



Multi-element coprecipitation for separation and enrichment of heavy metal ions for their flame atomic absorption spectrometric determinations

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ABSTRACT

A preconcentration–separation technique for lead(II), cadmium(II), chromium(III), nickel(II) and manganese(II) ions has been established. The procedure is based on coprecipitation of these ions by the aid of Cu(II)-dibenzylthiocarbamate precipitate. The precipitate was dissolved in 0.5 mL of concentrated HNO₃, and made up to 5 mL with distilled water. The heavy metals were determined by flame atomic absorption spectrometer. The effects of analytical parameters like pH, amounts of reagents, sample volume, etc. on the recoveries of heavy metals were investigated. The influences of matrix ions were also examined. The detection limits for the heavy metals based on 3 sigma ($N=21$) were found in the range of 0.34–0.87 $\mu\text{g L}^{-1}$. In order to validate the proposed method, two certified reference materials of NIST SRM 2711 Montana soil and NIST SRM 1515 Apple leaves were analyzed with satisfactory results. The proposed method was applied for the determination of lead, cadmium, chromium, nickel and manganese in environmental samples.

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1. Introduction

Heavy metals are important sources of environmental pollution and they can form compounds that are toxic even in very low concentrations [1–5]. Their accurate and precise determinations are one of the main parts of analytical chemistry. Due to lower analyte levels than the quantitation limits of instrumental techniques and interference effects of highly saline samples, separation and preconcentration techniques are used prior to determination step of the heavy metals ions [5–10]. Preconcentration–separation methods including solid phase extraction [11–13], cloud point extraction [14,15], membrane filtration [16,17], liquid–liquid extraction [18,19], electrochemical deposition [20,21], etc. have been widely used for the preconcentration–separation of heavy metal ions.

Coprecipitation has also an important place in the preconcentration and separation methods due to its some advantages including simplicity and short time period for the procedures [22–25]. In the coprecipitation procedure, a precipitate was occurred by the combination of a carrier element and a suitable inorganic or organic ligand. Various carrier elements including copper, nickel, aluminium, erbium, magnesium, indium, samarium, etc. have been

used for the coprecipitative preconcentration and separation of heavy metal ions at traces levels [26–30]. Inorganic ligands like hydroxide, thiocyanate and organic ligands like various ditiocarbamates, 5-methyl-4-(2-thiazolylazo) resorcinol, rubenic acid, etc. have been used for this purpose [31–35]. According to our literature survey, no coprecipitation study for trace heavy metal ions is performed by using the combination of copper(II) and dibenzylthiocarbamate.

The aim of presented work is to established a new precise and accurate coprecipitation procedure for lead(II), cadmium(II), chromium(III), nickel(II) and manganese(II) ions at ultra trace levels in environmental samples prior to their flame atomic absorption spectrometric determinations.

2. Experimental

2.1. Apparatus

A PerkinElmer AAnalyst 700 atomic absorption spectrometer (Norwalk, CT, USA) with deuterium background corrector was used. All measurements were carried out in an air/acetylene flame. A 10 cm long slot-burner head, a lamp and an air–acetylene flame were used. The operating parameters for working elements were set as recommended by the manufacturer.

A pH meter, Sartorius pp-15 Model glass-electrode was employed for measuring pH values in the aqueous phase. Milestone

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Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was used. Digestion conditions for microwave system were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, ventilation: 8 min [36,37].

2.2. Reagents and solutions

All the reagents used were of analytical grade. Deionized double distilled water was used throughout the experimental work. High purity reagents from Sigma (St. Louis, MO, USA) and Merck (Darmstadt, Germany) were used for all preparations of sample solution. The mono-elemental standard solutions (St. Louis, MO, USA) used for the calibration procedures were prepared before use by dilution of the stock solution with 1 mol L⁻¹ HNO₃. Stock solutions of matrix elements (St. Louis, MO, USA) were prepared from the high purity compounds (99.9%). A 1% (m/v) solution of sodium dibenzylthiocarbamate (Fluka no: 71485) was prepared by dissolving of 1.0 g of sodium dibenzylthiocarbamate in ethanol diluting to 100 mL with water.

The following buffer solutions were prepared for pH adjustment: (a) 3.8 g sodium dihydrogen phosphate and 9 mL 85% of phosphoric acid for pH 2; (b) 13.8 g sodium dihydrogen phosphate and 0.60 mL 85% of phosphoric acid for pH 3; (c) 77.0 g ammonium acetate and 413 mL acetic acid for pH 4; (d) 13.1 g sodium dihydrogen phosphate and 2.40 g disodium hydrogen for pH 5; (e) 58.5 g ammonium acetate and 2.5 mL acetic acid for pH 6; (f) 0.7 g sodium borate and 5 mL 1 mol L⁻¹ hydrochloric acid pH 7; (g) 53.5 g ammonium chloride and 4.0 mL ammonia for pH 8; (h) 500 mL of 0.1 mol L⁻¹ of ammonium chloride and 250 mL of 0.1 mol L⁻¹ of ammonia for pH 9; (i) 37.0 g ammonium chloride, 285 mL ammonia for pH 10; were taken then the final volume was completed to 500 mL with distilled water.

