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A membrane filtration procedure for the enrichment, separation, and flame atomic absorption spectrometric determinations of some metals in water, hair, urine, and fish samples

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ABSTRACT

A cellulose acetate membrane filter was applied for solid-phase extraction of Cd(II), Co(II), Cu(II), Fe(III), Ni(II), and Pb(II) from urine, hair, fish, and various water samples. The analyte ions were adsorbed on membrane filter as Cochenille red complexes and then eluted using 10 mL 3 M CH_3COOH. The matrix effects from concomitants and analytical parameters, including pH, sample volume, membrane type, and flow rates, were investigated. The analyte ion detection limit for the proposed method was in the range 1.0–5.2 μg/L. The preconcentration factors were calculated as 30 for Cu(II), 40 for Co(II), Ni(II), Cd(II) as well as Pb(II), and 50 for Fe(III). The proposed method was validated by analyzing certified reference materials. This method was successfully applied to water, hair, fish, and urine samples with good results.

Keywords: Membrane filtration; Preconcentration; Cochenille red; Metal; Food; Atomic absorption spectrometry

1. Introduction

Contamination by heavy metal ions poses a serious threat to human health and the environment. Heavy metals are toxic and accumulate in living organisms throughout their lifetime. Certain trace elements, such as copper, iron, and cobalt, are essential to organisms, which have a daily requirement of only a few milligrams. However, if ingested in high levels, such elements can be harmful to humans, animals, and plants. Recently, environmental pollution by heavy metals has received considerable attention. Wide technological use in industry and traffic are the primary source for traces metal ions in the environment [1–7]. Therefore, sensitive, reproducible, and accurate instrumental techniques are necessary to determine trace amounts of metals in such environmental samples. Quantifying such metal species in various matrices has been performed using different techniques, such as flame atomic absorption

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spectrometry (FAAS) [8,9], inductively coupled plasma atomic emission spectrometry (ICP-AES) [10], inductively coupled plasma mass spectrometry (ICP-MS) [5,11], and inductively coupled plasma optical emission spectrometry (ICP-OES) [12,13], which can determine the levels of trace metals with sufficient sensitivity for most applications. FAAS is preferred for determining trace levels of metal ions in environmental samples because it is simple and inexpensive compared with other instrumental techniques, such as ICP-MS [14,15]. However, analytes at lower levels than the detection limit of atomic absorption spectrometry and high salt content in the real samples are the two primary limitations in determining metal ion levels though atomic absorption spectrometry. Such techniques are not sufficiently sensitive and selective for certain analyses. Thus, methods for separating or preconcentrating trace elements may be necessary before spectrometric analysis [16,17].

Membrane filtration of trace heavy metals is effective for producing the concentration enrichment. Membrane filters, including cellulose nitrate and cellulose acetate, have been applied to solid-phase extraction (SPE) of trace species, such as organic species, certain anions, and heavy metal ions, in various media [18–21]. The most attractive features of membrane filtration are simplicity, speed, wide application of preconcentration methods, an easily attainable high preconcentration factor, and high precision [22,23].

Cochenille red (Acid Red 18) is a diazo compound (Fig. 1). It is used as a food dye in food industry. It has 1:1 complexes with metal ions [24]. According to our literature survey, Cochenille red-membrane filtration combination is first used for the preconcentration and separation of metal ions.

In this study, a method is introduced for enriching/separating Cd(II), Co(II), Cu(II), Fe(III), Ni(II), and Pb(II) ions as Cochenille red complexes on a cellulose acetate membrane filter for water, hair, fish, and urine samples with FAAS for analysis.

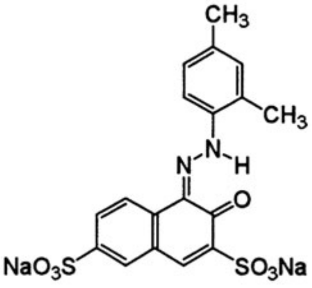

Fig. 1. Cochenille red.

2. Experimental

2.1. Apparatus

A Perkin–Elmer Model 3110 atomic absorption spectrophotometer was used for analyte measurements in standard and sample solutions. For each metal ion, its hollow cathode lamps and a 10 cm air-acetylene flame atomizer were used. The instrumental settings were recommended in the manufacturer's manual book. A PHS-3C pH meter (model Nel pH-900 Nel Company, Ankara, Turkey) with a combined glass electrode was used to measure the pH values. Ultra-pure de-ionized 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 model centrifuge (Buckinghamshire, England) was used.

