

Coprecipitative Preconcentration of Cr(III), Pb(II), Zn(II), Cd(II) and Mn(II) Ions with Al(III) and Fe(III) Carriers and Chromotrope 2B Reagent and their FAAS Determination in Various Water and Food Samples

Berrak Başbuğ and Şerife Tokaloğlu*

Chemistry Department, Faculty of Science, Erciyes University, TR 38039- Kayseri, Turkey

Métodos de coprecipitação utilizando Al(III) e Fe(III) como elementos carregadores e cromotrope 2B como agente co-precipitante foram descritos para a preconcentração dos íons Cr(III), Pb(II), Zn(II), Cd(II) e Mn(II). A morfologia da superfície dos coprecipitantes foi avaliada por microscopia eletrônica de varredura (SEM). As condições ideais para ambos os métodos de coprecipitação, tais como pH da solução, quantidades de carregadores e reagente, volume da amostra e efeito de íons interferentes, foram investigadas. Obtiveram-se resultados similares para ambos os carregadores. O pH ideal foi 9,0. Os limites de detecção (LOD) foram: 0,54 para Cr(III), 1,16 para Pb(II) e 0,08 $\mu\text{g L}^{-1}$ para Zn(II), quando o Al(III) foi usado como carregador, e 0,08, 0,17, 0,08 e 1,16 $\mu\text{g L}^{-1}$ para Cd(II), Mn(II), Zn(II) and Pb(II), respectivamente, para o carregador Fe(III). Para a precisão dos métodos, realizou-se a análise de materiais de referência certificados (águas fortificadas de lagos TMDA 54.4 and TMDA 70 e de farinha de arroz 1578a SRM) e estudos de recuperação foram realizados. O método foi aplicado na determinação de analitos em água (água da torneira, água de represa e água de rio) e em amostras de alimentos (damasco, menta e macarrão).

Coprecipitation methods using Al(III) and Fe(III) as carrier elements and chromotrope 2B as coprecipitative reagent were described for the preconcentration of Cr(III), Pb(II), Zn(II), Cd(II) and Mn(II) ions. The surface morphology of coprecipitants was examined by scanning electron microscopy (SEM). The optimum conditions for both coprecipitation methods, such as pH of the solution, amounts of carriers and reagent, sample volume and effect of interfering ions were investigated. Similar results were obtained for both carriers. The optimal pH was found at 9.0. The limits of detection (LOD) found were: 0.54 for Cr(III), 1.16 for Pb(II) and 0.08 $\mu\text{g L}^{-1}$ for Zn(II) when Al(III) carrier was used and 0.08, 0.17, 0.08 and 1.16 $\mu\text{g L}^{-1}$ for Cd(II), Mn(II), Zn(II) and Pb(II), respectively, when Fe(III) was the carrier. For the accuracy of the methods, the analysis of certified reference materials (TMDA 54.4 and TMDA 70 fortified lake waters and SRM 1578a rice flour) and recovery studies were performed. The method was applied for the determination of analytes in water (tap water, dam water and river water) and food (apricot, mint and macaroni) samples.

Keywords: Al(III) carrier, chromotrope 2B, Fe(III) carrier, flame atomic absorption spectrometry, scanning electron microscopy, water and food samples

Introduction

Trace heavy metals are major pollutants in the environment. Manganese is recognized as both an essential and a neurotoxic trace element. As an essential trace element, Mn plays an important role in bone and tissue formation, reproductive functions, and the activation of many enzymes, which are involved in vital metabolic processes. Element deficiency is not a common occurrence since dietary

sources provide an adequate supply of 2-8 mg of Mn *per day*.¹ Lead and cadmium are two of the most hazardous elements to human health because both metals cause adverse effects on the metabolic processes of human beings. Their widespread presence in the human environment comes from anthropogenic activities. Lead is proved to be a carcinogenic agent and to cause disturbances to several organs. Cadmium is highly toxic even at low concentrations, causing damages to organs such as the kidneys, liver and lungs.^{2,3}

Zinc is considered as an essential trace element in humans because zinc is a co-factor in more than

*e-mail: serifet@erciyes.edu.tr

200 enzymes and is necessary for the production of insulin. Zinc plays an important role in protein synthesis and cell division. Deficiency of zinc leads to several disorders such as growth retardation, diarrhea, immunological defense decreasing, eye and skin lesions, malfunctioning of wound healing, and other skin diseases. Moreover, metabolic disorders of zinc have now been closely associated with a number of neurological diseases, such as Alzheimer's disease, Parkinson's diseases, epilepsy and hypoxia-ischemia.^{4,5} Cr(III) is considered an essential trace element for the maintenance of effective glucose, lipid and protein metabolism in mammals.⁶