2.3. Model studies for coprecipitation

The copper(II)-dibenzylthiocarbamate coprecipitation procedure was tested with model solutions prior to its application to real samples. An aqueous solution containing 20 µg of lead(II), 5 µg of cadmium(II), 20 µg of chromium(III), 10 µg of nickel(II) and 10 µg of manganese(II), were placed in centrifuge tubes separately. One mL of 1000 mg L⁻¹ of copper(II) as a carrier element was added. Then 1.0 mL of 1% (m/v) dibenzylthiocarbamate was added. The pH was adjusted to pH 9 by the addition of 2.0 mL of ammonium buffer. After 10 min, the solution was centrifuged at 3500 rpm for 20 min. The precipitate remained adhering to the tube was dissolved with 0.5 mL of concentrated HNO₃, and made up to 5 mL with distilled water. Then the final volume of the supernatant was completed to 5.0 mL with distilled water. The heavy metals in final solution were determined by flame atomic absorption spectrometer.

2.4. Analysis of real samples

NIST SRM 2711 Montana soil and NIST SRM 1515 Apple leaves (250 mg), soil, sediment and river sediment (1.0 g) were digested with 6 mL of HCl (37%), 2 mL of HNO₃ (65%) in microwave digestion system and diluted to 50 mL with deionized water. Black tea and tobacco samples (1.0 g) were digested with 6 mL of concentrated HNO₃ (65%) and 2 mL of H₂O₂ (30%) in microwave system and diluted up to 50 mL with deionized water [36,37]. A blank digest was carried out in the same way. Then the preconcentration procedure given above was applied to the final solutions. The levels of heavy metals in the samples were determined by flame atomic absorption spectrometry.

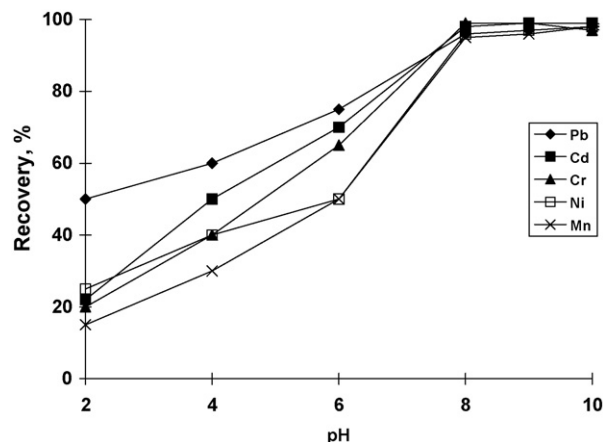


Fig. 1. The influences of pH on the recoveries of heavy metals (amounts of analytes: 20 µg of lead(II), 5 µg of cadmium(II), 20 µg of chromium(III), 10 µg of nickel(II) and 10 µg of manganese(II), amounts of carrier element: 1 mg copper(II), amounts of ligand: 10 mg dibenzylthiocarbamate, $N = 3$).

Natural water samples analyzed were filtered through Millipore cellulose membrane filter (0.45 µm pore size). The pH of the samples was adjusted to 9.0 with buffer solution. Then the preconcentration procedure given above was applied to the final solutions. The levels of heavy metal ions in the samples were determined by flame atomic absorption spectrometry.

3. Results and discussion

3.1. Influences of pH

The effect of pH on the quantitative recoveries of heavy metal ions on the copper(II)-dibenzylthiocarbamate precipitate were investigated in the pH range of 2–10. The pH adjustments were done by using different buffer solutions. Brown colored Cu(II)-dibenzylthiocarbamate precipitate was formed at the pH range of 8–10 in our working conditions. The results for influences of pH are depicted in Fig. 1. All the heavy metals ions were quantitatively recovered at the pH range of 8–10. Further works were performed at pH 9 by adjusting with ammonia buffer.

3.2. Effects of amount of Cu²⁺ as carrier element

The influences of amount of Cu²⁺ as carrier element on the recoveries of lead(II), cadmium(II), chromium(III), nickel(II) and manganese(II) ions were also investigated. The results are shown in Fig. 2. The recoveries were not quantitative without Cu²⁺. The recoveries increased and reach to quantitative values for all the investigated heavy metals at the range of 1.0–3.0 mg of Cu²⁺ due to the formation of Cu(II)-dibenzylthiocarbamate precipitate. In the light of these results, 1.0 mg of Cu²⁺ as carrier was used in all further works.

3.3. Amount of dibenzylthiocarbamate

The influences of amount of dibenzylthiocarbamate on the quantitative coprecipitation of heavy metal ions were also investigated in the range of 0.0–40.0 mg of dibenzylthiocarbamate. The results are depicted in Fig. 3. The optimum recoveries of lead(II), cadmium(II), chromium(III), nickel(II) and manganese(II) were obtained in the range of 10.0–40.0 mg of dibenzylthiocarbamate. For all further works, 10.0 mg of dibenzylthiocarbamate was used.