2.2. Reagents and solution

Stock solutions containing 1,000 mg/L of Cd(II), Co(II), Cu(II), Fe(III), Ni(II), and Pb(II) were prepared from nitrate salts (Merck, Darmstadt, Germany) in 1% of HNO_3 and were added to 1 L calibrated flasks. Diluted standard solutions were prepared from the stock standard solutions. Stock solutions with diverse elements were prepared from high-purity compounds. The cellulose acetate membrane filters used herein were purchased from Osmonics (Westborough, MA).

A 0.05% (w/v) solution of Cochenille red (Applichem GmbH, Darmstadt, Germany) was prepared by dissolving the required amount of Cochenille red in a water/ethanol (75/25, v/v) mixture. This solution was prepared daily. The pH values were adjusted by adding phosphate buffer ($H_2PO_4^-/H_3PO_4$), acetate buffer (CH_3COO^-/CH_3COOH), and ammonium buffer (NH_4^+/NH_3) solutions.

2.3. Test procedure

A 20–25 mL portion of an aqueous solution containing 5–20 μg of Cu(II), Co(II), Ni(II), Fe(III), Cd(II), and Pb(II) ions was placed in a glass beaker. Ten milliliters of the buffer solution in section 2.2 (to produce the desired pH between 2 and 8) and 75 μg of a 0.05% (w/v) Cochenille red solution were added. After 10 min, a metal-chelate solution was collected through a cellulose acetate membrane filter with a 0.45 μm pore size and a 47 mm diameter. The solution was collected by filtration under suction with an aspirator. The metal-chelates collected on the membrane filter were then eluted with 10 mL 3 mol/L of CH_3COOH. The analytes in the final solution were determined by FAAS.

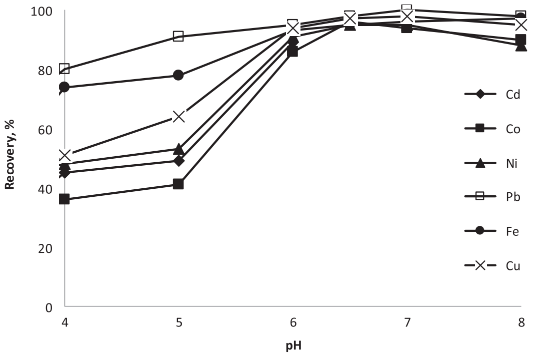

Fig. 2. The effect of pH on analyte ion recoveries ($N = 3$, eluent: 3 mol/L HAc; membrane: 0.45 μm pore size, 47 mm diameter cellulose acetate).

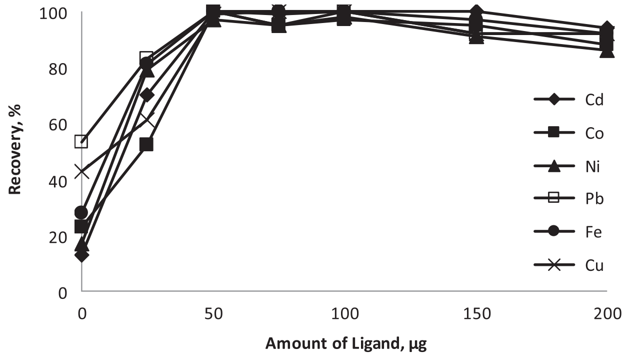

Fig. 3. The effect of ligand levels on analyte recovery ($N = 3$, eluent: 3 mol/L HAc).

2.4. Applications for real samples

Two-hundred fifty milliliter samples of tap, lake, sea, thermal spring, waste, and spring water were collected in a beaker, and the pH of the samples was adjusted to pH 6.5 with a buffer solution. One gram each of the hair and fish samples was digested with 12 mL of concentrated HNO_3 at 90˚C. The mixture was evaporated to almost dry and mixed with 4 mL of H_2O_2. It was then again evaporated to dry. After evaporation, 5–6 mL of distilled water was added, and the sample was mixed. The resident was diluted to 10 mL with distilled water. The separation/preconcentration method above was then applied. The analyte concentration for the final solution was determined by FAAS.

