

Separation and preconcentration of Pb(II) and Cu(II) ions via carrier element-free coprecipitation using an acetohydrazide derivative

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Abstract: A new method based on the combination of carrier element-free coprecipitation and flame atomic absorption spectrometric determination has been investigated for simultaneous separation and preconcentration of Pb(II) and Cu(II) ions in some environmental solid and liquid samples. The 2-{3-(4-methylbenzyl)-4-[2-(1H-indol-3-yl)ethyl]-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl} -N¹-(phenylmethylene) acetohydrazide (MITA) was utilized as an organic coprecipitating agent without using a carrier element for coprecipitation of the analyte ions. The effects of experimental conditions including aqueous solution pH, MITA quantity, sample volume, standing time, and centrifugation rate and time were investigated in detail and optimized. The influences of some foreign ions were also evaluated on the quantitative recoveries of the analyte ions. The preconcentration factors were 125 for both analyte ions. The detection limits were 1.32 $\mu\text{g L}^{-1}$ and 0.47 $\mu\text{g L}^{-1}$ for Pb(II) and Cu(II) ions, respectively, and the relative standard deviations (RSDs) were lower than 4% for both analyte ions. After the accuracy of the method was checked, it was applied to sea and stream water as liquid samples and waste tea and tobacco as solid samples to determine the levels of Pb(II) and Cu(II) ions.

Key words: Heavy metals, separation and preconcentration, coprecipitation, carrier element free coprecipitation

1. Introduction

The increasing industrial activities with the development of technology cause environmental pollution as well as improve living standards. Heavy metals, naturally occurring and indestructible elements in the earth's crust, are one of the major sources of environmental pollution. They spread into the environment by fuel gases, domestic waste, nuclear and thermal power plants, factories, mines, traffic, pesticides, and excessive fertilization.^{1,2} Heavy metals enter the human body through breathing, diet, or skin absorption and begin to accumulate in the tissues. These metals cannot be removed from the body and reach toxic values over time.^{3,4} Although some heavy metals such as copper, iron, selenium, and zinc are essential at certain concentration levels to maintain the living metabolism, when taken at high concentrations they may cause toxic effects.⁵ For example, a trace quantity of copper is necessary for human health since it is a cofactor of some important enzymes and plays an important role in carbohydrate and lipid metabolism. However, taking large amounts of copper damages the lungs, kidneys, liver, or other vital organs, and blood composition.⁶ On the other hand, lead is a nonessential

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and highly toxic element and it is harmful even at low concentrations.^{7,8} For these reasons, one of the main parts of analytical chemistry is the determination of heavy metal ion concentrations in environmental samples.^{9,10}

Flame atomic absorption spectrophotometry (FAAS) is a generally used instrumental technique for the determination of heavy metal ions at trace levels in environmental samples due to its low cost, easy instrument usage, and high specificity.^{11,12} Nevertheless, the analysis of trace elements in environmental samples with FAAS usually involves two types of problem: i) matrix effect, ii) concentration levels of trace elements lower than the detection limit of FAAS.^{13,14} In order to solve these problems and to obtain better results, a separation and preconcentration method like solid-phase extraction,^{15,16} ion exchange,¹⁷ cloud-point extraction,¹⁸ membrane filtration,^{19,20} liquid-liquid extraction,²¹ and coprecipitation^{22,23} is often required prior to determination of trace metals levels by both FAAS and other instrumental techniques.

Coprecipitation is one of the most preferred methods because of the following advantages: (i) the implementation of the method is simple and fast, (ii) high preconcentration factors that allow one to determine lower concentration levels of analyte ions in environmental samples can be obtained, (iii) a variety of analyte ions can be separated and preconcentrated simultaneously by using different organic or inorganic coprecipitating agents, (iv) the method is environmentally friendly since the consumption of organic solvents is lower.^{24,25} A variety of inorganic or organic coprecipitants with a large amount of carrier element can be used for preconcentration of trace metal ions in aqueous media. Carrier element-free coprecipitation (CEFC), which has been developed in recent years, has several advantages over other coprecipitation methods. In CEFC an organic compound that dissolves in an organic solvent such as dimethylsulfoxide, alcohol, acetone, and acetonitrile but is insoluble or only slightly soluble in water is used as a coprecipitating agent and the addition of carrier element for the formation of precipitate is not required. Thus there is no contamination and background adsorption risks for trace metal ions from carrier elements.^{26–36}

In the present study we developed a new CEFC method for accurate determination of Pb(II) and Cu(II) ions in environmental solid (tobacco and waste tea) and liquid (sea and stream water) samples. In order to obtain a precipitate, 2-{3-(4-methylbenzyl)-4-[2-(1H-indol-3-yl)ethyl]-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl} - N'-(phenylmethylene) acetohydrazide (MITA) was used as an organic coprecipitating agent without a carrier element. Although MITA, a triazole derivative, is harmful for human health when taken into the body via ingestion, inhalation, or skin contact, there is no information available about its carcinogenic, mutagenic, or teratogenic effects. According to our literature survey, MITA was not used previously for the separation and preconcentration of metal ions. The experimental conditions including aqueous solution pH, MITA quantity, sample volume, standing time, and centrifugation rate and time were investigated in detail and optimized before the method was applied to real samples.