In most samples, metals are generally present at levels lower than the limits of detection (LOD) of common analytical methods. For this reason, the determination of the metals generally requires separation and preconcentration steps due to insufficient sensitivity or matrix interference. The enrichment procedures developed for metal determination by various analytical techniques include mainly solid-phase extraction,^{7,8} liquid-liquid extraction,⁹ cloud-point extraction,^{10,11} or coprecipitation.¹² Among these preconcentration methods, coprecipitation is one of the most efficient separation and enrichment techniques for trace heavy metal ions. The mechanism of coprecipitation is usually considered to include mixed-crystal formation, occlusion and adsorption. Mixed-crystal formation involves substitution of ions in the crystal lattice of the carrier by coprecipitating ions. Occlusion involves mechanical entrapment of foreign ions and solvent molecules at the surface of the precipitate during the rapid growth of its crystal.¹³ The advantages of this technique are its simplicity, rapidity, ability to attain a high concentration factor and the fact that various analyte ions can be preconcentrated and separated simultaneously from the matrix.¹² Several coprecipitants, such as iron(III) hydroxide,^{14,15} scandium hydroxide,¹⁶ cerium(IV) hydroxide,¹⁷ terbium hydroxide,¹⁸ aluminum hydroxide,¹⁹ yttrium phosphate,²⁰ diethyldithiocarbamates of nickel²¹ and bismuth,²² Cu(II) and Ni(II) salicylaloximes¹² and copper(II) mercaptobenzothiazole²³ have been proposed. Among collecting precipitates, organic coprecipitants are the most attractive gathering precipitates because of their excellent multi-element trace recovery and sufficient separation factors especially for alkali and alkaline earth elements.

Chromotropic acid (CTA), with the chemical name 4,5-dihydroxy-2,7-naphthalenedisulfonic acid, is a phenolic compound with the ability to act as a bidentate ligand with the tendency to make complexes with "hard" metals. The two sulfonic groups of CTA dissociate in aqueous solutions to make the molecule as a doubly charged anion. Chromotropic acid is used for the preparation of azo dyes which are very famous indicators for the

spectrophotometric and chelatometric determination of metal ions.^{24,25} Tewari and Singh²⁶ reported a method for determining of Cd, Co, Cu, Ni, Fe and Zn ions by flame atomic absorption spectrometry (FAAS) after preconcentration on a column packed with chromotropic acid loaded Amberlite XAD-2. In literature, there are few studies done with chromotrope 2B (*p*-nitrobenzene azochromotropic acid). Satendra and Sangal²⁷ reported the results of the spectrophotometric determination of thorium using chromotrope 2B as a chromogenic reagent. Martín-Esteban *et al.*²⁸ have proposed a method based on selective retention of aluminium in a microcolumn packed with chromotrope 2B immobilized on AG 1-X8 ion exchange resin. As far as our group knows, there is no study on the coprecipitation of trace metal ions using chromotrope 2B.

In this study, two coprecipitation methods were developed by using Al(III) and Fe(III) carrier elements and the results were compared with each other. The influence of the various analytical parameters on the recovery of analytes for both coprecipitation methods that are pH, the amounts of carrier element and reagent, sample volume and the effect of matrix components was investigated.

Experimental

Apparatus

A Perkin Elmer AAnalyst 800 model atomic absorption spectrometer (Waltham, MA, USA) equipped with single element hollow cathode lamps and a 10 cm air acetylene burner were used for the determination of the metal ions. All instrumental settings were operated as recommended by the manufacturers. The pH adjustments were made by using WTW pH 315i pH meter (Weilheim, Germany). A centrifuge of MLTW 54 model to centrifuge and a Schleicher and Schuell filtration apparatus to filtrate the solutions were used. The membrane filter used was made of mixed cellulose ester (0.45 μm pore size and 47 mm diameter, Advantec MFS Inc., CA, USA). The surface morphology of the coprecipitants was examined using Leo 440 model scanning electron microscopy (SEM, USA).

Reagents and solutions

Analytical reagent-grade chemicals and distilled-deionized water were used in all the experiments. Stock solutions of the metals (1000 mg L⁻¹) were prepared from their nitrate salts in 1 mol L⁻¹ HNO₃. The working standard solutions were daily prepared by diluting from the stock standard solutions. For 0.5% (m/v) solution of chromotrope 2B (C2B), 0.05 g of C2B was daily dissolved

and it was made up to 10 mL with distilled-deionized water. The 1 mol L⁻¹ acetic acid-acetate buffer for pH 4.0-6.0 and 1 mol L⁻¹ ammonia/ammonium chloride buffer for pH 8.0-9.5 were used to determine optimal working pH.

Procedure

The coprecipitation methods were optimized with aqueous solutions. For the first coprecipitation method, 2 mL of 1000 mg L⁻¹ Al(III) solution and 2 mL of C2B reagent (0.5% m/v) were added to 20 mL of a solution containing 40 µg of Pb(II) and Cr(III) and 5 µg of Zn(II) in a centrifuge tube. The pH of the solution was adjusted to about 9.0 with ammonia/ammonium chloride buffer. To settle the resultant precipitate, the solution was allowed to stand for about 10 min. To separate the precipitate, the centrifugation process was performed at 3500 rpm for 10 min and then the supernatant was removed. The precipitate was dissolved with 1 mL of concentrated nitric acid by heating on a hot plate for a while. The final volume of the solution was made up to 5 or 10 mL with distilled-deionized water and analyzed by FAAS.

In the other coprecipitation method, Fe(III) was used as a carrier element. To 20 mL of a solution containing 5 µg Cd, 5 µg Mn, 40 µg Pb and 5 µg Zn, 2 mL of 1000 mg L⁻¹ Fe(III) solution and 2 mL of C2B reagent were added. The pH of the solution was adjusted to 9.0 with ammonia/ammonium chloride buffer solution by using the pH meter and the procedures mentioned above were applied.