One gram of certified reference material (NCS ZC 81002 b Human Hair) was digested with 12 mL concentrated HNO_3 at 95˚C. The mixture was evaporated to almost dry and mixed with 4 mL of H_2O_2. It was then again evaporated to dry. After evaporation 5–6 mL of distilled water was added, and the sample was mixed. The procedure in section 2.3 was then applied. Twenty five milliliters of TMDA-70 fortified water certified reference material was applied (see section 2.3). The analyte levels in the final solution were determined using FAAS.

3. Results and discussion

3.1. Effect of pH

Because the pH of the aqueous solution with Cu(II), Co(II), Ni(II), Fe(III), Cd(II), and Pb(II) ions influenced the quantitative recoveries, it was the first factor investigated in the enrichment-separation studies [25–31]. For the solutions used to recover the

Table 1
The influence of various eluents on analyte ion recovery ($N = 3$)

			Recovery (%)					
Eluent type	Concentration (mol/L)	Eluent volume (mL)	Cd	Co	Ni	Pb	Fe	Cu
HAc	1	10	35 ± 3	21 ± 3	69 ± 1	98 ± 2	69 ± 3	48 ± 2
	2	10	88 ± 2	48 ± 2	89 ± 2	100 ± 1	90 ± 2	70 ± 2
	3	10	99 ± 1	98 ± 2	94 ± 2	100 ± 1	96 ± 1	100 ± 1
	3	5	90 ± 2	89 ± 2	85 ± 1	96 ± 1	95 ± 2	96 ± 2
HNO_3	1	10	35 ± 2	31 ± 2	51 ± 2	76 ± 2	74 ± 2	46 ± 2
	2	10	42 ± 2	39 ± 2	65 ± 2	94 ± 1	86 ± 1	52 ± 1
	3	10	46 ± 2	50 ± 2	79 ± 2	100 ± 1	100 ± 2	73 ± 2
H_2SO_4	1	10	40 ± 2	35 ± 2	88 ± 2	69 ± 2	92 ± 3	46 ± 1
	2	10	51 ± 2	56 ± 2	90 ± 1	92 ± 2	98 ± 2	54 ± 2
HCl	1	10	67 ± 1	23 ± 3	95 ± 1	98 ± 1	95 ± 1	49 ± 2
	2	10	92 ± 2	75 ± 1	99 ± 2	95 ± 1	98 ± 2	55 ± 1
NH_3	1	10	25 ± 3	24 ± 1	19 ± 2	35 ± 2	39 ± 2	28 ± 2
	2	10	27 ± 3	18 ± 2	15 ± 2	38 ± 1	36 ± 2	32 ± 1

Note: mean ± standard deviation.

Table 2
The effect of membrane filter type on analyte recovery ($N = 3$)

	Recovery (%)					
Membrane filter type	Cd	Cu	Co	Ni	Fe	Pb
Cellulose acetate membrane filter	13 ± 2	25 ± 3	18 ± 2	51 ± 2	38 ± 1	58 ± 2
Cellulose acetate membrane filter + Cochenille red	99 ± 1	99 ± 1	97 ± 1	100 ± 1	96 ± 1	97 ± 1
Cellulose nitrate membrane filter	10 ± 1	41 ± 2	23 ± 3	15 ± 2	28 ± 3	52 ± 2
Polysulfone membrane filter	19 ± 1	28 ± 1	29 ± 1	21 ± 2	32 ± 2	56 ± 3

Cu(II), Co(II), Ni(II), Fe(III), Cd(II), and Pb(II) ions on the cellulose acetate membrane filter, the effect of pH was investigated in the range 2.0–8.0. The results are shown in Fig. 2. Quantitative recoveries were generated for Cu(II), Co(II), Ni(II), Fe(III) as well as Cd(II) in the pH range 6.0–8.0 and Pb (II) in the pH range 5.0–8.0. pH 6.5 was selected for further study. The samples were adjusted to pH 6.5 using phosphate buffer.

