chelates on the MWCNT disk. For further studies, a sample flow rate of 1.5 mL/min was selected.

The effect of elution rates from 0.5 to 4.0 mL/min was studied. The recoveries decreased with increasing the eluent flow rate above 3.0 mL/min. Thus, all further work was carried out using a 3.0 mL/min flow rate for the eluent solutions.

Effect of Sample Volume

The influence of sample volume on the recovery of Fe(III), Mn(II), Ni(II), and Zn(II) using MWCNT disk-SPE was investigated with sample solutions ranging from 25–400 mL. Figure 4 shows that the recoveries were found to be stable until 250 mL. The preconcentration factor was calculated by the ratio of the highest sample volume (250 mL) and the final volume (10 mL). The preconcentration factor was 25.

Interferences

“Matrix Effect” is a well-known problem for the flame atomic absorption spectrometric determination of metal ions in saline samples (31-39). The interference of cations and anions on the present enrichment-separation system were examined under optimized conditions. The results are summarized in Table III. Since the recovery values for the analyte elements are generally quantitative in the presence of the investigated foreign ions, it was found that the proposed extraction method can be applied to saline samples.

Performance of Proposed Method

The detection limits, defined as the concentration equivalent to three times the standard deviation ($N = 20$) of the reagent blank, are listed in Table IV. The precision of the present enrichment method, calculated as the relative standard deviation of the measurements carried out with the sample solutions ($N=9$), was below 2.3%.

Tests of addition/recovery in the experiments for analyte ions were performed using seawater, mineral water, and tap water samples. The results listed in Table V show that good agreement was obtained between the added and measured analyte values. The recoveries were quantitative and showed that the method can be applied for the separation/enrichment of analytes in real samples.

The present MWCNT disk-SPE procedure was applied to SPS SW1 Surface Water and NCS ZC 73012 Cabbage certified reference material. The results given in Table VI show that the certified values and the recoveries are in the acceptable range.

Applications

The applicability and reliability of the proposed method for the determination of iron, manganese, nickel, and zinc in food samples was investigated. The results listed in Table VII show that analyte elements at $\mu\text{g/g}$ levels can easily be determined by FAAS after using the

proposed solid phase extraction procedure.

CONCLUSION

A multiwalled carbon nanotube (MWCNT) disk-solid phase extraction (SPE) system coupled to FAAS was established for the separation, preconcentration, and determination of iron, manganese, nickel, and zinc in food and water samples. The Congo Red (CR) chelate worked well for these metal ions as complexing reagent. The method exhibited good precision, accuracy, sensitivity, and allows the determination of these elements in real and certified samples at $\mu\text{g/kg}$ levels. The multi-walled carbon nanotube (40 mg) can be reused until the end of a study without any loss in its adsorption properties. The procedure shows high tolerance to interference from matrix ions. The determination of elements in food and water samples using the proposed method is novel, rapid, easy, economical, and green.

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TABLE III
Influences of Matrix Ions

Ion	Conc.. (mg/L)	Added as:	Recovery (%)			
			Fe(III)	Mn(II)	Ni(II)	Zn(II)
Na ⁺	5000	NaCl	98	97	99	98
K ⁺	2500	KCl	99	100	97	100
Mg ²⁺	2500	Mg(NO ₃) ₂	96	98	98	99
Ca ²⁺	2500	CaCl ₂	88	91	89	90
Ca ²⁺	1000	CaCl ₂	97	96	96	97
Cu ²⁺	10	Cu(NO ₃) ₂ ·3H ₂ O	95	97	96	95
Cd ²⁺	10	Cd(NO ₃) ₂ ·4H ₂ O	97	96	95	100
Pb ²⁺	10	Pb(NO ₃) ₂	96	100	100	98
Co ²⁺	10	Co(NO ₃) ₂ ·6H ₂ O	99	98	97	99
Fe ³⁺	10	Fe(NO ₃) ₃ ·9H ₂ O	-	93	92	97
Mn ²⁺	10	MnSO ₄ ·H ₂ O	95	-	90	98
Ni ²⁺	10	Ni(NO ₃) ₂ ·6H ₂ O	94	91	-	96
Zn ²⁺	10	Zn(NO ₃) ₂	100	97	96	-
Cl ⁻	5000	NH ₄ Cl	98	95	97	94
CO ₃ ²⁻	2500	Na ₂ CO ₃	100	99	99	100
SO ₄ ²⁻	2500	Na ₂ SO ₄	98	97	98	99

