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Preconcentration via ion associated complexes combined with inductively coupled plasma optical emission spectrometry for determination of heavy metals

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ABSTRACT

A method of separation and preconcentration of cadmium, cobalt, copper, nickel, lead and zinc at trace level from plant matrix using 2,2′-bipyridyl and rose Bengal is proposed. The above heavy metals were determined after preconcentration by inductively coupled plasma optical emission spectrometry (ICP-OES). The results were compared with those obtained using flame atomic absorption spectrometry (F-AAS). The influence of several parameters such as pH, molar ratio of 2,2′-bipyridyl to rose Bengal, duration of co-precipitation was examined. Moreover, effects of inorganic matrix on recovery of the determined elements were studied. The detection limits (DL) for ICP-OES were 0.36, 0.66, 3.3, 1.4, 3.5 and 3.2 $\mu g\,L^{-1}$ for Cd, Co, Cu, Ni, Pb and Zn, respectively, whereas for F-AAS DL were 0.77, 5.8, 1.1, 3.2, 3.0 and 0.71 $\mu g\,L^{-1}$. The recovery of the method for the determined elements was better than 94% with relative standard deviation between 0.68% and 1.7%. The preconcentration factor was 40. The proposed method was applied for determination of Cd, Co, Cu, Ni, Pb, and Zn in plant materials. Accuracy of the proposed method was verified using certified reference material (NCS ZC85006 Tomato).

1. Introduction

Preconcentration–separation methods including chemical methods such as solid phase extraction [1–3], cloud point extraction [4–6], membrane filtration [7], liquid–liquid extraction [8], and physical method such as evaporation [9] have been widely used for preconcentration and separation of heavy metal ions from various matrices.

Co-precipitation has also an important place among preconcentration and separation methods, because it is a simple and non-time consuming procedure. Various carriers including copper [10], aluminum [11], erbium [12], europium [13], gadolinium [14], indium [15], samarium [16], cerium [17], lanthanum [18–20] have been used for preconcentration and separation of heavy metal ions at trace levels. Inorganic ligands, such as hydroxide ion [21], and organic ligands [22–25] like rubeanic acid, dithiocarbamates, mercaptobenzothiazole etc. have been used for this purpose.

Ionic associations are also used as organic carriers. Ionic associations can be formed in the following system: a cationic chelate metal complex – an anion of a non-chelating organic dye. They form sparingly soluble precipitations. These precipitates are insoluble in acids and well soluble in hydroxide solutions and in organic solvents. Till now, formation of ionic associates of metal–heterocyclic base–xanthene acidic dye type was used mainly for development of sensitive extraction-spectrophotometric methods for single element determination [26] and spectrofluorimetric methods [27]. In this work, the insoluble precipitates of ionic associations were applied to group separation and preconcentration of Cd, Co, Cu, Ni, Pb, and Zn. Analytes were co-precipitated with ionic associate La–2,2-bipyridyl–rose Bengal as a carrier. The developed method was applied in determination of heavy metals in plant material by inductively coupled plasma optical emission spectrometry (ICP-OES) and flame atomic absorption spectrometry (F-AAS). White and red cabbage, and potatoes were selected for the analysis. Accuracy of the developed method was tested using certified reference material NCS ZC85006 Tomato.

2. Experimental

2.1. Apparatus

An optical emission spectrometer, ICP Model M (Spectro Analytical Instruments, Germany) was used for determination of Cd, Co, Cu, Ni, Pb, and Zn. The sequential spectrometer was used with the following parameters: frequency, 27.12 MHz; power, 1.1 kW; demountable quartz torch, Ar/Ar/Ar; coolant gas Ar, 14.0 $L\,min^{-1}$; auxiliary gas Ar, 0.5 $L\,min^{-1}$; nebulizer gas Ar, 1.0 $L\,min^{-1}$; nebulizer pressure, 2.4 bar; glass spray chamber according to Scott, sample flow rate, 1.0 $mL\,min^{-1}$; observation height 11 mm; holographic grating, 2400 $grooves\,mm^{-1}$; dispersion of grating in

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the first reciprocal order, 0.55 nm mm^{-1}; wavelength range of monochromator 165–460 nm. The wavelengths (integration time) were 228.80 nm (3 s), 228.62 nm (4 s), 324.75 nm (3 s), 221.65 nm (5 s), 220.35 nm (5 s), 213.87 (4 s) for Cd, Co, Cu, Ni, Pb, and Zn, respectively.

A flame atomic absorption spectrometer (Solaar M6 TJA Solutions) with deuterium arc background correction, equipped with a hollow cathode lamp was used for determination of Cd, Co, Cu, Ni, Pb, and Zn. An air–acetylene burner was used. The wavelengths (spectral band pass) were 228.8 nm (0.5 nm), 240.6 nm (0.2 nm), 324.8 nm (0.5 nm), 232.0 nm (0.1 nm), 217.0 nm (0.5 nm), 213.9 nm (0.5 nm) for Cd, Co, Cu, Ni, Pb, and Zn, respectively. The nebulizer flow rate was 5.0 mL min^{-1}.