Application to the samples

The two proposed coprecipitation methods were applied for separation and preconcentration of analyte ions in tap water, dam water and river water samples. The dam water sample came from the Damsa Dam (Nevşehir Province, Turkey) and the river water sample from Kızılırmak River (Nevşehir Province, Turkey). The samples were immediately filtered through a Millipore cellulose membrane filter of 0.45 µm pore size and then acidified to pH 2 with concentrated nitric acid. The tap water sample from our research laboratory was analyzed without any pretreatment. The sample volumes of 100 and 250 mL were used for analysis. Both coprecipitation methods were applied to the water samples.

For the analysis of food (apricot, mint and macaroni) and SRM 1578a rice flour samples, 0.10 g of the SRM and 0.20 g of food sample were weighed and placed in a 100 mL beaker. The mixture was evaporated near to dryness on a hot plate. After cooling to room temperature, 3 mL of concentrated hydrogen peroxide were added. The mixture

was again evaporated near to dryness. The resulting solution was diluted to 25 mL with distilled-deionized water²⁹ and described coprecipitation procedures were applied.

Results and Discussion

Morphology of coprecipitants

SEM images of the Fe(III) and Al(III) coprecipitants both with and without reagent are given in Figures 1a-1f. From the figures, it can be seen that the surface morphology (both porosity and shape) of the precipitates is changed in the presence of reagent as well as analytes for both carriers.

Effect of pH

The effect of the pH on the coprecipitative preconcentration of metal ions (40 µg of Pb(II) and Cr(III), 5 µg of Cd(II), Mn(II) and Zn(II)) present in 20 mL of the model solutions was studied in the pH range of 4.0-9.5. 2 mg of Al(III) and 2 mL of 0.5% (m/v) C2B were added to the solution. For the other coprecipitation method, 2 mg of Fe(III) were used as a carrier element. 2 mL of 0.5% (m/v) C2B were added to the model solutions. The pH values of the solutions were adjusted to the range of 4.0-9.5 and the coprecipitation methods were applied separately. The results obtained for Al(III) and Fe(III) carrier elements are illustrated in Figures 2a and 2b, respectively. When Al(III) was used as a carrier element, Cr(III), Pb(II) and Zn(II) were recovered quantitatively at pH 9.0. When Fe(III) was used as a carrier element, the recoveries for Cd(II), Mn(II), Pb(II) and Zn(II) were ≥ 95% at pH 9.0. The recovery values of Zn(II) and Cr(III) for Al(III) carrier element and of Zn(II) and Cd(II) for Fe(III) carrier element decreased above pH 9.0 because of their dissolution as hydroxy complexes. In further experiments, pH 9.0 was selected as the working pH for both Al(III) and Fe(III) carrier elements.

Effect of reagent (C2B) amount

The effect of C2B (0.5% m/v) amount on quantitative coprecipitation of analyte ions was investigated in the range of 0-2.5 mL for a model solution including 2 mg of Al(III) carrier and in the range of 0-3.0 mL for a model solution including 2 mg of Fe(III) carrier. The pH values of the model solutions were adjusted to 9.0 and the coprecipitation methods were applied. As can be seen in Figure 3a, the ranges of C2B amount needed for quantitative precipitation using Al(III) carrier were found to be 0.5-2.5 mL for Cr(III), 1.0-2.5 mL for Zn(II), and 2.0 and 2.5 mL for Pb(II).

