



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

Mustafa Tuzen<sup>a</sup>, Mustafa Soylak<sup>b,\*</sup>

<sup>a</sup> Gaziosmanpasa University, Faculty of Science and Arts, Chemistry Department, 60250 Tokat, Turkey

<sup>b</sup> Erciyes University, Faculty of Art and Science, Department of Chemistry, 38039 Kayseri, Turkey

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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 HNO<sub>3</sub>, 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

\* Corresponding author. Tel.: +90 352 4374933; fax: +90 352 4374933.  
E-mail addresses: [msoylak@gmail.com](mailto:msoylak@gmail.com), [soylak@erciyes.edu.tr](mailto:soylak@erciyes.edu.tr) (M. Soylak).

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<sup>-1</sup> HNO<sub>3</sub>. 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.

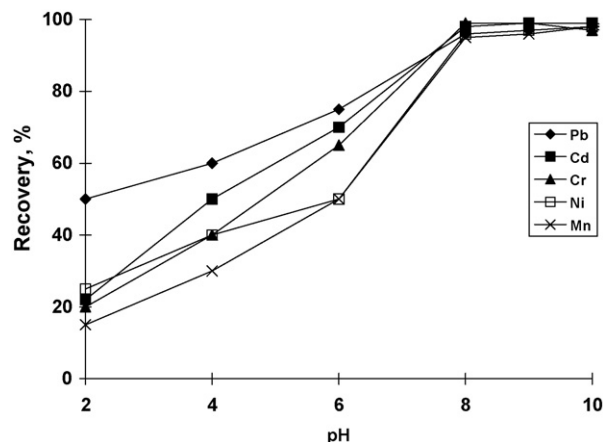
The following buffer solutions were prepared for pH adjustment: (a) 3.8 g sodium dihydrogen phosphate and 9 mL 85% of phosphoric acid for pH 2; (b) 13.8 g sodium dihydrogen phosphate and 0.60 mL 85% of phosphoric acid for pH 3; (c) 77.0 g ammonium acetate and 413 mL acetic acid for pH 4; (d) 13.1 g sodium 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<sup>-1</sup> 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<sup>-1</sup> of ammonium chloride and 250 mL of 0.1 mol L<sup>-1</sup> 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<sup>-1</sup> 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 HNO<sub>3</sub>, 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 HNO<sub>3</sub> (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 HNO<sub>3</sub> (65%) and 2 mL of H<sub>2</sub>O<sub>2</sub> (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 Cu<sup>2+</sup> as carrier element

The influences of amount of Cu<sup>2+</sup> 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 Cu<sup>2+</sup>. The recoveries increased and reach to quantitative values for all the investigated heavy metals at the range of 1.0–3.0 mg of Cu<sup>2+</sup> due to the formation of Cu(II)-dibenzylthiocarbamate precipitate. In the light of these results, 1.0 mg of Cu<sup>2+</sup> 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.

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