Coprecipitation of Fe(III), Mn(II), Cu(II), Pb(II), Co(II), and Ni(II) With Ytterbium Hydroxide for Separation and Preconcentration Prior to Determination by FAAS

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INTRODUCTION

Some trace elements such as copper(Cu) and cobalt (Co) are important nutritional elements for human health in very low quantities (1–3). However, some trace elements like lead (Pb) and cadmium (Cd) can be toxic to humans as well as the environment (3–5). While certain elements such as chromium (Cr) are essential at low levels, when in excess this can result in deleterious effects to human health (6–7). Trace elements are also one of the main sources of environmental pollution resulting from industry, traffic, mining, etc. (8–10). Thus, an accurate and precise determination of trace elements in foods, biological and environmental samples is very important in order to monitor trace element levels in these samples. The instrumental detection systems including UV-Vis spectrometry, atomic absorption spectrometry (AAS), and atomic emission spectrometry (AES) (11–14) are widely used for the determination of trace elements. However, due to the limitation in detection limits of the instruments and the interference effects of the matrix components of the samples, these types of analyses are generally combined with a separation/preconcentration system (15–18). Various sample pretreatment procedures that combine separation and preconcentration include liquid-liquid extraction (19), cloud point extraction (20–22), solid phase extraction (23–25), membrane filtration (26, 27), and electroanalyti-

ABSTRACT

A coprecipitation procedure for the separation and preconcentration of trace amounts of Fe(III), Mn(II), Cu(II), Pb(II), Co(II), and Ni(II) is described. The analytical parameters including pH, ytterbium amount, centrifugation rate and time for the quantitative recovery of the analyte elements were optimized. The effect of matrix components of highly saline samples was also investigated. The limit of detection of the procedure was in the range of 2.1 µg/L for copper, 8.2 µg/L for nickel, and the preconcentration factor was 80. The accuracy of the method was checked by the addition recovery tests to real samples and by the analysis of the certified reference materials NIST SRM1570a Trace Elements in Spinach Leaves and SPS-WW2 Wastewater Level 2. The application of the method was performed for the determination of analyte elements in food and water samples.

cal systems (28, 29). These methods often require large amounts of high purity organic solvents (30–32).

Coprecipitation is usually considered as a separation/preconcentration method due to its simplicity, speed, and the ability to attain high concentration efficiency for metal ions at trace levels. Coprecipitation with metal hydroxides has been widely used for enrichment/separation of metals at trace levels. Coprecipitation by hydroxide of analyte elements including magnesium, indium, lanthanum, samarium, terbium, erbium, gallium, hafnium, dysprosium, thulium,

gadolinium, cerium, europium, neodymium, and iron has been reported for the separation/preconcentration of trace elements (32–35). The use of ytterbium hydroxide in the preconcentration studies is very limited (36–38). Due to its low solubility in water (39), for this work we selected ytterbium hydroxide as the coprecipitant for the separation/preconcentration of trace elements.

For this study, a separation/preconcentration procedure has been established for some metal ions in environmental samples based on coprecipitation. The analytical parameters including pH, amount of reagents, etc., were optimized.

EXPERIMENTAL

Instrumentation

A PerkinElmer® Model 3110 flame atomic absorption spectrometer (PerkinElmer, Inc., Shelton, CT, USA) was used for the analyte measurements in standard and sample solutions. For each metal ion, a hollow cathode lamp and a 10-cm air-acetylene flame atomizer were used. The instrumental settings as recommended by the manufacturer are listed in Table I.

TABLE I
FAAS Instrumental Conditions

Element	Wavelength (nm)	Lamp Current (mA)
Mn	279.5	20
Fe	248.3	30
Pb	283.3	13
Ni	232.0	23
Co	240.7	23
Cu	324.8	15

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For pH measurements, a Nel pH-900 meter (Nel Company, Ankara, Turkey) with a glass electrode was used. Ultrapure deionized water was prepared by reverse osmosis and filtration using a Milli-Q® Direct 16 system (Millipore Australia Pty Ltd., North Ryde, Australia). An ALC PK 120 centrifuge (ALC International, Italy) was used during the centrifugation processes.

Solutions and Reagents

All solutions were made with reverse osmosis purified water. All reagents were of analytical grade. Distilled water was used throughout this work. The chemicals were of analytical reagent grade unless otherwise stated. Plastic and glassware were cleaned by soaking in a 10% HNO₃ solution, then rinsing with distilled water prior to use.