2. Results and discussion

2.1. Effect of pH

The effect of solution pH on the recovery of the analyte ions was investigated in the pH range of 3.0–10.0. For that purpose, 1.5 mg of MITA was added to 50 mL of aqueous solutions containing 10.0 μg of Pb(II) and 3.0 μg of Cu(II) ions. After that, pH values of the solutions were adjusted in the range of 3.0–10.0 by the addition of dilute HNO_3 and NaOH solutions. Then the coprecipitation procedure given in section “3.2. Procedure of the method” was applied to these solutions. The results showed that maximum recoveries for both metal ions (98%) were obtained at pH 7.0 (Figure 1). Hence during all experiments, pH 7.0 was selected as the working pH value.

2.2. Effect of MITA amount

The effect of MITA amount as the coprecipitating agent on the recovery of analyte ions was evaluated in the MITA amount range of 0–6.0 mg. It was seen that the quantitative separation and preconcentration of Cu(II) and Pb(II) ions were not possible without adding MITA (Figure 2). The recovery values for Pb(II) and Cu(II) ions increased from 68% to 98% and 53% to 95%, respectively, with the increase in MITA amount from 0 to 6.0 mg. The lowest MITA amount at which quantitative recovery values for both analyte ions were obtained was 1.5 mg; hence all the further experiments were performed using 1.5 mg (1.5 mL of 0.1% w/v) of MITA.

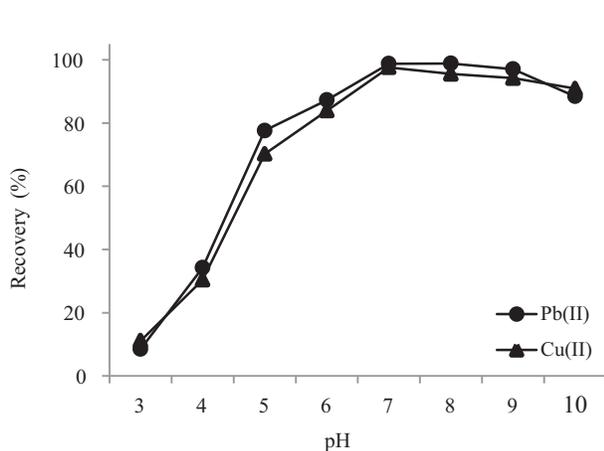


Figure 1. Effect of pH on the recovery of Pb(II) and Cu(II) ions ($N: 3$, sample volume: 50 mL, final volume: 2.0 mL, ligand amount: 1.50 mg, standing time: 10 min, centrifugation rate: 2000 rpm, centrifugation time: 10 min).

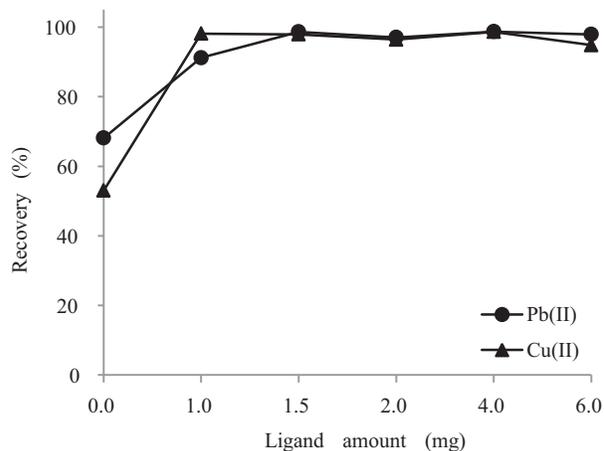


Figure 2. Effect of ligand amount on the recovery of Pb(II) and Cu(II) ions ($N: 3$, pH: 7.0, sample volume: 50 mL, final volume: 2.0 mL, standing time: 10 min, centrifugation rate: 2000 rpm, centrifugation time: 10 min).