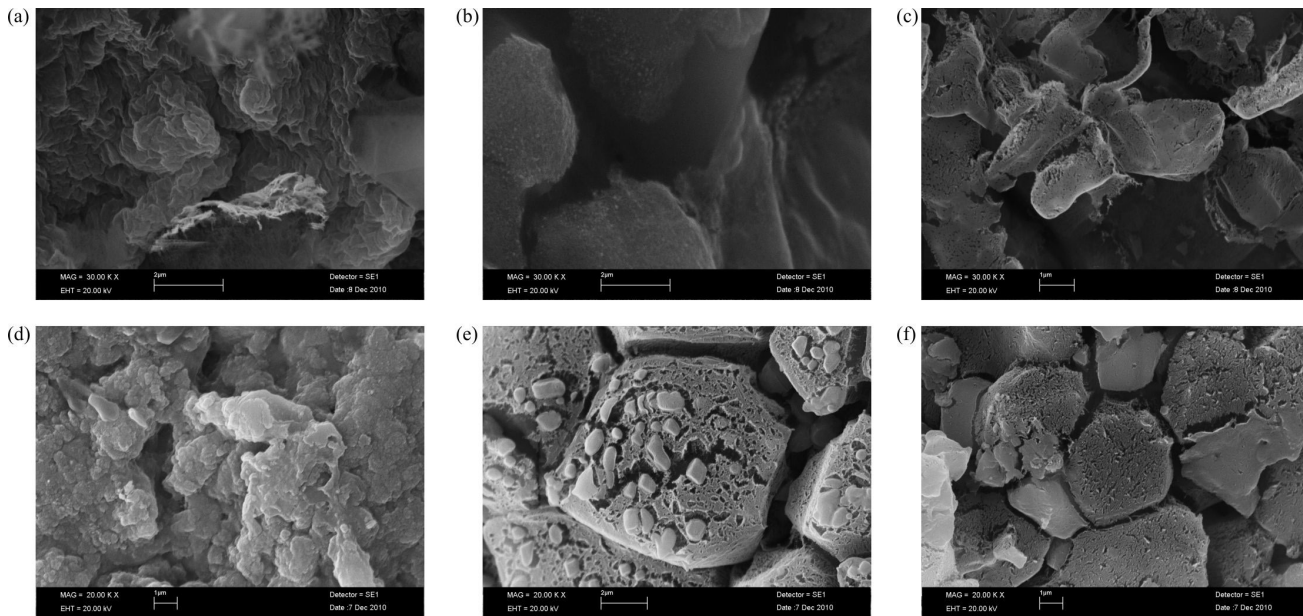


Figure 1. SEM images of (a) Al(OH)₃ precipitate, (b) Al(OH)₃ precipitate with analytes; Cr(III), Pb(II) and Zn(II), (c) Al(III)-C2B coprecipitant with analytes; Cr(III), Pb(II) and Zn(II), (d) Fe(OH)₃ precipitate, (e) Fe(OH)₃ precipitate with analytes; Cd(II), Mn(II), Pb(II) and Zn(II), and (f) Fe(III)-C2B coprecipitant with analytes; Cd(II), Mn(II), Pb(II) and Zn(II).

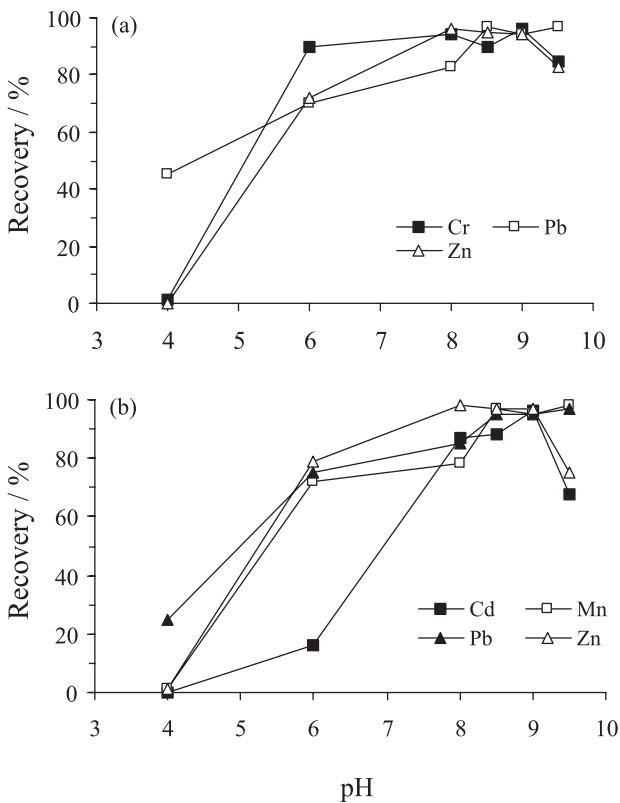


Figure 2. Effect of pH on the recovery of (a) Cr(III), Pb(II) and Zn(II) ions (carrier element: 2 mg of Al(III), reagent amount: 2 mL of 0.5% (m/v) C2B), and (b) Cd(II), Mn(II), Pb(II) and Zn(II) ions (carrier element: 2 mg of Fe(III), reagent amount: 2 mL of 0.5% (m/v) C2B).

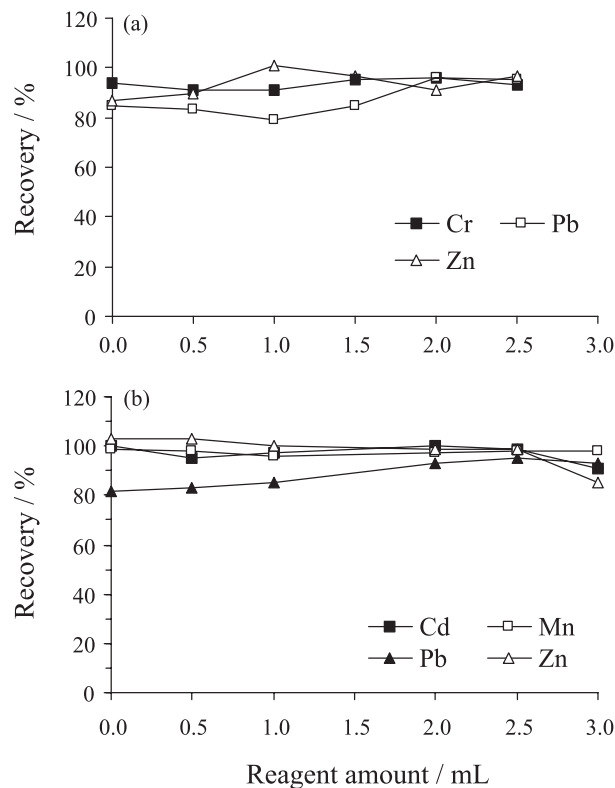


Figure 3. Effect of reagent amount on the recovery of (a) Cr(III), Pb(II) and Zn(II) ions (pH 9.0, carrier element: 2 mg of Al(III), n = 3), and (b) Cd(II), Mn(II), Pb(II) and Zn(II) ions (pH 9.0, carrier element: 2 mg of Fe(III), n = 3).