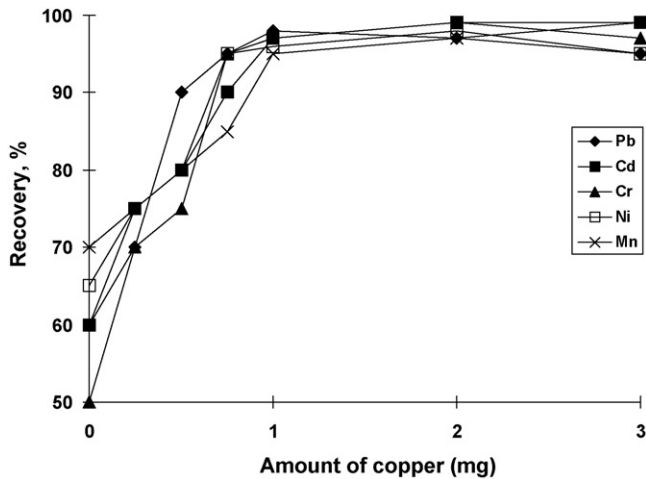


Fig. 2. The influences of amount of Cu^{2+} on the recoveries of heavy metal ions (pH 9, amounts of analytes: 20 μg of lead(II), 5 μg of cadmium(II), 20 μg of chromium(III), 10 μg of nickel(II) and 10 μg of manganese(II), amounts of ligand: 10 mg dibenzylthiocarbamate, $N=3$).

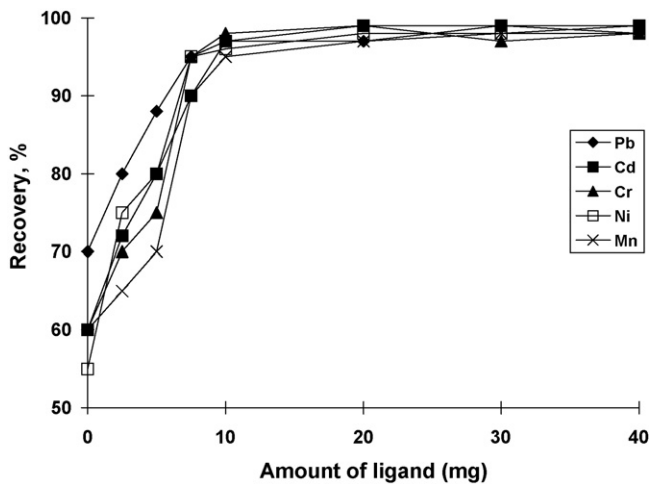


Fig. 3. Influences of the amounts of dibenzylthiocarbamate on the recoveries of heavy metals (pH 9, amounts of analytes: 20 μg of lead(II), 5 μg of cadmium(II), 20 μg of chromium(III), 10 μg of nickel(II) and 10 μg of manganese(II), amounts of ligand: 10 mg dibenzylthiocarbamate, $N=3$).

3.4. Influences of sample volume

The effects of sample volume were examined in range of 25–250 mL, to possible application of the coprecipitation procedure for natural water samples. The results are depicted in Table 1. The recoveries of heavy metal ions were found quantitative in the sam-

Table 1

The effects of sample volume on the recoveries of heavy metals (pH 9, amounts of analytes: 20 μg of lead(II), 5 μg of cadmium(II), 20 μg of chromium(III), 10 μg of nickel(II) and 10 μg of manganese(II), amounts of carrier element: 1 mg copper(II), amounts of ligand: 10 mg dibenzylthiocarbamate, $N=3$)

mL	Recovery (%)				
	Pb	Cd	Cr	Ni	Mn
25	98 ± 3 ^a	97 ± 2	99 ± 3	96 ± 2	98 ± 3
50	97 ± 2	98 ± 3	97 ± 2	97 ± 3	98 ± 2
100	95 ± 3	96 ± 2	96 ± 3	95 ± 2	96 ± 3
150	90 ± 2	85 ± 3	80 ± 2	90 ± 3	83 ± 2
250	70 ± 3	60 ± 2	50 ± 3	75 ± 2	77 ± 3

^a Mean ± standard deviation.

Table 2

Influences of matrix ions on the recoveries of heavy metals ($N=3$)

Ion	Added as	Concentration (mg L ⁻¹)	Pb	Cd	Cr	Ni	Mn
Na^+	NaCl	10,000	97 ± 2	96 ± 3	96 ± 3	95 ± 3	99 ± 3
K^+	KCl	3,000	95 ± 2	95 ± 2	95 ± 2	96 ± 2	95 ± 2
Ca^{2+}	CaCl_2	3,000	96 ± 3	96 ± 3	96 ± 3	96 ± 4	96 ± 3
Mg^{2+}	MgCl_2	3,000	95 ± 3	97 ± 3	99 ± 1	97 ± 3	97 ± 2
Cl^-	NaCl	25,000	96 ± 3	98 ± 3	96 ± 2	96 ± 2	98 ± 2
F^-	NaF	2,000	95 ± 2	96 ± 4	96 ± 2	98 ± 4	96 ± 2
NO_3^-	KNO_3	3,000	95 ± 2	97 ± 3	97 ± 3	97 ± 3	97 ± 4
SO_4^{2-}	Na_2SO_4	3,000	96 ± 3	97 ± 2	95 ± 2	97 ± 2	96 ± 2
PO_4^{3-}	Na_3PO_4	1,000	97 ± 4	96 ± 4	95 ± 3	95 ± 3	95 ± 3
Al^{3+}	$\text{Al}_2(\text{SO}_4)_3$	50	96 ± 2	97 ± 2	96 ± 2	95 ± 2	97 ± 2
Fe^{3+}	FeCl_3	50	98 ± 2	96 ± 3	96 ± 3	96 ± 3	96 ± 3
Cu^{2+}	CuSO_4	50	97 ± 3	97 ± 2	97 ± 2	97 ± 2	97 ± 2
Co^{2+}	CoSO_4	50	96 ± 3	98 ± 3	98 ± 3	98 ± 3	98 ± 3
Zn^{2+}	ZnSO_4	50	95 ± 3	96 ± 3	96 ± 3	96 ± 2	96 ± 2