TABLE IV
The Detection Limit for the
Analyte Elements by the
Proposed Method
(V_{sample} = 200 mL
and V_{final} = 10 mL)

Analyte	Limit of Detection (ng/mL)
Fe(III)	4.2
Mn(II)	1.2
Ni(II)	2.1
Zn(II)	1.8

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TABLE V
Test of Addition/Recovery for Analyte Elements for Water Samples
(N = 3) (V_{sample} = 200 mL and V_{final} = 10 mL)

	Mineral Water 1		Mineral Water 2		Seawater from Black Sea		Tap Water from Beytepe	
	Added (µg)	Found (µg)	Added (µg)	Found (µg)	Added (µg)	Found (µg)	Added (µg)	Found (µg)
Fe(III)	0	55.0 ± 1.3	0	43.0 ± 1.7	0	35.9 ± 1.6	0	67.4 ± 1.8
	20	73.0 ± 2.0	10	52.0 ± 2.1	10	44.0 ± 1.2	20	85.0 ± 1.3
	40	96.0 ± 2.4	20	61.0 ± 1.5	20	55.5 ± 1.9	40	108.7 ± 2.4
Mn(II)	0	2.9 ± 0.4	0	1.9 ± 0.6	0	15.9 ± 1.3	0	10.5 ± 0.8
	5	7.7 ± 0.5	5	6.5 ± 0.3	20	36.2 ± 2.1	5	15.6 ± 1.4
	10	13.1 ± 0.8	10	10.9 ± 0.6	40	54.9 ± 2.6	10	21.2 ± 1.7
Ni(II)	0	BDL	0	BDL	0	5.4 ± 0.5	0	BDL
	10	11.1 ± 0.7	10	10.7 ± 0.8	10	15.1 ± 1.0	5	5.2 ± 0.4
	20	22.0 ± 1.3	20	21.5 ± 1.0	20	26.0 ± 1.9	10	10.7 ± 0.8
Zn(II)	0	3.4 ± 0.5	0	24.0 ± 1.3	0	4.9 ± 0.6	0	267.0 ± 2.5
	5	8.7 ± 0.8	10	36.0 ± 1.1	5	10.1 ± 0.5	25	289.6 ± 2.3
	10	13.9 ± 0.9	20	43.0 ± 0.7	10	14.2 ± 1.3	50	313.5 ± 2.7

^a Mean ± standard deviations.

BDL: Below the detection limit.

TABLE VI
Levels of Analyte Ions in CRMs
After Application of Proposed SPE Method (N = 2)

Sample	Ion	Certified Value	Found Value	Recovery (%)
NCS ZC 73012 (Cabbage)	Fe(III)	98 ± 10 µg/g	100 ± 5 µg/g	102
	Mn(II)	18.7 ± 0.8 µg/g	17.6 ± 1 µg/g	94
	Ni(III)	0.93 ± 0.10 µg/g	0.89 ± 0.15 µg/g	96
	Zn(II)	26 ± 2 µg/g	25.2 ± 0.9 µg/g	97
SPS SW1 (Surface Water)	Fe(III)	20 ng/mL	19.8 ± 0.3 ng/mL	99
	Mn(II)	10 ng/mL	10.3 ± 0.5 ng/mL	103
	Ni(III)	10 ng/mL	9.8 ± 0.4 ng/mL	98
	Zn(II)	20 ng/mL	19.5 ± 0.7 ng/mL	98

TABLE VII
Levels of Analytes in Various Food Samples (N = 2)
(V_{sample} = 200 mL and V_{final} = 10 mL)

Sample	Fe	Concentration (µg/g)			Zn
		Mn	Ni		
Tomato	53.0 ± 1.1	6.6 ± 0.5	BDL		9.5 ± 0.9
Zucchini	86.0 ± 1.2	18.9 ± 1.1	3.6 ± 0.2		53.1 ± 1.5
Lettuce	79.9 ± 1.0	47.7 ± 1.6	1.4 ± 0.1		68.8 ± 0.9
Bread	60.0 ± 0.9	5.9 ± 0.4	BDL		4.7 ± 0.7
Almond	87.2 ± 0.5	23.6 ± 1.9	0.78 ± 0.01		47.2 ± 0.6

BDL: below the detection limit.

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