3.2. The influence of Cochenille red levels

The influence of Cochenille red levels on retaining Cu(II), Co(II), Ni(II), Fe(III), Cd(II), and Pb(II) on the cellulose acetate membrane filter was also examined in the range 0–200 μg. The results are shown in Fig. 3. The recoveries for Cu(II), Co(II), Ni(II), Fe(III), Cd(II), and Pb(II) were quantitative (>95%) for Cochenille red in the 0.50–150.0 μg range. The studies were also performed at pH 6.5 without Cochenille red. As can be seen in Fig. 3, the recoveries for Cu(II), Co(II), Ni(II), Fe(III), Cd(II), and Pb(II) ions on a cellulose acetate membrane filter were less than 55% without Cochenille red for all analyte ions. Adding 75 μg of Cochenille red is recommended.

3.3. Elution process from membrane filter

Herein, the elution process was applied to elute-adsorbed Cu(II), Co(II), Ni(II), Fe(III), Cd(II), and Pb(II) ions on the cellulose acetate membrane filter. After

Table 3
The effect of matrix ions on membrane filtration ($N = 3$)

		Recovery (%)						
Ions	Concentration (μg/mL)	Added	Cd	Cu	Co	Ni	Fe	Pb
K^+	5,000	KCl	98 ± 2	95 ± 1	95 ± 0	96 ± 1	96 ± 1	97 ± 2
Mg^{2+}	3,000	$Mg(NO_3)_2.6H_2O$	94 ± 2	97 ± 2	94 ± 1	97 ± 1	96 ± 2	97 ± 1
Ca^{2+}	1,000	$CaCl_2$	99 ± 1	99 ± 1	97 ± 1	100 ± 1	96 ± 1	97 ± 1
CO_3^{2-}	7,000	Na_2CO_3	97 ± 1	100 ± 1	98 ± 1	97 ± 2	97 ± 1	96 ± 1
NO_3^-	3,000	KNO_3	94 ± 1	96 ± 1	99 ± 1	95 ± 1	96 ± 2	93 ± 2
F^-	500	NaF	94 ± 0	95 ± 2	97 ± 2	96 ± 1	98 ± 1	100 ± 2
I^-	500	NaI	97 ± 1	94 ± 2	95 ± 1	95 ± 2	100 ± 1	99 ± 1
SO_4^{2-}	2,500	Na_2SO_4	95 ± 2	96 ± 2	95 ± 2	94 ± 1	93 ± 2	95 ± 1
Cl^-	11,000	NaCl	92 ± 2	99 ± 1	98 ± 2	94 ± 2	100 ± 1	99 ± 1
PO_4^{3-}	2,000	$Na_3PO_4.12H_2O$	96 ± 1	96 ± 1	96 ± 2	95 ± 1	98 ± 1	97 ± 1
Al^{3+}	30	$Al(NO_3)_3.9H_2O$	97 ± 1	98 ± 1	94 ± 2	95 ± 2	98 ± 2	98 ± 1
Cu^{2+}	20	$Cu(NO_3)_2.3H_2O$	96 ± 1	–	100 ± 2	92 ± 2	95 ± 2	97 ± 2
Co^{2+}	20	$Co(NO_3)_2.6H_2O$	98 ± 1	97 ± 1	–	98 ± 2	97 ± 2	100 ± 1
Mn^{2+}	20	$MnSO_4.H_2O$	98 ± 1	96 ± 1	100 ± 1	96 ± 0	94 ± 2	98 ± 1
Ni^{2+}	20	$Ni\ (NO_3)_2.6H_2O$	97 ± 2	100 ± 1	98 ± 1	–	95 ± 1	99 ± 1
Pb^{2+}	25	$Pb(NO_3)_2$	95 ± 1	98 ± 1	94 ± 1	96 ± 1	92 ± 0	–
Zn^{2+}	25	$Zn(NO_3)_2.6H_2O$	98 ± 1	96 ± 1	95 ± 2	99 ± 1	98 ± 1	95 ± 1
Cr^{3+}	75	$Cr(NO_3)_3.9H_2O$	100 ± 1	98 ± 1	94 ± 1	95 ± 3	99 ± 1	98 ± 2
Cd^{2+}	25	$Cd(NO_3)_2.4H_2O$	–	97 ± 1	95 ± 1	95 ± 1	100 ± 1	97 ± 1
Fe^{2+}	20	$Fe(NO_3)_2$	98 ± 1	95 ± 2	96 ± 2	95 ± 2	–	95 ± 1

Note: mean ± standard deviation.