ple volume range of 25–100 mL. The high sample volumes may be behaved as eluent. The preconcentration factor is calculated by the ratio of the highest sample volume with the analytes under study (100 mL) and the lowest eluent volume (2 mL). The preconcentration factor was 50. The time required for the coprecipitation and determination was about 45 min.

3.5. Matrix effects

The interferences of matrix components of real samples especially highly saline samples including seawater, urine are important problem in the determination of heavy metals [36–42]. The effect of some foreign ions (Table 2) which interfere with the determination of metal ions by the proposed method or/and often accompany heavy metal ions in various real samples was examined. A fixed amount of metal ions was taken with different amounts of foreign ions and recommended procedure was followed. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of investigated heavy metal ions. The results are summarized in Table 2. The recoveries of heavy metal ions were affected by the matrix ions. This results show that the presented procedure could be applied to the multi-element separation and preconcentration of heavy metals.

3.6. Analytical figures of merit

The reproducibility of the presented procedure was evaluated by model solution containing heavy metal ions ($N=7$). The relative standard deviations (R.S.D.) of these determinations were below 10%.

The limits of detection (LOD) of the proposed procedure for the determination of analyte heavy metal were studied under the optimal experimental conditions. The detection limits, defined as the concentration equivalent to 3 times the standard deviation of blank ($N=21$, $X_L = X_b + 3s$, X_L : limit of detection, X_b : blank value) of the reagent blank, were 0.87, 0.34, 0.75, 0.060 and 0.45 $\mu\text{g L}^{-1}$ for lead, cadmium, chromium, nickel and manganese, respectively.

3.7. Applications

Tests of addition/recovery in the experiments for heavy metal ions were performed in three water samples. The results are given in Table 3. A good agreement was obtained between the added and measured heavy metal amounts. The recovery values for the heavy metal ions were greater than 95%. These values were quantitative and it shows that the presented procedure could be applied for the preconcentration of heavy metal ions in real samples.

Table 3

The results for tests of addition/recovery for heavy metals determination in water samples (sample volume: 25 mL, final volume: 5 mL, N=4)

Element	Added (μg)	Tap water		Sea water		Spring water	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Pb	0	ND	–	ND	–	ND	–
	10	9.9 ± 0.4 ^a	99	9.9 ± 0.5	99	9.8 ± 0.3	98
	20	19.6 ± 0.7	98	19.4 ± 0.8	97	19.2 ± 0.5	96
	40	38.9 ± 0.9	97	38.1 ± 1.2	95	38.5 ± 0.8	96
Cd	0	ND	–	ND	–	ND	–
	2.5	2.5 ± 0.1	100	2.4 ± 0.2	96	2.4 ± 0.1	96
	5	4.8 ± 0.2	96	4.9 ± 0.3	98	4.9 ± 0.2	98
	10	10.1 ± 0.6	101	9.9 ± 0.5	99	9.6 ± 0.4	96
Cr	0	ND	–	ND	–	ND	–
	10	9.8 ± 0.4	98	9.7 ± 0.5	97	9.8 ± 0.4	98
	20	19.4 ± 0.5	97	19.6 ± 0.7	98	19.1 ± 0.5	96
	40	38.5 ± 0.9	96	38.2 ± 1.5	96	38.7 ± 0.9	97
Ni	0	ND	–	ND	–	ND	–
	5	4.9 ± 0.2	98	4.7 ± 0.3	94	4.8 ± 0.2	96
	10	10.2 ± 0.5	102	9.8 ± 0.4	98	9.7 ± 0.3	97
	20	19.6 ± 0.9	98	19.3 ± 0.9	97	19.2 ± 0.8	96
Mn	0	ND	–	ND	–	ND	–
	2.5	2.4 ± 0.1	96	2.5 ± 0.2	100	2.4 ± 0.1	96
	5	4.9 ± 0.2	98	4.8 ± 0.3	96	4.9 ± 0.2	98
	10	9.8 ± 0.8	98	9.9 ± 0.4	99	9.7 ± 0.5	97

^a Standard deviation, ND: not detected.**Table 4**

The results for reference standard materials (N=4)

Element	NIST SRM 2711 Montana soil ($\mu\text{g g}^{-1}$)		NIST SRM 1515 Apple leaves ($\mu\text{g g}^{-1}$)	
	Certified value	Our value	Certified value	Our value
Pb	1162	1100 ± 50 ^a	0.47	0.45 ± 0.03
Cd	41.7	40.2 ± 2.5	0.013	0.020 ± 0.002
Cr	(47) ^b	45.8 ± 3.2	(0.3)	0.32 ± 0.02
Ni	20.6	20.2 ± 1.5	0.91	0.87 ± 0.05
Mn	638	615 ± 23	54	52.5 ± 3.2

