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5-Chloro-2-hydroxyaniline–copper(II) coprecipitation system for preconcentration and separation of lead(II) and chromium(III) at trace levels

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Abstract

A separation–preconcentration procedure based on the coprecipitation of lead(II) and chromium(III) ions with copper(II)–5-chloro-2-hydroxyaniline system has been developed. Effects of pH, sample volume and interferences on the recovery of the metal ions were investigated. The detection limits corresponding to three times the standard deviation of the blank were found to be 2.72 $\mu g\,L^{-1}$ for lead and 1.20 $\mu g\,L^{-1}$ for chromium. The preconcentration factor is 50. The effectiveness of the present method was assessed by determining analyte metals in GBW 07309 stream sediment and NIST SRM 1633b coal fly ash certified reference materials. The method was successfully applied to the determination of trace lead and chromium in environmental samples.

Keywords: Coprecipitation; 5-Chloro-2-hydroxyaniline; Metal ion; Environmental sample; Natural water

1. Introduction

Heavy metals occur naturally at trace concentrations in our environment; however, the levels of heavy metals are increased in the environment due to mining, industrial activities and traffic [1–4]. Heavy metal contamination of soils through anthropogenic activities is a widespread and serious problem confronting scientists and regulators throughout the world. Many works by many chemists around the world are been performed for the determination of traces heavy metals [5–10]. In these works, flame atomic absorption spectrometry (FAAS) is the main instrumental technique due to its simplicity and its lower costs than other instruments [11–14]. However the direct determinations of heavy metal ions at $\mu g\,L^{-1}$ levels by FAAS are not possible due to detection limits of FAAS [15–17]. Also other main problem in FAAS determinations of metals is the interference effects of matrix components of the sample [18,19]. The use of a separation–preconcentration step prior to heavy metal determination is usually necessary since the presence of heavy metals in environmental samples is at low levels. Methods including cloud point extraction, membrane filtration, solvent extraction, solid phase extraction, ion-exchange, solvent sublation, and electroanalytical techniques are widely used to solve these problems [20–27].

Coprecipitation is a useful technique for isolation of traces of heavy metals determination with flame furnace atomic absorption spectrometry. Short analysis time, high preconcentration factors and low consumption of organic solvent are the main advantages of the coprecipitation technique [28–37]. For the present work, 5-chloro-2-hydroxyaniline and copper(II) were selected as organic reagent and carrier element, respectively. According to our literature survey, this combination is not used for the coprecipitation of heavy metal ions, until now.

In this work, a coprecipitation technique for lead(II) and chromium(III) has been developed. The analytical parameters including pH of the working media, amount of copper(II), amount of 5-chloro-2-hydroxyaniline, sample volume, matrix effects, etc., were investigated.

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2. Experimental

2.1. Instruments

PerkinElmer AAnalyst 700 atomic absorption spectrometer was used in the studies. All measurements were carried out in an air/acetylene flame. 10-cm long slot-burner heads, hollow cathode lamps were used. A pH meter, Nel pH-900 model glass-electrode was employed for measuring pH values in the aqueous phase. Nuve NF 800 model centrifuge was used to centrifuge of solutions.

Milestone 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 [38–40].

2.2. Reagents and solutions

All the reagents used were of analytical reagent grade. Deionised double distilled water was used throughout. Laboratory glassware was kept overnight in a 10% (v/v) HNO_3 solution and then rinsed with deionised double distilled water. 5-Chloro-2-hydroxyaniline solution (1.0% (w/v)) was daily prepared in ethanol.

A stock solution of copper(II) (1000 mg L^{-1}) was prepared by dissolving 0.378 g of $Cu(NO_3)_2 \cdot 3H_2O$ (E-Merck, Germany) in deionised doubly distilled water in 100 mL; it was prepared daily. Stock standard solutions of analytes, 1000 mg L^{-1}, were prepared by dissolving appropriate amount of nitrate salts of analytes in 1% nitric acid. Stock metal ion solutions were diluted daily for obtaining reference and working solutions. The calibration curve was established using the standard solutions prepared in 1 mol L^{-1} HNO_3 by dilution from stock solutions.

The buffer solutions were prepared for pH adjustment: (a) 3.79 g sodium dihydrogen phosphate and 9 mL 85% of phosphoric acid for pH 2; (b) 13.78 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) 0.69 g sodium borate and 5 mL 1 mol L^{-1} hydrochloric acid for 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 volume was completed to 500 mL with distilled water.

2.3. Preconcentration work

25.0 mL portion of an aqueous solution containing 20 μg of Pb(II) and Cr(III) was placed in a centrifuge tube. The pH of solution was adjusted with an appropriate buffer solution. For pH adjustment, different buffer solutions given in Section 2.2 were used for each pH that was worked. Then 1.0 mL of 1000 mg L^{-1} of copper(II) as a carrier element was added to this solution. The required volume of 5-chloro-2-hydroxyaniline solution was poured into the tube. After 10 min, the solution was centrifuged at 2500 rpm for 20 min. The supernatant was removed. The precipitate in the tube was dissolved with 500 μL of concentrated HNO_3. Then it was completed to 2.0 mL with deionised water. The analytes in the final solution were determined by flame atomic absorption spectrometry.

2.4. Application to real samples

The water samples were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size. The pH of the samples was adjusted to 8.0 with ammonia/ammonium buffer solution. Then the preconcentration–separation procedure given above was applied to all the samples. The levels of analyte ions in the final solutions were determined by flame atomic absorption spectrometry.

GBW 07309 stream sediment (250 mg) and NIST SRM 1633b coal fly ash (250 mg) certified reference materials, river sediment from Kizilirmak (1.0 g), soil sample from Tokat City (1.0 g) and coal from Tokat City (1.0 g) were digested with 6 mL HCl (37%), 2 mL of HNO_3 (65%) in microwave digestion system and diluted to 50.0 mL with deionised water. A blank digest was carried out in the same way. Then the preconcentration procedure given above was applied to the final solutions.

3. Results and discussion

3.1. Effects of pH on the coprecipitation

The effect of pH of working media on the recoveries of chromium(III) and lead(II) ions on copper–5-chloro-2-hydroxyaniline precipitate were studied in the pH range of 2.0–10.0. Each pH was adjusted by using related buffer solutions given in Section 2. The results for this work are depicted in Fig. 1. The recoveries of analytes were increased with the increasing pH. The quantitative recovery values were obtained for chromium(III) and lead(II) ions in the pH range of 8–10. pH 8 was selected as working pH for all further coprecipitation works.

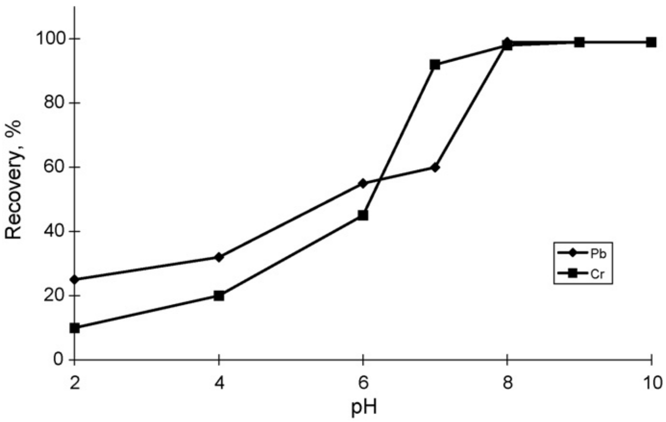

Fig. 1. Influences of pH on the recoveries of lead(II) and chromium(III) on the coprecipitation method ($N = 3$).