Stock solutions (1000 mg/L) of the analyte ions were diluted daily for obtaining reference and working solutions. The calibration standards were not subjected to the preconcentration procedure. A 0.1% (m/v) ytterbium(III) solution (0.1% mv) was prepared fresh daily by dissolving Yb₂O₃ (No: 1124100005, Merck, Darmstadt, Germany) in small amounts of 1 mol/L HNO₃ and diluting to 100 mL with distilled water.

Two certified reference materials, SRM 1570a - Trace Elements in Spinach Leaves and SPS-WW2 Wastewater Level 2, were purchased from the National Institute of Standards & Technology (NIST, Gaithersburg, MD, USA) and from Spectrapure Standards AS (Oslo, Norway), respectively.

Preconcentration Procedure

In order to optimize the coprecipitation system, 15 mL of deionized water containing analyte elements and 1.0 mL of 0.1% Yb₂O₃ (m/v) solution was used. The pH of the solutions was adjusted to the

corresponding pH by the addition of 1 mol/L NaOH solution. The solutions were centrifuged at 4000 rpm for seven minutes. The supernatant was removed. The precipitate adhering to the tube was dissolved with 1 mL of 1 mol/L HNO₃. The final volume was completed to 2.0–10.0 mL with distilled water. The metal concentrations of the final solutions were determined by flame AAS (FAAS).

Application to Real and Certified Samples

A 1.0-g sample amount of certified reference sample (SRM 1570A Spinach Leaves), water, fruit, or spices was digested with 10 mL concentrated HNO₃ at 95 °C. The mixture was evaporated to form a semi-dry mass, mixed with 3 mL of H₂O₂, and then again evaporated to near dryness. After evaporation, 8–9 mL of ultrapure water was added and the sample mixed. The resulting mixture was filtered through a blue band filter paper. The filtrate was diluted to 20 mL with ultrapure water, and the procedure described above was applied. The analytes in the final solution were determined by FAAS.

The certified reference material, SPS-WW2 Wastewater Level 2, was used directly and the coprecipitation procedure listed above applied after adjusting the pH to 11.0 by using 1 mol L⁻¹ NaOH solution.

The proposed method was also applied to different water samples which were obtained from the Kayseri area: tap water, bottled mineral water, and wastewater. The samples were collected in pre-washed polyethylene bottles. Before analysis, the pH of the water samples was adjusted to 11.0 by using 1 mol L⁻¹ NaOH solution. The preconcentration procedure listed above was applied to the final solutions. All determinations were carried out by FAAS.

RESULTS AND DISCUSSION

The recovery (%) value for the analyte ions of the proposed coprecipitation procedure was calculated using the following equation:

$$\text{Recovery}(\%) = (w_o/w_f) \times 100$$

where w_o (μg) is the amount of analyte in the final solution and w_f (μg) is the amount of analyte in the beginning solution, respectively.

Effect of pH

The influence of pH on the recovery of the analyte elements using coprecipitation with ytterbium(III) hydroxide was investigated in the 8.0–12.0 range. The pH of the working solutions was adjusted by using 1 mol/L NaOH. The results are given in Figure 1. Since the Fe(III), Mn(II), Cu(II), Pb(II), Co(II), and Ni(II) ions were quantitatively (>95%) recovered at pH 11.0, all further studies were performed at this pH.

Effect of Amount of ytterbium(III)

The influence of the amount of ytterbium(III) on the coprecipitation efficiency of Fe(III), Mn(II), Cu(II), Pb(II), Co(II), and Ni(II) was investigated in the 0–200 μg range at pH 11.0 (see Figure 2). It was found that without ytterbium(III), the recovery of the analyte ions was not quantitative (< 80%). Quantitative recovery for the analytes was tested in the range of 100–200 μg of ytterbium(III). The optimum amount of ytterbium(III) selected for further experiments was 100 μg.

Centrifugation Speed and Time

The effect of centrifugation speed on the recovery of the analytes was studied in the 1000–4000 rpm range. Quantitative values were obtained in the range of 2000–4000 rpm. For the present work, 2500 rpm was selected as the optimum centrifugation speed.

Fig. 1. Recovery(%)–pH relation on the proposed coprecipitation system (sample volume: 15 ml, N=3).

Fig. 2. Relation between amounts of ytterbium and recovery (%), (sample volume: 15 ml, N=3).

The influence of centrifugation time on the present coprecipitation work for the analyte elements was studied from 2–15 minutes. The recovery values were found to be quantitative in the time range of 10–15 minutes. Thus, 10 minutes were selected as the optimum centrifugation time.