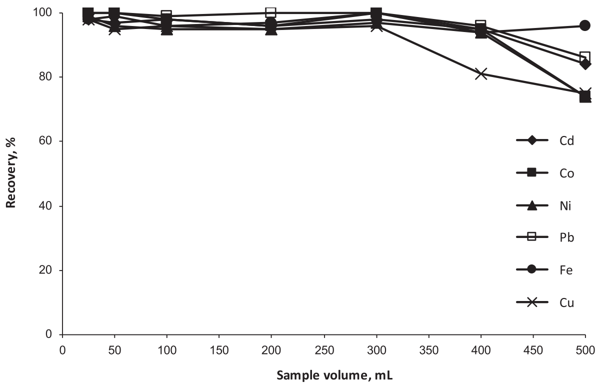

Fig. 4. The effect of sample volume on analyte recovery ($N = 3$).

collecting the analytes-Cochenille red chelates on the cellulose acetate membrane filter, the eluents shown in Table 1 were used separately to elute the analytes. Cu (II), Co(II), Ni(II), Fe(III), Cd(II), and Pb(II) ions were quantitatively (95%) recovered by using 3 mol/L CH_3COOH as eluent. In further studies, 10 mL of 3 mol/L CH_3COOH was used as the eluent.

A cellulose acetate membrane filter could be used at least 15 times without a loss in collection properties for the metal chelates through elution. The analyte ions were quantitatively recovered at a 4 mL/min flow rate for the sample solutions and a 6 mL/min flow rate for the eluent solutions.

3.4. Effects of membrane filter type

Various membrane filter types were used to recover Cu(II), Co(II), Ni(II), Fe(III), Cd(II), and Pb(II). The results are depicted in Table 2. The recovery values were 13% for Cd(II), 25% for Cu(II), 18% for Co(II), 51% for Ni(II), 38% for Fe(III), and 58% for Pb(II) using only cellulose acetate membrane filter. Cu(II), Co(II), Ni(II), Fe(III), Cd(II), and Pb(II) were quantitatively recovered using a combination of cellulose acetate membrane filter and Cochenille red.

3.5. Matrix effects

The interferon effects of cation and anions on SPE studies are important [32–36]. In our work, the influence of interfering ions in FAAS was investigated. Various levels of metal ions were added to a solution containing fixed levels of Cu(II), Co(II), Ni(II), Fe(III), Cd(II), and Pb(II) ions, and the procedure herein was followed. The results from this study are summarized in Table 3. The tolerance limit was defined as the ion concentration with a relative error lower than ± 5% related to membrane filtration and characterization of

Table 4
Addition/recovery test for application of the method herein ($N = 5$, final volume = 5 mL)

	Urine 1			Hair 1		Tap water	
	Added (μg)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Pb	0	9.9 ± 0.4	–	17.2 ± 0.6	–	–	–
	10	19.9 ± 0.6	100	26.9 ± 0.9	97	9.4 ± 0.2	94
	20	30.0 ± 0.9	101	36.4 ± 0.9	96	19.5 ± 0.5	98
Fe	0	78.3 ± 1.2	–	25.8 ± 0.8	–	61.2 ± 1.3	–
	10	88.0 ± 1.5	97	35.8 ± 0.8	100	71.0 ± 1.5	98
	20	97.1 ± 1.6	94	45.6 ± 1.1	99	80.2 ± 1.9	95
Cu	0	11.7 ± 0.5	–	24.1 ± 0.6	–	17.4 ± 0.5	–
	10	21.2 ± 0.7	95	33.5 ± 0.7	94	26.7 ± 0.6	93
	20	30.5 ± 0.8	94	42.9 ± 0.8	98	38.1 ± 0.8	103
Co	0	6.9 ± 0.3	–	5.0 ± 0.1	–	BDL	–
	10	16.9 ± 0.5	100	14.4 ± 0.4	94	10.1 ± 0.3	101
	20	26.7 ± 0.7	99	24.1 ± 0.4	95	19.6 ± 0.4	98
Cd	0	BDL	–	4.8 ± 0.2	–	BDL	–
	10	9.5 ± 0.3	95	14.5 ± 0.4	97	9.4 ± 0.3	94
	20	19.6 ± 0.5	98	23.4 ± 0.6	93	19.6 ± 0.5	98
Ni	0	3.8 ± 0.1	–	4.3 ± 0.1	–	10.2 ± 0.2	–
	10	13.6 ± 0.4	98	13.9 ± 0.3	96	20.1 ± 0.4	99
	20	23.8 ± 0.7	100	23.1 ± 0.5	94	29.5 ± 0.5	96

Notes: N.D.: not detected, mean ± standard deviation.