2.3. Effect of standing time, centrifugation time, and centrifugation rate

The experimental parameters standing time, and centrifugation time and rate are important for quality precipitate formation; hence these parameters should also be optimized. For that purpose, 1.5 mg of MITA was added to a series of solutions containing Cu(II) and Pb(II) ions. After pH values were adjusted to 7.0, the procedure developed was applied to these solutions in the standing time range 0–30 min, centrifugation rate range of 1000–3500 rpm, and centrifugation time range of 0–20 min. As a result, quantitative recoveries were observed after 10 min of standing time, 2000 rpm of centrifugation rate, and 10 min of centrifugation time; hence these values were determined as optimum conditions.

2.4. Effect of the sample volume on the metal recovery

High preconcentration factors provide the opportunity to analyze low levels of analyte ions in environmental samples. Therefore, the effect of sample volume on the recovery of the analyte ions was evaluated in the sample volume range of 50–1000 mL by using the model solutions. Both Pb(II) and Cu(II) ions' recovery was quantitative up to 250 mL (Figure 3). The ratio of the highest sample volume (250 mL) and the lowest final volume (2 mL) was utilized to calculate the preconcentration factor and it was 125 for both metal ions.

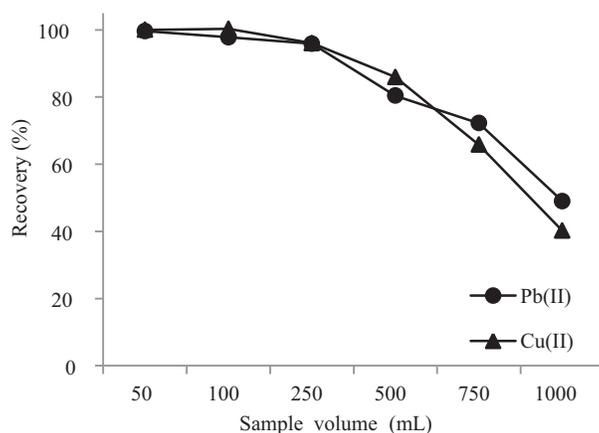


Figure 3. Effect of sample volume on the recovery of Pb(II) and Cu(II) ions ($N: 3$, pH: 7.0).

2.5. Effect of matrix ions on quantitative recovery

The interference effects of matrix components cause significant problems in all instrumental analysis methods. Therefore, the effects of concomitant ions on the recovery efficiency of analyte ions were examined by utilizing model solutions containing 10 μg of Pb(II) and 3 μg of Cu(II) ions and different amounts of interfering ions that may be present in sea and stream waters together with the analyte ions. The experiments were performed at predetermined optimum conditions. The results demonstrated that the presence of common interfering ions and also some transition metal ions has no explicit impact on the separation and preconcentration of Pb(II) and Cu(II) ions in the presented CEFC method (Table 1).

Table 1. Influences of some interfering ions on the recovery of Pb(II) and Cu(II) ions ($N: 3$, pH: 7.0, sample volume: 50 mL, final volume: 2.0 mL, standing time: 10 min, centrifugation rate: 2000 rpm, centrifugation time: 10 min).

| Ions | Added as | Conc. (mg L^{-1}) | Recovery (%) | |
|---|----------------------------|------------------------------|-----------------|-----------------|
| | | | Pb(II) | Cu(II) |
| Na^+ | NaCl | 12650 | 94.9 ± 3.3 | 99.3 ± 4.4 |
| K^+ | KCl | 1000 | 95.3 ± 2.5 | 99.1 ± 0.9 |
| Ca^{2+} | CaCl_2 | 1000 | 98.8 ± 1.5 | 97.3 ± 3.8 |
| Mg^{2+} | $\text{Mg}(\text{NO}_3)_2$ | 1000 | 98.9 ± 4.2 | 98.6 ± 2.4 |
| NH_4^+ | NH_4NO_3 | 250 | 101.1 ± 1.3 | 100.1 ± 3.7 |
| NO_3^- | NaNO_3 | 6050 | 96.5 ± 0.5 | 94.8 ± 2.9 |
| Cl^- | NaCl | 16200 | 96.2 ± 1.9 | 94.7 ± 2.1 |
| CO_3^{2-} | Na_2CO_3 | 1000 | 96.5 ± 3.5 | 95.4 ± 5.5 |
| SO_4^{2-} | Na_2SO_4 | 1000 | 95.4 ± 1.1 | 96.2 ± 4.6 |
| PO_4^{3-} | Na_3PO_4 | 1000 | 100.2 ± 1.7 | 95.3 ± 3.0 |
| F^- | NaF | 250 | 101.5 ± 2.0 | 96.4 ± 5.5 |
| $\text{Fe}^{3+}, \text{Al}^{3+}, \text{Cr}^{3+}, \text{Zn}^{2+}, \text{Mn}^{2+}, \text{V}^{5+}$ | * | 50 | 100.2 ± 3.5 | 95.6 ± 1.4 |

*Added as their nitrate salts.