Sample Volume

In order to achieve a high pre-concentration factor, the sample volume of the working media is a key factor in preconcentration studies (40–45). The influence of sample volume of the aqueous solution on the recovery of the analyte elements was also investigated in the sample volume range of 10–500 mL. The elements were quantitatively (95%) recovered in the sample volume ranging from 10–400 mL. The final volume of the coprecipitation work was 5.0 mL. It was found that a preconcentration factor of 80 can be achieved when the final volume was 5.0 mL.

Effect of Concomitant Ions

Due to the interference effects of alkaline metals and the detection capability of the instrument at trace levels, earth alkaline metal ions and some cations and anions are a big problem for analytical chemists (46–53). The influence of these

ions on the proposed coprecipitation procedure was investigated, and the results are listed in Table II. The ions normally present in water do not interfere under the experimental conditions used.

Analytical Performance

The accuracy of the proposed coprecipitation procedure for trace metal ions was checked by using addition/recovery tests for real samples. The results in Table III show that good agreement was obtained between the added and found analyte concentrations. The recovery values calculated for the standard additions were generally > 95%, thus confirming the accuracy of the proposed procedure and the absence of matrix effects.

The relative standard deviations for atomic absorption spectrometric measurements for analyte ions are below 5.0%. The detection limits, defined as the concentration equivalent to three times the standard deviation (n=10) of the reagent blank, are listed in Table IV. The optimum concentration ranges and regression equations for the analytes are also listed in Table IV. The detection limits for the analyte elements ranged from 2.1–8.2 µg/L.

Application

The developed method was applied to certified reference materials: SRM 1570a - Trace Elements in Spinach Leaves and SPS-WW2 Wastewater Level 2 for the determination of analyte metals. The results listed in Table V are based on the average of three replicates for the analytes and show that they are in good agreement with the certified values.

The presented procedure was applied to the determination of analyte elements in water, fruit, and spice samples from Kayseri, Turkey. The results are listed in Table VI.

CONCLUSION

Coprecipitation with ytterbium hydroxide offers a useful separation/preconcentration technique for food and water analysis. The procedure has been successfully applied to the analyte elements Fe(III), Mn(II), Cu(II), Pb(II), Co(II), and Ni(II) with acceptable accuracy and precision. The coprecipitated analyte ions can be sensitively determined by flame atomic absorption spectrometry without any influence caused by ytterbium hydroxide. Accuracy of the method was verified by analysis of the certified reference materials.

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TABLE II
Effects of Matrix Ions on the Recovery of the Analyte Elements (Sample Volume: 15 mL, N=3)

Ion	Added as	Concentration (mg/L)	Recovery(%)					
			Mn	Fe	Pb	Ni	Co	Cu
Na ⁺	NaCl	20,000	100±2	99±2	98±1	100±1	100±1	96±2
Ca ²⁺	CaCl ₂	5000	97±1	102±1	98±2	98±1	98±1	99±2
Cl ⁻	NaCl	35,000	100±1	99±2	98±1	100±1	100±1	96±2
K ⁺	KCl	6000	96±2	101±1	99±1	97±1	96±1	99±2
SO ₄ ²⁻	Na ₂ SO ₄	2000	98±1	99±1	98±1	96±1	101±1	99±1
Mn ²⁺	MnSO ₄ ·H ₂ O	20	-	101±1	97±1	96±1	100±1	99±1
Cr ³⁺	Cr(NO ₃) ₃ ·9H ₂ O	20	100±1	99±2	96±1	91±1	97±1	99±1
Fe ³⁺	Fe(NO ₃) ₃ ·9H ₂ O	10	97±1	-	100±1	96±1	97±1	100±1
Pb ²⁺	Pb(NO ₃) ₂	20	100±1	101±1	-	99±1	99±1	100±1
Ni ²⁺	Ni(NO ₃) ₂ ·6H ₂ O	10	96±1	100±1	99±2	-	99±1	99±1
Co ²⁺	Co(NO ₃) ₂ ·6H ₂ O	10	99±1	100±1	97±2	96±1	-	99±1
Cu ²⁺	Cu(NO ₃) ₂ ·3H ₂ O	20	99±1	101±1	98±1	97±1	100±2	-
Zn ²⁺	Zn(NO ₃) ₂ ·6H ₂ O	40	97±1	98±1	100±1	98±1	100±1	100±1

TABLE III
Addition/Recovery Test for Real Samples (Sample Volume: 15 mL, N=3)