^a Mean expressed as 95% tolerance limit.^b The value in the parentheses are not certified.**Table 5**

Trace element levels of natural water samples (sample volume: 100 mL, final volume: 2 mL, N=4)

Element	Tap water ($\mu\text{g L}^{-1}$)	Sea water ($\mu\text{g L}^{-1}$)	Spring water ($\mu\text{g L}^{-1}$)	River water ($\mu\text{g L}^{-1}$)
Pb	5.4 ± 0.3 ^a	4.5 ± 0.2	7.2 ± 0.5	6.7 ± 0.4
Cd	2.3 ± 0.2	2.6 ± 0.2	4.4 ± 0.3	3.5 ± 0.2
Cr	BDL	5.5 ± 0.3	3.7 ± 0.2	4.2 ± 0.2
Ni	BDL	6.7 ± 0.4	8.3 ± 0.6	7.5 ± 0.4
Mn	4.9 ± 0.2	3.8 ± 0.2	4.2 ± 0.2	5.9 ± 0.3

BDL: Below the detection limit.

^a Mean expressed as 95% tolerance limit.**Table 6**

The application of presented method in real samples for contents of heavy metal ions (N=4)

Element	Soil from Tokat City ($\mu\text{g g}^{-1}$)	Black tea ($\mu\text{g g}^{-1}$)	Tobacco ($\mu\text{g g}^{-1}$)	River sediment ($\mu\text{g g}^{-1}$)
Pb	16.5 ± 0.9 ^a	1.2 ± 0.1	1.6 ± 0.1	21.5 ± 0.8
Cd	1.5 ± 0.1	0.85 ± 0.05	1.8 ± 0.1	3.4 ± 0.2
Cr	24.6 ± 1.3	0.50 ± 0.04	2.9 ± 0.2	10.5 ± 0.7
Ni	15.1 ± 1.1	4.6 ± 0.2	2.4 ± 0.2	19.5 ± 1.5
Mn	96.8 ± 7.6	1045 ± 65	72.9 ± 5.4	75.1 ± 5.3

^a Mean expressed as 95% tolerance limit.**Table 7**

Comparative data from some recent studies on preconcentration–separation of heavy metal ions

Technique	Analytes	System	Eluent/dissolving media	PF	Detection limit ($\mu\text{g L}^{-1}$)	R.S.D. (%)	References
Coprecipitation	Cu, Fe, Pb, Mn, Zn, Cd, Ni, Bi, Cr	Cobalt-diethyldithiocarbamate	1.0 mL conc. HNO ₃	225	4–64	<7	[34]
Coprecipitation	Pb	Manganese dioxide	HNO ₃ /H ₂ O ₂	–	3.2	<5	[43]
Coprecipitation	Cd, Cu, Pb	Aluminium hydroxide	4 mol L ⁻¹ HNO ₃	125	3–16	2–3	[44]
Coprecipitation	Au, Pd, Pb	Nickel(II)-5-methyl-4-(2-thiazolylazo)resorcinol	1.0 mL conc. HNO ₃	25	1.5–2.6	<10	[45]
Coprecipitation	Fe, Pb, Bi	Yttrium phosphate	6 mol L ⁻¹ HNO ₃	–	0.008–0.137 μg	1.2–4.1	[46]
Coprecipitation	Cu, Co, Pb, Cd, Ni	Cerium(IV) hydroxide	0.5 mL conc. HNO ₃	375	0.18–7	<9	[47]
Coprecipitation	Co, Mn	Copper(II)-8-hydroxyquinoline	0.5 mL conc. HNO ₃	25	0.86–0.98	<10	[48]
SPE	Cd, Cu	Amberlite XAD-2/2-aminothiophenol	0.5 mol L ⁻¹ HCl	14–28	0.14–0.54	<5	[49]
SPE	Pb	Octadecyl bonded silica membrane disk modified with Cyanex302	1 mol L ⁻¹ HNO ₃	400	1.0	0.4	[50]
Coprecipitation	Pb, Cd, Cr, Ni, Mn	Copper(II)-dibenzylthiocarbamate	0.5 mL conc. HNO ₃	50	0.34–0.87	<10	This study

SPE: solid phase extraction, PF: preconcentration factor.

The validation of the presented coprecipitation procedure is performed by the analysis of two CRMs (NIST SRM 2711 Montana soil and NIST SRM 1515 Apple leaves). The certified and observed values for certified reference materials are given in Table 4. The results found were in good agreement with the certified values of certified reference materials.

The procedure presented for lead, cadmium, chromium, nickel and manganese was applied to three different water samples. The results were given in Table 5. The method has been combined with the microwave assisted digested samples including soil, sediment, black tea and tobacco samples. The results are given in Table 6.