Cr(III) was quantitatively recovered without reagent due to the formation of hydroxy precipitates of aluminum and chromium with low solubility at pH 9.0 (K_{sp} Al(OH)₃ <

K_{sp} Cr(OH)₃ << K_{sp} Zn(OH)₂ < K_{sp} Pb(OH)₂). Figure 3b shows the effect of C2B amount for Fe(III) carrier. While Zn(II), Cd(II) and Mn(II) were quantitatively recovered

without reagent due to the formation of hydroxy precipitates of Fe(III), the required reagent amounts for quantitative precipitation of Pb(II) were found in the range of 2-3 mL. The quantitative recovery values for Zn(II), Cd(II) and Mn(II) did not change by increasing reagent amount (except for 3 mL of reagent for Zn). So, 2 mL of C2B was used in subsequent studies for the two methods.

Effect of amounts of carrier elements

The effect of Al(III) and Fe(III) amounts as carrier elements on the recoveries of analyte ions was examined. The results are shown in Figures 4a and 4b. The recoveries of the metal ions were not quantitative without carrier elements (between 12 and 58%). The recovery value for Pb(II) was quantitative in the range of 2-3 mg of Al(III) amount. But this amount for Cr(III) and Zn(II) was only 2 mg. For Fe(III) carrier, the recoveries of Zn(II) and Cd(II) were found to be in range of 92-96% for 1-3 mg Fe(III) amounts. While Mn was almost quantitatively recovered in range of 0.5-3 mg of Fe(III), this range for Pb was found to be 2-3 mg Fe(III). Because of this, the amounts

of Al(III) and Fe(III) carriers were chosen to be 2 mg. The recoveries of elements without both carrier element and reagent were also studied at pH 9.0. The recoveries changed from 12 to 54% due to the formation of hydroxy precipitates of the studied elements.

Effect of sample volume

The effects of sample volume on the quantitative coprecipitation of the trace metal ions were examined in the volume ranges of 40-1000 mL for both methods. The carrier element and reagent amounts were increased with an increasing sample volume. For both Al(III) and Fe(III) carriers, the recoveries of the elements were quantitative for volume ranges of 40-500 mL. Above this volume, the recoveries changed between 81 and 90%. When a 500 mL of sample solution was preconcentrated to 5 mL of the final solution, a preconcentration factor (PF) of 100 could be achieved.

Effect of matrix ions

The preconcentration procedures for trace metals can be strongly affected by other constituents of the samples. For this reason, the reliability of the proposed method was examined in the presence of possible interfering ions of the water and food samples. The interfering elements, in the range of 25-1000 $\mu\text{g mL}^{-1}$, were added to the model solutions containing 40 μg of Pb(II) and Cr(III), 5 μg of Cd(II), Mn(II), and Zn(II) ions as their nitrate or chloride salts. Tables 1 and 2 show the effect of interfering ions when Al(III) and Fe(III) were used as carrier elements, respectively. The large amounts of the matrix components have no serious interfering effect on the recovery of the elements for both methods. As can be seen in Table 1, the recovery value of Cr(III) was affected by the chloride ions ($R = 68\%$). Mn(II), Cu(II), SO_4^{2-} and Cl^- ions interfered in the determination of Zn(II) when they existed in the concentrations of 10, 10, 100 and 1000 $\mu\text{g mL}^{-1}$, respectively. 1000 $\mu\text{g mL}^{-1}$ of Cl^- also interfered in the determination of Cd(II) (Table 2).

Analytical performance

LODs of the method calculated as three times the standard deviation of the blank solutions divided by the slope of the calibration curve ($n = 10$, $3s/b$) were found to be 0.54 for Cr(III), 1.16 for Pb(II) and 0.08 $\mu\text{g L}^{-1}$ for Zn(II) when Al(III) carrier was used. For Fe(III) carrier, it was found to be 0.08, 0.17, 0.08 and 1.16 $\mu\text{g L}^{-1}$ for Cd(II), Mn(II), Zn(II) and Pb(II), respectively. In the calculation

