Journal of Industrial and Engineering Chemistry 20 (2014) 1030–1034

Contents lists available at SciVerse ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Separation and preconcentration of lead, chromium and copper by using with the combination coprecipitation-flame atomic absorption spectrometric determination

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ARTICLE INFO

Article history:
Received 5 April 2013
Received in revised form 29 May 2013
Accepted 15 June 2013
Available online 1 July 2013

Keywords:
Carrier element free coprecipitation
Flame atomic absorption spectrometry
Preconcentration
Separation

ABSTRACT

A coprecipitation method was developed for the quantitative separation and preconcentration of Pb(II), Cr(III) and Cu(II) ions. Analytes were coprecipitated using a triazole derivative (2-{4-[2-(1H-indol-3-yl)ethyl]-3-(4-chlorobenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl}-*N*-aryl methylidene acetohydrazid). The analytes were analyzed by flame atomic absorption spectrometry. The parameters such as sample pH, amount of reagent, sample volume, matrix effects etc. were investigated. The enrichment factor for the analyzed metal ions was obtained as 50. The relative standard deviations (RSD) were in the range of 2.8–4.1%. The accuracy of the proposed procedure was checked by the analysis of the CRM-C-Sandy Soil C. The method was successfully applied to real samples.

1. Introduction

The detection of heavy metal ions in natural waters and foods is a great concern in analytical chemistry due to their toxicity for living organism [1–4]. The main sources of metal contamination are industrial development and human activities [5]. Lead is an environmentally pollutant heavy metal that can damage to vital organs such as liver, kidney, lung and brain [6,7]. Although the adverse health effects of Pb(II) are known, it is widely used in paint and gasoline industry [8]. Cr(III) is an essential nutrient for humans. Cr(III) is effective on the mechanism of the glucose and cholestroled metabolism, whereas Cr(IV) is especially toxic to human health owing to its mutagenic features. Cr(IV) is highly water soluble and easily penetrate to biological membranes. Its familiar harmful effects involve cardiovascular and liver system [9,10]. Copper is a major micronutrient for all living organism it may activate many enzyme in protein metabolism [11]. However, when taken in excess, Cu(II) can damage intestinal and stomach systems [12]. The precise determination of heavy elements is needed improved analytical techniques, such as inductively coupled plasma optical emission spectrometry (ICP-OES) [13], flame atomic absorption spectrometry (FAAS) [14] and inductively coupled plasma-mass spectrometry (ICP-MS) [15]. Flame atomic absorption spectrometry (FAAS) is the most suitable analytical technique for sensitive determination of trace metal levels in environmental materials due to its simplicity and selectivity [16,17]. Nevertheless, the lower concentration of Pb(II), Cr(III) and Cu(II) ions together with a high concentration of matrix components in food and water samples are not match with the detection limits (LODs) of FAAS [18]. To overcome these problems, a separation and preconcentration step such as, liquid–liquid extraction [19], solid phase extraction [20], coprecipitation [21], and cloud point extraction [22] are widely used prior to heavy metals detection by FAAS technique. Among the above-mentioned methods, coprecipitation procedure combined with FAAS is specially preferred for preconcentration and sepeartion of heavy metal ions from interfering media [23].

The coprecipitation method has some important advantages such as it is a simple, effective, selective and low cost method. In addition high preconcentration factors can be obtained and analyte ions can be separated from the matrix simultaneously. A precipitate can be obtained by a proper organic and inorganic

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1226-086X/$ – see front matter
http://dx.doi.org/10.1016/j.jiec.2013.06.039

ligand in the separation and preconcentration procedure. A number of inorganic ligands such as praseodymium [24], magnesium [25], iron hydroxides [26] and organic coprecipitants, commonly dithiocarbamates [27] have been widely used.

In present study a coprecipitation method with the use of organic or inorganic coprecipitants has been supported by using a carrier element. Recently, the carrier element free coprecipitation (CEFC) method has been developed for separation and preconcentration of metal ions. The CEFC method has many advantages for preconcentration of trace metals such that in this method the contamination and adsorption risks for the interested analyte ions from a carrier element can be eliminated [28].

Triazole derivatives are important for various analytical studies. Various derivatives of triazoles have been used by our working group as indicator for acid bases titrations [29,30], coprecipitant for coprecipitation of metal ions at trace level [28,30,31] and complexing agent for solid phase extraction of metal ions [32].

In this work, we carried out the CEFC procedure by using a triazole compound, 2-{4-[2-(1H-indol-3-yl)ethyl]-3-(4-chlorobenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl}-*N*-aryl methylidene acetohydrazid (ICOTMA), as an organic coprecipitant without any carrier element for preconcentration and determination of lead, chromium and copper in some food and water samples.

2. Materials and methods

2.1. Chemicals and apparatus

All reagents used in this work were of analytical reagent grade. Ultra pure water was used in all the dilutions. Stock solutions of the metal ions (1000 mg L^{-1}) in 0.5 M HNO_3 were diluted daily for obtaining reference and working solutions. High purity stock solutions of Pb(II), Cr(III) and Cu(II) ions were obtained from Sigma (St. Louis, MO, USA). All glass and plastic materials were soaked with 10% (v/v) HNO_3 before use, and then cleaned with double distilled water. ICOTMA was synthesized in the Karadeniz Technical University organic chemistry research laboratory [33] and its solution was prepared in dimethyl sulfoxide and ethanol (1:4). The sandy soil (CRM-SA-C) certified reference material, used in the coprecipitation studies, was acquired from High-Purity Standard Inc.