4. Conclusions

The presented procedure is simple and rapid with good precision and accuracy. Heavy metal ions were quantitatively recovered by the investigated matrix ions. The comparisons of the presented procedure and some works on preconcentration and separation of heavy metal ions in literature are given in Table 7. The proposed procedure is superior to reported methods of heavy metal for separation–preconcentration in term of no need to consumption of organic solvents and enrichment factor. The method is relatively rapid as compared with previously reported procedures for the enrichment of heavy metal ions [48–56].

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References

- M.G.A. Korn, E.S.B. Morte, D.C.M.B. dos Santos, J.T. Castro, J.T.P. Barbosa, A.P. Teixeira, A.P. Fernandes, B. Welz, W.P.C. dos Santos, E.B.G.N. dos Santos, M. Korn, Sample preparation for the determination of metals in food samples using spectroanalytical methods—a review, *Appl. Spectrosc. Rev.* 43 (2008) 67–92.
- M. Soylak, O. Turkoglu, Trace metal accumulation caused by traffic in an agricultural soil near a motorway in Kayseri, Turkey, *J. Trace Microprobe Tech.* 17 (1999) 209–217.
- M.B. Arain, T.G. Kazi, M.K. Jamali, H.I. Afridi, N. Jalbani, Factorial designs for As, Cd and Pb ultrasound-assisted pseudodigestion of fish muscles followed by electrothermal atomic absorption spectrophotometer, *J. AOAC Int.* 90 (2007) 470–478.
- G. Hoeksema, L. Cheperdak, K. Ikehata, M.G. El-Din, W.B. Kindzierski, A.G. El-Din, Automotive wastes, *Water Environ. Res.* 79 (2007) 1613–1629.
- S.J. Shahtaheri, M. Khadem, F. Golbabaei, A. Rahimi-Froushani, Solid phase extraction for monitoring of occupational exposure to Cr (III), *Anal. Chem. Insign.* 2 (2007) 125–132.
- A.R. Turker, New sorbents for solid-phase extraction for metal enrichment, *Clean* 35 (2007) 548–557.
- I. Narin, M. Soylak, K. Kayakirilmaz, M. Dogan, Preparation of a chelating resin by immobilizing 1-(2-pyridylazo) 2-naphthol on amberlite XAD-16 and its application of solid phase extraction of Ni(II), Cd(II), Co(II), Cu(II), Pb(II), and Cr(III) in natural water samples, *Anal. Lett.* 36 (2003) 641–658.
- F.A.L. De Moura, Avaliação Da Digestão De Amostras De Piche Assistida Por Radiação De Microondas E Determinação De Metais Por Icp Oes, Dissertação Apresentada Ao Curso De Pós-Graduação Em Química na Universidade Federal Fluminense, 2006.
- I. Narin, M. Tuzen, M. Soylak, Aluminium determination in environmental samples by graphite furnace atomic absorption spectrometry after solid phase extraction on Amberlite XAD-1180/pyrocatechol violet chelating resin, *Talanta* 63 (2004) 411–418.
- M. Ghaedi, Pyrimidine-2-thiol as selective and sensitive ligand for preconcentration and determination of Pb²⁺, *Chem. Anal.* 51 (2006) 593–602.
- H. Askun, B. Gulbakan, O. Celikbicak, C. Uzun, O. Guven, B. Salih, Preconcentration and matrix elimination for the determination of Pb(II), Cd(II), Ni(II), and Co(II) by 8-hydroxyquinoline anchored poly(styrene-divinylbenzene) microbeads, *J. Appl. Polym. Sci.* 107 (2008) 2714–2722.
- M. Soylak, Solid phase extraction of Cu(II), Pb(II), Fe(III), Co(II) and Cr(III) on chelex 100 column prior to their flame atomic absorption spectrometric determinations, *Anal. Lett.* 37 (2004) 1203–1217.
- H. Refiker, M. Merdivan, R.S. Aygun, Solid-phase extraction of silver in geological samples and its determination by FAAS, *Sep. Sci. Technol.* 43 (2008) 179–191.
- F. Bai, Z. Fan, Flow injection micelle-mediated methodology for determination of lead by electrothermal atomic absorption spectrometry, *Microchim. Acta* 159 (2007) 235–240.
- X.B. Yin, Dual-cloud point extraction as a preconcentration and clean-up technique for capillary electrophoresis speciation analysis of mercury, *J. Chromatogr.* 1154A (2007) 437–443.
- I. Narin, M. Soylak, Enrichment and determinations of nickel(II), cadmium(II), copper(II), cobalt(II) and lead(II) ions in natural waters, table salts, tea and urine samples as pyrrolidine dithiocarbamate chelates by membrane filtration-flame atomic absorption spectrometry combination, *Anal. Chim. Acta* 493 (2003) 205–212.
- A. Moghimi, M. Saber-Tehrani, S. Waqif-Husain, M. Mohammadhosseini, Preconcentration and determination of chromium species using octadecyl silica membrane disks and flame atomic absorption spectrometry, *Chin. J. Chem.* 25 (2007) 1859–1865.
- J. Komarek, R. Cervenka, T. Ruzicka, V. Kuban, ET-AAS determination of aluminium in dialysis concentrates after continuous flow solvent extraction, *J. Pharmaceut. Biomed. Anal.* 45 (2007) 504–509.