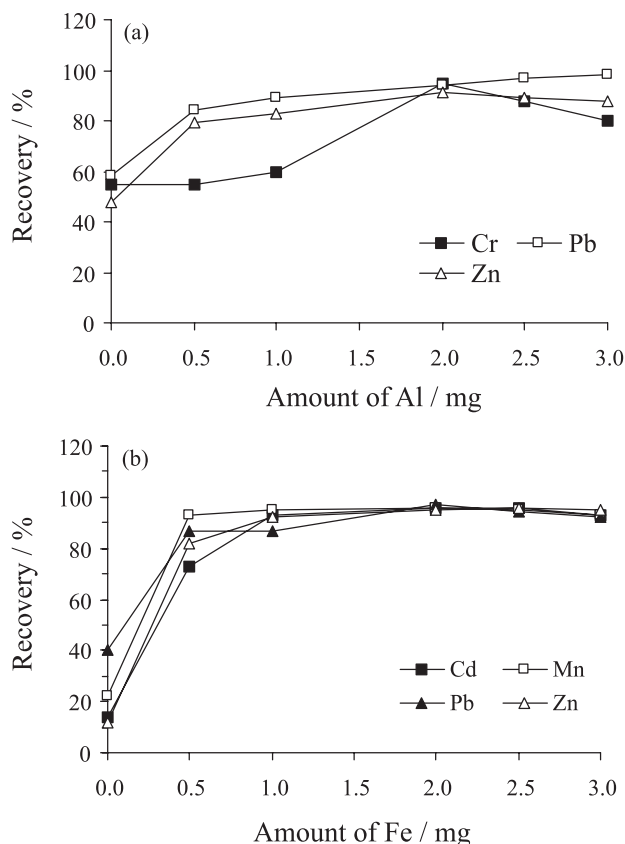


Figure 4. (a) Effect of Al(III) carrier element amount on the recovery of Cr(III), Pb(II) and Zn(II) ions (pH 9.0, reagent amount: 2 mL of 0.5% (m/v) C2B). (b) Effect of Fe(III) carrier element amount on the recovery of Cd(II), Mn(II), Pb(II) and Zn(II) ions (pH 9.0, reagent amount: 2 mL of 0.5% (m/v) C2B).

Table 1. Effect of interfering ions on the coprecipitation of Cr(III), Pb(II) and Zn(II) ions by using Al(III) carrier element (pH = 9.0, n = 3)

Ion	Concentrations studied ^a / (mg L ⁻¹)	Cr(III)		Pb(II)		Zn(II)	
		Concentration / (mg L ⁻¹)	R ± s / %	Concentration / (mg L ⁻¹)	R ± s / %	Concentration / (mg L ⁻¹)	R ± s / %
Na ⁺	25, 50, 100, 250, 500, 1000	25	90 ± 1	1000	91 ± 5	500	97 ± 6
K ⁺	25, 50, 100, 250, 500, 1000	25	91 ± 0	1000	95 ± 2	500	104 ± 5
Ca ²⁺	25, 50, 100, 250, 500, 1000	1000	96 ± 2	1000	98 ± 4	50	96 ± 3
Mg ²⁺	25, 50, 100, 250, 500, 1000	25	93 ± 1	500	95 ± 3	50	94 ± 3
Mn ²⁺	10	10	97 ± 2	10	95 ± 5	10	101 ± 2
Pb ²⁺	10	10	91 ± 2	–	–	10	93 ± 6
Ni ²⁺	10	10	93 ± 2	10	97 ± 0	10	95 ± 3
Cr ³⁺	10	10	–	10	94 ± 5	10	98 ± 3
Cu ²⁺	10	10	96 ± 4	10	100 ± 0	10	95 ± 3
Zn ²⁺	10	10	97 ± 4	10	100 ± 4	10	–
Fe ³⁺	10	10	99 ± 0	10	100 ± 3	10	93 ± 5
SO ₄ ²⁻	100, 250	100	80 ± 2	250	96 ± 7	100	83 ± 5
NO ₃ ⁻	100, 250	100	86 ± 2	250	101 ± 2	100	88 ± 2
Cl ⁻	1000	1000	68 ± 1	1000	82 ± 2	1000	101 ± 2
PO ₄ ³⁻	100	100	97 ± 2	250	99 ± 2	250	88 ± 4

R: recovery; s: standard deviation.

Table 2. Effect of interfering ions on coprecipitation of Cd(II), Zn(II), Mn(II) and Pb(II) ions by using Fe(III) carrier element (n = 3)

Ion	Cd(II)		Mn(II)		Pb(II)		Zn(II)	
	Concentration / (mg L ⁻¹)	R ± s / %	Concentration / (mg L ⁻¹)	R ± s / %	Concentration / (mg L ⁻¹)	R ± s / %	Concentration / (mg L ⁻¹)	R ± s / %
Na ⁺	500	98 ± 4	500	94 ± 3	500	94 ± 4	500	101 ± 3
K ⁺	500	104 ± 4	500	96 ± 2	1000	97 ± 2	500	95 ± 0
Ca ²⁺	100	82 ± 3	1000	95 ± 3	1000	99 ± 2	500	107 ± 4
Mg ²⁺	500	84 ± 2	500	92 ± 5	1000	98 ± 4	500	102 ± 0
Al ³⁺	10	90 ± 2	10	92 ± 2	10	105 ± 5	10	93 ± 7
Pb ²⁺	10	94 ± 2	10	94 ± 1	–	–	10	101 ± 5
Ni ²⁺	10	91 ± 3	10	93 ± 2	10	104 ± 5	10	88 ± 1
Cr ³⁺	10	99 ± 1	10	92 ± 1	10	106 ± 5	10	82 ± 2
Mn ²⁺	10	93 ± 2	–	–	10	100 ± 4	10	73 ± 3
Cu ²⁺	10	92 ± 3	10	96 ± 3	10	98 ± 6	10	66 ± 4
Zn ²⁺	10	89 ± 2	10	96 ± 5	10	95 ± 4	–	–
SO ₄ ²⁻	100	90 ± 1	250	96 ± 0	250	101 ± 2	250	65 ± 3
NO ₃ ⁻	100	92 ± 2	250	96 ± 0	250	105 ± 0	250	97 ± 3
Cl ⁻	1000	77 ± 0	1000	104 ± 2	1000	101 ± 2	1000	76 ± 2
PO ₄ ³⁻	100	94 ± 0	250	98 ± 1	250	97 ± 2	100	90 ± 3

R: recovery; s: standard deviation.

of LODs of the method, the preconcentration factor of 100 was taken into consideration. The precision of the method based on the relative standard deviation (RSD, in %) was evaluated by using model solutions under the optimum experimental conditions ($n = 10$). When Al(III) was used as a carrier element, the mean recoveries were found to be $98 \pm 2\%$ for Cr(III), $97 \pm 1\%$ for Pb(II) and $94 \pm 2\%$ for Zn(II), and also it was found to be $97 \pm 2\%$ for Cd(II), $96 \pm 3\%$ for Mn(II), $96 \pm 1\%$ for Pb(II) and $95 \pm 2\%$ for Zn(II) when Fe(III) was used as a carrier element.