Table 5
Analyte levels of certified reference materials after application of the proposed method ($N = 3$)

TMDA-70 water	Certified value (μg/L)	Found (μg/L)	Recovery (%)
Cu	399	391	98
Co	285	273.6	96
Pb	443	438.5	99
Ni	328	305.0	93
Cd	145	134.8	93
Fe	368	371.6	101c
NCS ZC 81002 b Human Hair	Certified value (μg/g)	Found (μg/g)	Recovery (%)
Cu	33.6 ± 2.3	32.6 ± 1.9	97
Fe	160 ± 16	153.6 ± 11	96
Ni	5.77 ± 0.2	5.65 ± 0.2	98
Pb	3.83 ± 0.18	3.60 ± 0.15	94

Note: mean ± standard deviation.

the examined elements. The results should be applicable to real samples, which include various salts at high concentrations.

3.6. Effect of sample volume

The influence of sample volume on the recovery of Cu(II), Co(II), Ni(II), Fe(III), Cd(II), and Pb(II) ion on an cellulose acetate membrane filter was studied by varying the sample volume from 25 to 500 mL. The results are shown in Fig. 4. The sample volume does not affect quantitative recoveries in the range 25–300 mL for Cu(II) and 25–400 mL for Co(II), Ni(II), Cd(II) as well as Pb(II) and 25–500 mL for Fe(III), respectively. The preconcentration factors were calculated as 30 for Cu (II), 40 for Co(II), Ni(II), Cd(II) as well as Pb(II) and 50 for Fe(III) when the eluent volume is 10 mL.

3.7. Detection limit

The limit of detection (LOD) for the proposed procedure to measure analyte elements was studied under the optimal experimental conditions. The detection limit is defined as the concentration 3 times the standard deviation of the blank ($n = 10$, $X_L = (X_b + 3s)/PF$, where X_L: LOD, and X_b: blank value, PF: preconcentration factor), which was 1.9 μg/L for Cu(II),

Table 6
Analyte levels for real samples after application of the proposed method ($N = 6$)

Samples	Pb	Cu	Fe	Ni	Cd	Co
Concentration (μg/g)						
Hair 1	17.2 ± 0.6	24.1 ± 0.6	25.8 ± 0.8	4.3 ± 0.1	4.8 ± 0.2	5.0 ± 0.1
Hair 2	281.2 ± 7.8	34.7 ± 1.1	43.7 ± 1.3	5.2 ± 0.1	6.4 ± 0.1	9.1 ± 0.3
Esox lucius	BDL	8.3 ± 0.3	22.7 ± 1.3	BDL	5.8 ± 0.1	BDL
Cyprinus carpio	9.2 ± 0.5	10.1 ± 0.6	19.8 ± 0.9	BDL	5.1 ± 0.1	5.3 ± 0.1
Salmo trutta	7.8 ± 0.3	9.8 ± 0.4	32.3 ± 1.4	8.2 ± 0.4	6.3 ± 0.2	6.2 ± 0.2
Concentration (μg/L)						
Urine 1	9.9 ± 0.4	11.7 ± 0.5	78.3 ± 1.2	3.8 ± 0.1	BDL	6.9 ± 0.3
Urine 2	147.3 ± 4.2	33.6 ± 1.1	157.1 ± 4.4	12.5 ± 0.3	10.5 ± 0.2	23.1 ± 0.4
Spring water	BDL	49.2 ± 3.1	76.1 ± 4.2	BDL	BDL	BDL
Tap water	BDL	17.4 ± 0.5	61.2 ± 1.3	10.2 ± 0.2	BDL	BDL
Mineral water	BDL	12.1 ± 0.3	49.9 ± 0.8	7.2 ± 0.2	BDL	BDL
Wastewater	121 ± 9	62.7 ± 3.1	108 ± 6	11.9 ± 0.8	3.9 ± 0.7	BDL
Lake water	BDL	19.3 ± 0.8	47.6 ± 1.9	BDL	BDL	BDL
Thermal spring water	BDL	31.1 ± 2.3	123.7 ± 6.9	BDL	5.9 ± 0.2	BDL
Sea water	BDL	44.2 ± 1.8	83.2 ± 2.8	BDL	6.4 ± 0.3	BDL

Note: mean ± standard deviation.