- Y. Shijo, M. Suzuki, T. Shimizu, S. Aratake, N. Uehara, Determination of trace amounts of molybdenum in rainwater and snow by graphite-furnace atomic absorption spectrometry after solvent extraction and micro-volume back-extraction, *Anal. Sci.* 12 (1996) 953–957.
- G. Yang, X. Qu, M. Shen, C. Wang, Q. Qu, X. Hu, Electrochemical behavior of lead(II) at poly(phenol red) modified glassy carbon electrode, and its trace determination by differential pulse anodic stripping voltammetry, *Microchim. Acta* 160 (2008) 275–281.
- B. Zawisza, R. Sitko, Determination of Te, Bi, Ni, Sb and Au by X-ray fluorescence spectrometry following electroenrichment on a copper cathode, *Spectrochim. Acta* 62B (2007) 1147–1152.
- C. Li, T.Y. Chen, Y.S. Yan, Study on the determination of trace Cu and Mn in foodstuff preconcentration by precipitate flotation and FAAS, *Spectrosc. Spect. Anal.* 27 (2007) 2127–2130.
- D. Atanassova, V. Stefanova, E. Russeva, Co-precipitative pre-concentration with sodium diethyldithiocarbamate and ICP-AES determination of Se, Cu, Pb, Zn, Fe, Co, Ni, Mn, Cr and Cd in water, *Talanta* 47 (1998) 1237–1243.
- D.S.K. Peker, O. Turkoglu, M. Soylak, Dysprosium(III) hydroxide coprecipitation system for the separation and preconcentration of heavy metal contents of table salts and natural waters, *J. Hazard. Mater.* 143 (2007) 555–560.
- S. Kagaya, Y. Serikawa, R. Yashima, T. Tanaka, K. Hasegawa, A simple preconcentration-storing technique based on sulfide precipitation for multipoint monitoring of mercury in rainwater and snow by cold vapor atomic absorption spectrometry, *Bull. Chem. Soc. Jpn.* 79 (2006) 1719–1724.
- M. Hiraide, Z.S. Chen, H. Kawaguchi, Coprecipitation of traces of heavy metals with indium hydroxide for graphite-furnace atomic absorption spectrometry, *Anal. Sci.* 7 (1991) 65–68.
- Z. Zhuang, X. Wang, P. Yang, C. Yangand, B. Huang, On-line flow injection cobalt-ammonium pyrrolidine-1-ylidithioformate coprecipitation for preconcentration of trace amounts of metals in waters with simultaneous determination by inductively coupled plasma atomic emission spectrometry, *J. Anal. At. Spectrom.* 9 (1994) 779–783.
- T. Minami, Y. Sohrin, J. Ueda, Determination of chromium, copper and lead in river water by graphite-furnace atomic absorption spectrometry after coprecipitation with terbium hydroxide, *Anal. Sci.* 21 (2005) 1519–1521.
- Y.C. Sun, Determination of antimony (III, V) in natural waters by coprecipitation and neutron activation analysis, *Anal. Chim. Acta* 276 (1993) 33–37.
- L. Elci, M. Soylak, B. Ozcan, Coprecipitation of Cu(II), Ni(II), Fe(III), Cd(II), Pb(II) and Co(II) in wastewater, sediment and metallic zinc samples with HMDTC-HMA for flame atomic absorption spectrometric determination, *Anal. Lett.* 36 (2003) 987–999.
- O. Kujirai, K. Yamada, Application of cobalt ammine complexes for the simultaneous determination of traces of As, Fe, Ti, V and Zr in high-purity cobalt metal by lanthanum hydroxide coprecipitation and inductively coupled plasma-atomic emission spectrometry, *Fresenius J. Anal. Chem.* 354 (1996) 428–431.
- M. Vircavs, V. Rone, D. Vircava, Coprecipitation study of As(III), Cu(II) and Cd(II) from aqueous solution using 5-bromo and 2-methylthioquinoline-8-thiol, *Fresenius J. Anal. Chem.* 350 (1994) 650–651.
- S. Saracoglu, M. Soylak, D.S.K. Peker, L. Elci, W.N.L. dos Santos, V.A. Lemos, S.L.C. Ferreira, A pre-concentration procedure using coprecipitation for determination of lead and iron in several samples using flame atomic absorption spectrometry, *Anal. Chim. Acta* 575 (2006) 133–137.
- L. Elci, U. Sahin, S. Oztas, Determination of trace amounts of some metals in samples with high salt content by atomic absorption spectrometry after cobalt-diethyldithiocarbamate coprecipitation, *Talanta* 44 (1997) 1017–1023.
- I. Atsuya, K. Itoh, I. Ariu, Preconcentration by coprecipitation of lead and selenium with Ni/pyrrolidine-dithiocarbamate complex and their simultaneous determination by internal standard atomic absorption spectrometry with the solid sampling technique, *Pure Appl. Chem.* 63 (1991) 1221–1226.
- M. Tuzen, K. Parlar, M. Soylak, Enrichment/separation of cadmium(II) and lead(II) in environmental samples by solid phase extraction, *J. Hazard. Mater.* 121 (2005) 79–87.
- M. Tuzen, H. Sari, M. Soylak, Microwave and wet digestion procedures for atomic absorption spectrometric determination of trace metals contents of sediment samples, *Anal. Lett.* 37 (2004) 1925–1936.