2.2. Reagents and solutions

All chemicals were of analytical reagent grade. All reagents were dissolved and diluted with high purity water obtained from Milli-Q system. The following reagents were used in the experiment: 2,2′-bipyridyl (POCh, Gliwice, Poland), rose Bengal–disodium salt of tetrachlorotetraiodofluoresceine (Serva, Heidelberg, Germany), lanthanum(III) nitrate(V) (Loba Feinchemie, Fischamend, Austria), nitric acid, hydrochloric acid, sodium hydroxide, ammonia, nitrates(V) of sodium, potassium, magnesium, calcium, strontium, barium, aluminum, iron(III), manganese (all from POCh, Gliwice, Poland), stock standard solutions of cadmium, cobalt, copper, nickel, lead, and zinc at a concentration of 1000 mg L^{-1} (Merck, Darmstadt, Germany). Sodium acetate buffer solution was prepared by adding an appropriate amount of acetic acid to sodium acetate solution until pH 4 was obtained. The accuracy of the method was assessed by analyzing the certified reference material (CRM): NCS ZC85006 Tomato (China National Analysis Center for Iron & Steel 2000).

2.3. Procedures

2.3.1. General procedure of co-precipitation

0.2 mg of lanthanum(III), 5 mL of 0.01 mol L^{-1} solutions of 2,2′-bipyridyl and 5 mL of 0.01 mol L^{-1} solutions of rose Bengal were added to 100 mL of a solution containing 2 μg of Cd and Co, 10 μg of Pb and Ni, and 20 μg of Cu and Zn. The pH value of the obtained solution was adjusted to 4 using the acetate buffer. Then, the solution was heated in a water bath for 20 min in the temperature of 60 °C. Precipitate formed under these conditions was then centrifuged and the solution was decanted. Precipitate was digested in 1 mL of 0.2 mol L^{-1} solution of sodium hydroxide for ICP-OES measurement or in 1 mL of ammonia solution (1 + 1) for F-AAS measurement. The solution was diluted to 5 mL with water (final volume) and analyzed.

The calibration samples were prepared using 100 mL of standard solution containing analytes in the ranges: 0.2–4 μg of Cd and Co, 1–20 μg of Ni and Pb, 2–40 μg of Cu and Zn. The standard solutions were prepared using co-precipitation procedure described above.

2.3.2. Preparation of the plant material

Potatoes and white and red cabbage were selected for the analysis. The analyzed material was cleaned, broken up and dried in a laboratory drier at the temperature of 45 °C. Dried cabbage leaves and potato bulbs were ground in a high-speed rotor mill (Fritsch, Germany), in order to obtain a homogeneous sample with grain diameter of 1 mm. The plant material was stored in labeled, tightly sealed polyethylene containers.

The plant material was mineralized in the following way: 1 g of the sample was digested in 10 mL of concentrated nitric acid using a microwave pressure mineralizer. The following program was applied: step 1 (time: 3 min, power: 60%), step 2 (time: 5 min, power: 80%) and step 3 (time: 7 min, power: 100%). Then, the obtained solution was diluted to a volume of about 50 mL. Next, the sample was prepared using the co-precipitation procedure. The same procedure was used for the blank solutions.

In the case of certified reference material (NCS ZC85006 Tomato), 0.5 g of the sample was digested in 6 mL of concentrated nitric acid using a microwave pressure mineralizer and the program described above.

3. Results and discussion

The method developed for preconcentration of cadmium, cobalt, copper, nickel, lead, and zinc is based on reactions of ionic associates formation. The mechanism of traces concentration is as follows:

- The metal cation reacts with a heterocyclic base, forming a chelate complex with positive charge:

$$M^{2+} + n\text{bip} \rightarrow [M(\text{bip})_n]^{2+}$$

- The complex formed is coupled with an anion of xanthene dye, which results in formation of a new ionic associate:

$$[M(\text{bip})_n]^{2+} + \text{RB}^{2-} \rightarrow [M(\text{bip})_n]\text{RB}$$

- In the presence of lanthanum(III), an excess of the heterocyclic base and an excess of the acidic dye form a precipitate of an ionic associate performing as a carrier:

$$2\text{La}^{3+} + 2n\text{bip}_{\text{excess}} + 3\text{RB}^{2-}_{\text{excess}} \rightarrow [\text{La}(\text{bip})_n]_2\text{RB}_3\downarrow$$

- Ionic associates containing traces of heavy metals co-precipitated with the precipitate formed according to surface adsorption mechanism:

$$[M(\text{bip})_n]\text{RB} + [\text{La}(\text{bip})_n]_2\text{RB}_3\downarrow \rightarrow$$

$$\{[M(\text{bip})_n]\text{RB} + [\text{La}(\text{bip})_n]_2\text{RB}_3\}\downarrow$$

where M^{2+} – Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}; bip – 2,2′-bipyridyl; RB – rose Bengal.

3.1. Optimization of operating conditions

3.1.1. Precipitation

The La–2,2′-bipyridyl–rose Bengal ionic associate precipitates in acidified solution. Influence of pH in the range from 2 to 7 on the recovery of the determined elements was examined. Fig. 1

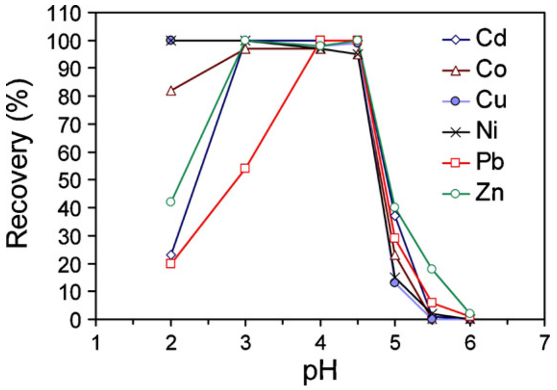

Fig. 1. Effect of pH on the quantitative co-precipitation of the elements studied.