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Bi(III)4-methylpiperidinedithiocarbamate coprecipitation procedure for separation–pre-concentration of trace metal ions in water samples by flame atomic absorption spectrometric determination

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Abstract

A pre-concentration method was developed for determination of trace amounts of cadmium, copper and lead in water samples by FAAS after coprecipitation by using potassium 4-methylpiperidinedithiocarbamate (K4-MPDC) as a chelating agent and Bi(III) as a carrier element. This procedure is based on filtration of the solution containing precipitate on a cellulose nitrate membrane filter following Cd(II), Cu(II) and Pb(II) coprecipitation with Bi(III)4-MPDC and then the precipitates together with membrane filter were dissolved in concentrated nitric acid. The metal contents of the final solution were determined by FAAS. Several parameters including pH of sample solution, amount of carrier element and reagent, standing time, sample volume for precipitation and the effects of diverse ions were examined. The accuracy of the method was tested with standard reference material (MBH, C31XB20 and CRM BCR-32) and Cd, Cu and Pb added samples. Determination of Cd, Cu and Pb was carried out in sea water, river water and tap water samples. The recoveries were >95%. The relative standard deviations of determination were less than 10%.

Keywords: Dithiocarbamate; Coprecipitation; Pre-concentration; FAAS

1. Introduction

Since several heavy metals are generally present at trace concentration in environmental and metallurgical samples such as wastewater, sediment, soils, pure metal and alloy, sensitive and selective methods of the determination are needed for the samples including these complex matrices.

Flame atomic absorption spectrometry (FAAS) is one of the most reliable techniques to determine metal ions at trace concentrations. However, the detection limits of FAAS is usually insufficient for determining μg/L concentration levels of metal ions. Therefore, FAAS is frequently combined with pre-concentration techniques to improve the detection limit and/or selectivity.

Many techniques have been proposed to pre-concentrate trace metals from matrices that adversely influence atomic absorption spectrometric detection. The various pre-concentration procedures include extraction [1–3], ion exchange supports [4], chelating resins [5,6] and coprecipitation [7–15]. The combination of coprecipitation and filtration offer a simple and rapid pre-concentration method mainly in water analysis.

Among the pre-concentration techniques used, the coprecipitation method is a useful means of enrichment and variety of coprecipitants have been proposed. Dithiocarbamates have been widely used as chelating agents for separation, pre-concentration and determination of trace metals with coprecipitation method [16–18]. Dithiocarbamate compounds have sulfur atoms as electron-donor in their structures. Uncharged chelates form when metal ions react with bifunctional ligands. The high molar absorptivities of metal dithiocarbamate complexes make them useful spectrometric reagents for trace metals analysis. Also, metal dithiocarbamates are more useful than ammonium or alkali metal salt of dithiocarbamic acids [19,20].

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Table 1
Operating conditions for FAAS

Metal	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Flame type	Fuel flow rate (L s^{-1})
Cd	228.8	0.5	10	Air/acetylene	1.2
Cu	324.8	0.5	5	Air/acetylene	1.2
Pb	217.1	0.5	10	Air/acetylene	1.2

In the presented work, a coprecipitation procedure has been proposed for the separation–pre-concentration of Cd(II), Cu(II) and Pb(II) ions prior to their flame atomic absorption spectrometric determinations. The procedure was based on coprecipitation of analytes by Bi(III)4-methylpiperidinedithiocarbamate (Bi(III)4-MPDC) and it was applied to the various water samples.

2. Experimental

2.1. Apparatus

A Unicam 929 model flame atomic absorption spectrophotometer was used for determination of Cd(II), Cu(II) and Pb(II), following the instrumental parameters recommended by the manufacturer were given in Table 1. pH measurements were performed with a Jenway 3040 model digital pH-meter.