Application and accuracy of the method

In order to evaluate accuracy of the proposed coprecipitation methods, the analytes were determined in certified reference materials (TMDA 54.4 and TMDA 70 fortified lake waters and SRM 1578a rice flour) and spiked water and food samples. For recovery studies, the aliquots of 100 and 250 mL of tap water, dam water and river water samples were used and the analytes were added to the water samples at changing concentrations. The results are given in Tables 3 and 4. The metal ions were recovered in the range

Table 3. The recoveries (R) of the analytes in the spiked tap, dam and river water samples by using Al(III) carrier (sample volume: 100 and 250 mL, pH 9.0, $n = 3$)

Element	Sample volume / mL	Tap water			Dam water			River water		
		Added / ($\mu\text{g L}^{-1}$)	Found / ($\mu\text{g L}^{-1}$)	R / %	Added / ($\mu\text{g L}^{-1}$)	Found / ($\mu\text{g L}^{-1}$)	R / %	Added / ($\mu\text{g L}^{-1}$)	Found / ($\mu\text{g L}^{-1}$)	R / %
Cr	100	–	< LOD	–	–	< LOD	–	–	< LOD	–
		400	390 ± 4	98	600	595 ± 12	99	400	408 ± 8	102
	250	–	< LOD	–	–	< LOD	–	–	< LOD	–
		240	237 ± 2	99	240	232 ± 6	97	240	234 ± 2	98
Pb	100	–	< LOD	–	–	< LOD	–	–	< LOD	–
		400	382 ± 10	96	400	380 ± 20	95	400	378 ± 4	95
	250	–	< LOD	–	–	< LOD	–	–	< LOD	–
		240	222 ± 6	93	240	230 ± 6	96	240	230 ± 6	96
Zn	100	–	50.4 ± 3.7	–	–	12.2 ± 1.2	–	–	9.05 ± 0.78	–
		50	101 ± 7	101	50	62.5 ± 2.8	101	50	56.1 ± 1.0	94
	250	–	31.4 ± 0.8	–	–	14.0 ± 0.2	–	–	13.2 ± 1.8	–
		16	48.9 ± 0.2	109	16	28.9 ± 0.6	93	16	29.8 ± 1.2	104

LOD: limit of detection.

Table 4. The recoveries (R) of the analytes in the spiked tap, dam and river water samples by using Fe(III) carrier (sample volume: 100 mL and 250 mL, pH 9.0, $n = 3$)

Element	Sample volume / mL	Tap water			Dam water			River water		
		Added / ($\mu\text{g L}^{-1}$)	Found / ($\mu\text{g L}^{-1}$)	R / %	Added / ($\mu\text{g L}^{-1}$)	Found / ($\mu\text{g L}^{-1}$)	R / %	Added / ($\mu\text{g L}^{-1}$)	Found / ($\mu\text{g L}^{-1}$)	R / %
Cd	100	–	< LOD	–	–	< LOD	–	–	< LOD	–
		50	47.2 ± 1.0	94	50	46.4 ± 2.4	93	50	48.4 ± 1.6	97
	250	–	< LOD	–	–	< LOD	–	–	< LOD	–
		40	41.6 ± 1.6	104	40	40.0 ± 0.4	100	40	40.8 ± 1.1	102
Mn	100	–	6.14 ± 0.70	–	–	5.70 ± 0.65	–	–	8.5 ± 1.0	–
		50	56.5 ± 0.8	101	50	56.1 ± 1.4	101	50	58.8 ± 1.6	100
	250	–	12.6 ± 0.5	–	–	13.3 ± 0.5	–	–	14.3 ± 0.8	–
		40	53.6 ± 0.2	103	40	55.2 ± 0.4	105	40	54.7 ± 0.3	101
Pb	100	–	< LOD	–	–	< LOD	–	–	< LOD	–
		400	378 ± 16	95	400	376 ± 6	94	400	406 ± 12	102
	250	–	< LOD	–	–	< LOD	–	–	< LOD	–
		240	$248 \pm$	103	240	240 ± 4	100	240	242 ± 4	101
Zn	100	–	51.5 ± 3.8	–	–	13.3 ± 2.1	–	–	11.7 ± 1.8	–
		50	96.2 ± 2.2	89	50	60 ± 11	94	50	58.1 ± 3.8	93
	250	–	42.1 ± 1.5	–	–	13.8 ± 1.6	–	–	18.5 ± 1.6	–
		16	56.6 ± 1.1	90	16	31.1 ± 0.8	108	16	33.5 ± 1.2	94

LOD: limit of detection.