- [38] R.M. Cespon-Romero, M.C. Yebra-Biurrun, Determination of trace metals in urine with an on-line ultrasound-assisted digestion system combined with a flow-injection preconcentration manifold coupled to flame atomic absorption spectrometry, *Anal. Chim. Acta* 609 (2008) 184–191.
- [39] M. Ghaedi, M.R. Fathi, A. Shokrollahi, S. Gharaghani, F. Ahmadi, M. Soylak, Cloud point extraction for the determination of copper in environmental samples by flame atomic absorption spectrometry, *Quim. Nova* 31 (2008) 70–74.
- [40] Q. He, X. Chang, X. Huang, Z. Hu, Determination of trace elements in food samples by ICP-AES after preconcentration with *p*-toluenesulfonylamide immobilized on silica gel and nanometer SiO₂, *Microchim. Acta* 160 (2008) 147–152.
- [41] L. Morales, M.I. Toral, Simultaneous determination of Cu(II) and Ag(I) on SP Sephadex C25 as complexes with 1-phenyl-1,2-propanedione-2-oximethiosemicarbazone by derivative spectrophotometry, *J. AOAC Int.* 90 (2007) 1695–1700.
- [42] M. Ghaedi, A. Shokrollahi, Chromosorb, an alternative suitable support for trace copper ion enrichment using 2-mercaptobenzoxazole as modifier, *Fresenius Environ. Bull.* 15 (2006) 1373–1381.
- [43] M.S. Bispo, E.S. da Boa Morte, M.G.A. Korn, L.S.G. Teixeira, M. Korn, A.C.S. Costa, Determination of Pb in river water samples by inductively coupled plasma optical emission spectrometry after ultrasound-assisted co-precipitation with manganese dioxide, *Spectrochim. Acta Part B* 60 (2005) 653–658.
- [44] G. Doner, A. Ege, Determination of copper, cadmium and lead in seawater and mineral water by flame atomic absorption spectrometry after coprecipitation with aluminum hydroxide, *Anal. Chim. Acta* 547 (2005) 14–17.
- [45] M. Tuzen, M. Soylak, Coprecipitation of gold(III), palladium(II) and lead(II) for their flame atomic absorption spectrometric determinations, *J. Hazard. Mater.* 152 (2008) 656–661.
- [46] S. Kagaya, Y. Araki, N. Hirai, K. Hasegawa, Coprecipitation with yttrium phosphate as a separation technique for iron(III), lead, and bismuth from cobalt, nickel, and copper matrices, *Talanta* 67 (2005) 90–97.
- [47] U. Divrikli, L. Elci, Determination of some trace metals in water and sediment samples by flame atomic absorption spectrometry after coprecipitation with cerium (IV) hydroxide, *Anal. Chim. Acta* 452 (2002) 231–235.
- [48] M. Soylak, B. Kaya, M. Tuzen, Copper(II)-8-hydroxyquinoline coprecipitation system for preconcentration and separation of cobalt(II) and manganese(II) in real samples, *J. Hazard. Mater.* 147 (2007) 832–837.
- [49] V.A. Lemos, P.X. Baliza, Amberlite XAD-2 functionalized with 2-aminothiophenol as a new sorbent for on-line preconcentration of cadmium and copper, *Talanta* 67 (2005) 564–570.
- [50] M. Karve, R.V. Rajgor, Solid phase extraction of lead on octadecyl bonded silica membrane disk modified with Cyanex302 and determination by flame atomic absorption spectrometry, *J. Hazard. Mater.* 141 (2007) 607–613.
- [51] X.J. Liu, Z.F. Fan, Determination of trace Pb in water samples by electrothermal atomic absorption spectrometry after single-drop microextraction, *Atom. Spectrosc.* 28 (2007) 215–219.
- [52] D. Bingol, M. Akcay, Determination of trace elements in leach solution by flame atomic absorption spectrometry after pre-concentration on amberlite XAD-4, *Asian J. Chem.* 20 (2008) 4031–4036.
- [53] A.A. Ensafi, A.R. Ghaderi, Preconcentration, separation determination of lead(II) with methyl thymol blue adsorbed on activated carbon using flame atomic absorption spectrometry, *J. Korean Chem. Soc.* 52 (2008) 16–22.
- [54] A. Moghimi, Preconcentration ultra trace of Cd(II) in water samples using dispersive liquid-liquid microextraction with Salen(*N,N*-bis(salicylidene)-ethylenediamine) and determination graphite furnace atomic absorption spectrometry, *J. Chin. Chem. Soc.* 55 (2008) 369–376.
- [55] V.A. Lemos, C.G. Novaes, A. da Silva Lima, D.R. Vieira, Flow injection preconcentration system using a new functionalized resin for determination of cadmium and nickel in tobacco samples, *J. Hazard. Mater.* 155 (2008) 128–134.
- [56] V.A. Lemos, M.S. Santos, G.T. David, M.V. Maciel, M.A. Bezerra, Development of a cloud point extraction method for copper and nickel determination in food samples, *J. Hazard. Mater.* 159 (2008) 245–251.