Table 7
Comparison of the preconcentration procedures with presented method

Technique	System	Detection system	PF	DL (μg/L)	Ref.
SPE	Amberlite XAD-7 resin and-pyro-catechol	FAAS	22 for Cd(II), 23 for Co(II), 25 for Ni(II)	0.27 for Cd(II), 0.59 for Co(II) 1.29 for Ni(II)	[13]
Membrane filtration	PAN complexes on cellulose acetate membrane filter	FAAS	60 for Cu(II) and 20 for Pb(II)	1.2 for Cu(II) and 3.5 for Pb(II)	[16]
Co-precipitation	Ultrasound-assisted co-precipitation with manganese dioxide	ICP-OES	–	3.2 for Pb(II)	[17]
Membrane filtration	Calmagite complexes on a soluble cellulose nitrate membrane filter	FAAS	50 for Co(II), 250 for Cu(II), 250 for Fe(III), 150 for Pb(II)	0.06 for Cu(II), 0.76 Co(II), 0.33 for Fe(III), 2.5 Pb(II)	[22]
SPE	Microcolumn packed with single-walled carbon nanotubes	ICP-MS	–	3.9 for Cu(II), 1.2 for Co(II), 5.4 for Pb(II)	[29]
Membrane filtration	Cochenille red complexes on cellulose acetate membrane filter	FAAS	30 for Cu(II), 40 for Co(II), Ni(II), 50 for Fe(III), Pb(II)	1.9 for Cu(II), 2.4 for Ni(II), 1.5 for Cd(II), 3.6 Pb(II), 2.6 for Co (II), 3.1 for Fe (III)	This work

2.4 μg/L for Ni(II), 1.5 μg/L for Cd(II), 3.6 μg/L Pb(II), 2.6 μg/L for Co, and 3.1 μg/L for Fe(III).

3.8. Addition/recovery tests

Tests for addition/recovery of Cu(II), Co(II), Ni(II), Fe(III), Cd(II), and Pb(II) ions were performed for urine 1, hair 1, and tap water samples. The results are shown in Table 4. The added and measured analyte levels were consistent. The recovery values for Cu(II), Co(II), Ni(II), Fe(III), Cd(II), and Pb(II) were in the range 93–103%. These values were quantitative and demonstrate that the method herein can be performed for separation-preconcentration of analyte ions in real samples.

The membrane filtration procedure herein was validated by analyzing two certified reference materials (NCS ZC 81002 b Human Hair, TMDA-70 fortified water certified reference material) for Cu(II), Co(II), Ni(II), Fe (III), Cd(II), and Pb(II) values. The certified and observed values for the certified reference materials are in Table 5. The results are consistent with the certified values.

3.9. Application to real samples

The procedure herein was applied to various water (tap, natural spring, thermal spring, mineral, lake, sea, and wastewater), urine, hair, and fish samples, including *Salmo trutta*, *Cyprinus carpio*, and *Esox lucius*. The results are summarized in Table 6. The relative standard deviations were less than 7%.

4. Conclusion

The procedure herein for copper(II), cobalt(II), nickel(II), iron(III), cadmium(II), and lead(II) in real samples was characterized with good reproducibility and accuracy. Analyte ions were quantitatively recovered by the investigated matrix ions. The recoveries were quantitative (93–103%). The method developed herein was successfully employed to analyze various samples after a successful validation. The method is simple, rapid, inexpensive, as well as environmentally friendly, and has a lower LOD and higher enrichment factor than other methods reported in the literature (Table 7). The proposed method was also free of interference compared with conventional methods used to determine Cu(II), Co(II), Ni(II), Fe(III), Cd(II), and Pb (II) ion content.

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