2.2. Reagent and solution

The stock solutions containing 1000 mg/L of Cd(II), Cu(II), Pb(II) and Bi(III) were prepared by dissolving appropriate amount of $Cd(NO_3)_2 \cdot 5H_2O$ (Merck), $Cu(NO_3)_2 \cdot 3H_2O$ (Merck), $Pb(NO_3)_2$ (Merck) and $Bi_5O(OH)_9(NO_3)_4$ (Merck) in 1 mol/L HNO_3. Diluted standard solutions and model solutions were daily prepared from the stock standard solutions.

The potassium 4-methylpiperidinedithiocarbamate (K4-MPDC) was synthesised according to the method given in the literature [22]. A solution of K4-MPDC (2%, m/v) was daily prepared by dissolving solid K4-MPDC in deionized water.

Two certified reference materials were used to investigate accuracy of the method: phosphate rock standard reference material BCR-32 (Cd: 20.8 μg/g; Cu: 33.7 μg/g) and standard metal alloy MBH C31XB20 (Pb: 0.21%).

The membrane filter used was made of cellulose nitrate (Sartorius AG 37070 and 0.45 μm pore).

2.3. General procedure

An aqueous solution containing 4.0 mg Bi(III) and 2 mL of a 2% K4-MPDC solution was added while stirring to a sample solution (up to 1000 mL) containing 5.0 μg of Cd, 12.5 μg of Cu and 25.0 μg of Pb, and the pH was adjusted with acetate buffer. After the precipitate has settled, the mixture was filtered through a cellulose nitrate membrane filter under vacuum. The precipitate was washed with the deionized water. The precipitate together with the membrane was dissolved 1–2 mL of concentrate HNO_3 and the solution was evaporated almost to dryness. The residue was dissolved in 1 mL concentrate HNO_3 and diluted up to 5 mL with deionized water. The analytes in the solution were determined by FAAS.

3. Results and discussion

3.1. Effect of pH on coprecipitation

The effect of the pH on coprecipitation with Bi(III)4-MPDC was studied with a solution containing 12.5 μg of Cu, 5.0 μg of Cd and 25.0 μg of Pb. The maximum recoveries were obtained over a pH range from 4.0 to 11.5 (Fig. 1). A pH of about 5 was used for coprecipitation of Cd(II), Cu(II) and Pb(II) and adjusted with acetate buffer for further experiments.

3.2. Effect of the amounts of Bi(III) as carrier element

Bi(III) is a suitable matrix for the determination of elements of interest by AAS. This reason was tested with a preliminary experiment. As a result, the atomic absorption of Cd(II), Cu(II) and Pb(II) was not affected even if 8.0 mg of Bi(III) was used for coprecipitation. Thus, 4.0 mg of Bi(III) was used in subsequent experiments.

The experiments were also repeated without Bi(III). In this case, the recovery yields were less than 50% (Fig. 2). As the concentration of trace elements is at the μg/mL level or even lower, they cannot form completely their own independent solid phases. Also K4-MPDC cannot precipitate in water [21]. Probably, the low recoveries are due to these two reasons. Therefore, for precipitation of trace elements from aqueous solution, a solid phase must be formed.

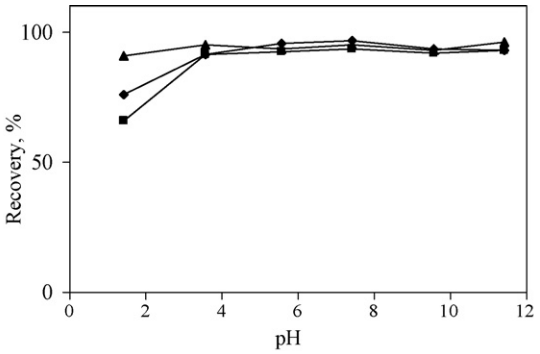

Fig. 1. Effect of pH on the recovery of copper, cadmium and lead from 250 mL of a sample solution containing 12.5 μg of Cu (▲) 5.0 μg of Cd (■) and 25.0 μg of Pb (♦) (amounts of carrier element and ligand: 4.0 mg Bi(III), 400.0 mg K4-MPDC, respectively. Final volume: 5 mL, $N = 3$).