All absorbance measurements were made using Perkin Elmer AAnalyst400 flame atomic absorption spectrometer in an air/acetylene flame with a 10-cm-long burner head. A pH meter, Hanna pH-211model digital glass electrode, was used for measuring pH values of the aqueous phase. The pH meter was calibrated with standard buffer solutions. A Sigma 3-16P model centrifuge (Sigma laborzentrifugen GmbH, Germany) was employed to centrifuge the solutions. Distilled water was obtained from Sartorius Milli-Q system (arium® 611UV). Milestones Ethos D (Milestore Inc., Italy) with closed vessel microwave system was standardized for digestion of the solid samples.

2.2. Coprecipitation procedure

The coprecipitation method was checked with model solutions. Firstly, 25.0 mL portion of a solutions containing of 20.0 μg Cr(III), 25.0 μg Pb(II) and 15.0 μg Cu(II) and 1.0 mL of coprecipitating agent (0.1%, w/v) were added to a beaker. The pH of the solutions was adjusted to 7.0 by using diluted NaOH and/or HNO_3 solutions. After stand for 10 min the precipitate was centrifuged at 3500 rpm for 10 min and then the supernatant was removed. The precipitate was dissolved with 0.5 mL of concentrated HNO_3. Finally, the volume was completed to 5.0 mL with distilled water and the analytes were determined by FAAS.

2.3. Application to real samples

Two fifty millilitres of sea and stream water samples were filtered through a 0.45 μm cellulose nitrate with membrane, then their pH values were adjusted to 7.0. Then 1.0 mL of 0.1% coprecipitating agent was added to the water samples and the CEFC method was applied to the solutions. After enrichment, the final volume was diluted to 5.0 mL with distilled water and levels of the analytes were determined by FAAS.

The digestion of black tea (0.750 mg) and tobacco (0.750 mg) was carried out using 4.0 mL of HNO_3, and 2.0 mL of H_2O_2 and the digestion of CRM-SA-C Sandy Soil C Standard material (0.500 mg) was carried out with 1.5 mL of HNO_3, 4.5 mL of HCl, 1.0 mL of HF and 2.0 mL of H_2O_2 in a closed microwave digestion system. After microwave digestion process, the proposed coprecipitation procedure was performed to the samples. The final volume was completed to 5.0 mL and then, the content of analytes was analyzed by FAAS.

3. Results and discussion

3.1. Effect of pH

The pH effect is one of the most important analytical parameter on the recovery of analyte ions on the coprecipitation of metal ions [34–36]. The effects of pH were examined in the pH range of 2.0–10.0 for the quantitative recoveries of Pb(II), Cr(III) and Cu(II) ions. The results are given in Fig. 1. The quantitative recoveries for Pb(II), Cr(III) and Cu(II) ions were obtained at pH 7.0 so for all further works, the pH of the solutions was adjusted to 7.0.

3.2. Influences of amounts of ICOTMA

The amount of the ICOTMA was studied in the ICOTMA amount range of 0–3.0 mg (0–3 mL, 0.1% w/v) for evaluation of its influences on the recovery of the analyte ions. The results are indicated in Fig. 2. When the coprecipitation studies were carried out without ICOTMA at pH 7.0, the recoveries of the Pb(II), Cr(III) and Cu(II) ions were below than 85%. The recoveries of metal ions were quantitative (>95%) after adding 1.0 mg of ICOTMA. All experiments were performed by using 1.0 mg (1.0 mL of 0.1% (w/v)) of ICOTMA amount at optimal pH value.

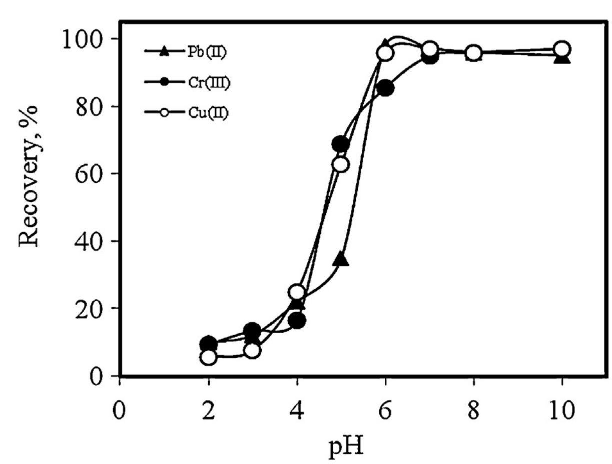

Fig. 1. Effect of pH on the recoveries of analyte ions (N: 3, sample volume: 50 mL, quantity of ICOTMA: 1.0 mg (1.0 mL 0.1% (w/v)), standing time: 10 min, centrifugation rate: 3500 rpm, centrifugation time: 10 min).