Table 5. The analysis results of some food samples (pH 9.0, sample amount: 0.20 g, final volume: 5 mL, n = 3)

Element	Apricot			Mint			Macaroni		
	Added / ($\mu\text{g g}^{-1}$)	Found ^a / ($\mu\text{g g}^{-1}$)	R / %	Added / ($\mu\text{g g}^{-1}$)	Found ^a / ($\mu\text{g g}^{-1}$)	R / %	Added / ($\mu\text{g g}^{-1}$)	Found ^a / ($\mu\text{g g}^{-1}$)	R / %
Cd(II) ^b	–	< LOD		–	< LOD		–	< LOD	
	12.5	12.3 ± 0.2	98	12.5	12.3 ± 0.1	98	12.5	12.3 ± 0.2	98
Mn(II) ^b	–	5.08 ± 0.19		–	4.87 ± 0.51		–	4.02 ± 0.18	
	12.5	17.3 ± 0.2	98	12.5	17.2 ± 0.10	99	12.5	15.8 ± 0.2	94
Pb(II) ^b	–	< LOD		–	< LOD		–	< LOD	
	50	49.6 ± 0.3	99	50	49.5 ± 0.2	99	50	49.5 ± 0.1	99
Zn(II) ^b	–	4.21 ± 0.26		–	4.86 ± 0.44		–	5.37 ± 0.20	
	12.5	17.0 ± 0.5	102	12.5	17.9 ± 0.5	104	12.5	17.6 ± 0.5	98
Cr(III) ^c	–	< LOD		–	< LOD		–	< LOD	
	50	49.0 ± 0.2	98	50	49.5 ± 0.2	99	50	49.4 ± 0.2	99
Pb(II) ^c	–	< LOD		–	< LOD		–	< LOD	
	50	49.4 ± 0.1	99	50	49.4 ± 0.3	99	50	50.0 ± 0.2	100
Zn(II) ^c	–	4.54 ± 0.43		–	4.71 ± 0.32		–	5.41 ± 0.31	
	12.5	17.4 ± 0.3	103	12.5	17.7 ± 0.2	104	12.5	17.4 ± 0.2	96

^aMean values ± standard deviation, n = 3; ^bFe(III) was used as a carrier element; ^cAl(III) was used as a carrier element. R: recovery; LOD: limit of detection.

Table 6. The analysis results of standard reference materials (sample volume: 25 mL, sample amount: 0.10 g, final volume: 5 mL, n = 3)

Element	Certified lake water		R / %	SRM 1568a rice flour		R / %
	Certified ^a / ($\mu\text{g L}^{-1}$)	Found ^b / ($\mu\text{g L}^{-1}$)		Certified ^a / ($\mu\text{g g}^{-1}$)	Found ^b / ($\mu\text{g g}^{-1}$)	
Cd(II) ^c	145 ± 0.84	148 ± 3	102	0.022 ± 0.002	< LOD	–
Mn(II) ^c	302 ± 1.6	271 ± 3	90	20.0 ± 1.6	19.6 ± 0.3	98
Pb(II) ^c	444 ± 2.7	482 ± 3	109	–	< LOD	–
Zn(II) ^c	477 ± 3.1	482 ± 11	101	19.4 ± 0.5	19.4 ± 1.0	100
Cr(III) ^d	438 ± 4	398 ± 14	91	–	< LOD	–
Pb(II) ^d	514 ± 5	505 ± 26	98	–	< LOD	–
Zn(II) ^d	537 ± 6	505 ± 53	94	19.4 ± 0.5	20.3 ± 0.2	106

^aAt 95 % confidence level; ^bmean values ± standard deviation, n = 3; ^cFe(III) as a carrier element and TMDA 70 as a certified reference material were used; ^dAl(III) as a carrier element and TMDA 54.4 as a certified reference material were used. R: recovery; LOD: limit of detection.

of 89-104%. Also, the recovery studies for apricot, mint and macaroni samples were made. As can be seen in Table 5, the recovery values for the analyte ions were quantitative (94-104%). The analysis results of certified reference materials are given in Table 6. A good agreement was obtained between the certified and found values (90-109%).

Comparison of the present methods with other coprecipitation methods

The methods proposed in this work may be compared with other works described in the literature in terms of

preconcentration factors. For example, they are superior to those of Cu(II) salicylaldoxime (PF:15),¹² zirconium(IV) hydroxide (PF:25),³⁰ Cu(II)-9-phenyl-3-fluorene (PF:30),³¹ sodium diethyldithiocarbamate (PF:40),³² manganese dioxide (PF:80)³³ and La-2,2'-bipyridyl-erythrosine (PF:50).³⁴

Conclusions

New and rapid coprecipitation methods were described for the determination of Cr(III), Pb(II), Zn(II), Cd(II) and Mn(II) ions by FAAS. Analytical parameters were

investigated for both Al(III) and Fe(III) carriers. The optimum conditions (pH 9.0, carrier amount: 2 mg, reagent amount: 2 mL of C2B of 0.5% (m/v) and sample volume: 500 mL) were found to be similar for both methods. Pb(II) and Zn(II) elements were quantitatively recovered for both Fe(III) and Al(III) carrier elements. The time required for the coprecipitation method was about 30 min. The proposed coprecipitation methods provide simple, sensitive, precise, reliable and accurate techniques. Both methods could be successfully applied for determination of Cr(III), Pb(II), Zn(II), Cd(II) and Mn(II) ions in various water and food samples.

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