	Added (µg)	Black Tea		Tap Water		Bottled Mineral Water	
		Found (µg)	Rec.(%)	Found (µg)	Rec.(%)	Found (µg)	Rec.(%)
Pb	0	BDL	-	BDL		BDL	
	10	9.9±0.0	99	9.8±0	98	9.8±0	98
	20	20.6±0.3	103	20.0±0	100	20.0±0	100
Mn	0	BDL	-	BDL		BDL	
	10	10.2±0.3	102	10.2±0.6	102	10.2±2	102
	20	19.7±0.3	99	19.6±1	98	19.8±1	99
Ni	0	BDL		BDL		BDL	
	10	9.7±0.6	97	10.5±0.6	105	10.5±0	105
	20	20.3±0.0	101	20.5±0.6	103	20.5±1.2	103
Fe	0	BDL		BDL		BDL	
	10	10.3±0.6	103	10.1±0	101	9.6±1	96
	20	20.1±0.6	100	20.1±0.6	100	20.1±0.6	100
Cu	0	BDL		BDL		BDL	
	10	10.2±0.0	102	10.2±1	102	10.4±1	104
	20	20.0±0.0	100	20.2±2	100	20.0±1	100
Co	0	BDL		BDL		BDL	
	10	9.9±0.6	99	9.6±0.6	96	9.6±0	96
	20	19.6±0.3	98	19.6±0.6	98	19.6±1.0	98

Rec.(%) = Recovery(%). BDL : Below the detection limit.

TABLE IV
Analytical Characteristics of Proposed Method

Analyte	Correlation Coefficient	Linear Range (mg/L)	Regression Equation	Limit of Detection (µg/L)
Mn	0.999	0.1-2.0	A=0.058C - 0.0006	2.5
Fe	0.999	0.5-5.0	A=0.024C - 0.0011	7.4
Pb	0.999	1.0-10.0	A=0.006C + 0.0013	3.7
Ni	0.991	0.5-5.0	A=0.024C - 0.0011	8.2
Co	0.998	0.5-5.0	A=0.032C - 0.0040	4.5
Cu	0.999	0.5-5.0	A=0.033C + 0.0020	2.1

A = absorbance, C = concentration of analyte.

TABLE V
Application of Proposed Method to CRMs (Sample Volume: 15 mL)

Element	SRM 1570a - Trace Elements in Spinach Leaves			SPS-WW2 Wastewater Level 2		
	Certified Value (µg/g)	Found Value (µg/g)	Rec.(%)	Certified Value (µg/mL)	Found Value (µg/mL)	Rec.(%)
Cu	12.2	12.1 ± 0.6	99	0.4	0.4 ± 0.1	100
Mn	75.9	75.7 ± 0.2	99	0.4	0.4 ± 0.2	100
Co	0.39	0.38 ± 0.04	97	-	-	-
Pb	0.2	0.2 ± 0.0	100	-	-	-
Ni	2.14	2.1 ± 0.1	98	1.0	1.04 ± 0.02	104
Fe	-	-	-	1.0	1.02 ± 0.01	102

BDL : below the detection limit.

ND: not determined.

TABLE VI
Levels of Analyte Elements in Real Samples (Sample Volume: 15 mL, N=3)

Sample	Pb (µg/L)	Ni (µg/L)	Mn (µg/L)	Co (µg/L)	Cu (µg/L)	Fe (µg/mL)
Wastewater	21.6 ± 0.04	5.38 ± 0.02	2.48 ± 0.06	3.05 ± 0.01	3.82 ± 0.01	28.8 ± 0.04
	Pb (µg/g)	Ni (µg/g)	Mn (µg/g)	Co (µg/g)	Cu (µg/g)	Fe (µg/g)
Grape	0.31 ± 0.02	2.14 ± 0.06	10.5 ± 0.1	0.43 ± 0.06	11.2 ± 0.01	25.3 ± 0.02
Cherry	0.31 ± 0.01	1.08 ± 0.02	4.53 ± 0.02	0.49 ± 0.04	13.0 ± 0.02	15.3 ± 0.01
Mulberry	0.15 ± 0.01	1.61 ± 0.04	1.47 ± 0.01	0.31 ± 0.02	18.4 ± 0.04	21.1 ± 0.04
Pepper Flakes	0.23 ± 0.02	1.34 ± 0.02	BDL	0.37 ± 0.06	5.8 ± 0.01	4.6 ± 0.02
Black Pepper	0.31 ± 0.04	1.08 ± 0.04	BDL	0.24 ± 0.01	7.6 ± 0.02	BDL

BDL: below the detection limit.

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