2.6. Analytical performance of the method

The analytical performance of the method was calculated by FAAS measurements. The linear concentration ranges were 0.30–8.0 mg L^{-1} and 0.10–5.0 mg L^{-1} for Pb(II) and Cu(II) ions, respectively, with a correlation coefficient 0.999 for both analyte ions. In order to assess the precision of the method given as relative standard

deviations (RSDs), the developed method was carried out ten times with model solutions containing 3 μg of Cu(II) and 10 μg of Pb(II) ions under optimum conditions. The RSD values were 3.25% and 2.96% for Pb(II) and Cu(II) ions, respectively. The detection limits, defined as the concentration equivalent to three times the standard deviation of ten replicate measurements of blank samples (50 mL of aqueous solutions at pH 7.0 containing 1.5 mg of MITA) at optimum conditions, were 1.32 $\mu\text{g L}^{-1}$ and 0.47 $\mu\text{g L}^{-1}$ for Pb(II) and Cu(II) ions, respectively, when the sample volume was 250 mL and the final volume was 2.0 mL.

2.7. Method validation and application to real samples

Before applying the presented CEFC method to real samples, the accuracy of the method was investigated by spike/recovery tests and certified reference material analyses. For that purpose, suitable amounts of the analyte ions were spiked with 50 mL of sea and stream water (Table 2) and 0.750 g of waste tea and tobacco samples (Table 3). Then the method was applied to the samples under optimum conditions. All of the observed recovery values were $>90\%$ (Tables 2 and 3). Good agreement was also obtained for both analyte ions between the certified and the found values when using CRM-Sandy Soil C as a certified reference material (Table 4). The present CEFC method was finally applied to the real solid (waste tea and tobacco) and liquid samples (sea and stream water) to determine their Pb(II) and Cu(II) levels and the results obtained from the real samples are summarized in Table 5.

Table 2. Spiked recoveries of Pb(II) and Cu(II) ions from water samples (N : 3, pH: 7.0, MITA amount: 1.5 mg, sample volume: 50 mL, final volume: 2.0 mL).

| Element | Added (μg) | Stream Water | | Seawater | |
|---------|-------------------------|-------------------------|--------------|-------------------------|--------------|
| | | Found (μg) | Recovery (%) | Found (μg) | Recovery (%) |
| Pb(II) | 0 | BDL | - | BDL | - |
| | 12.50 | 11.73 \pm 0.13 | 93.8 | 11.60 \pm 0.54 | 92.8 |
| | 25.00 | 23.13 \pm 0.69 | 92.5 | 23.35 \pm 0.44 | 93.4 |
| Cu(II) | 0 | BDL | - | BDL | - |
| | 6.25 | 5.92 \pm 0.67 | 94.7 | 5.83 \pm 0.81 | 93.3 |
| | 12.50 | 11.88 \pm 0.27 | 95.0 | 11.93 \pm 0.94 | 95.4 |

BDL: Below detection limit

Table 3. Spiked recoveries of Pb(II) and Cu(II) ions from solid samples (N : 3, pH: 7.0, MITA amount: 1.5 mg, final volume: 2.0 mL).

| Element | Added (μg) | Tobacco | | Waste tea | |
|---------|-------------------------|-------------------------|--------------|-------------------------|--------------|
| | | Found (μg) | Recovery (%) | Found (μg) | Recovery (%) |
| Pb(II) | 0 | BDL | - | BDL | - |
| | 12.50 | 11.87 \pm 0.02 | 95.0 | 11.91 \pm 0.11 | 95.3 |
| | 25.00 | 23.47 \pm 0.10 | 93.9 | 23.66 \pm 0.60 | 94.6 |
| Cu(II) | 0 | 1.46 \pm 0.22 | - | 5.39 \pm 0.40 | - |
| | 6.25 | 7.35 \pm 0.10 | 94.2 | 11.67 \pm 0.85 | 100.5 |
| | 12.50 | 13.48 \pm 0.97 | 96.2 | 17.60 \pm 0.62 | 97.7 |

BDL: Below detection limit

Table 4. Application of the present method to the certified reference materials (N : 3, pH: 7.0, MITA amount: 1.5 mg, quantity of CRM-SA-C Sandy Soil C: 0.250 g, final volume: 5.0 mL).

| Element | CRM-SA-C Sandy Soil C | | |
|---------|---|--------------------------------------|----------------|
| | Certificated value ($\mu\text{g g}^{-1}$) | Found value ($\mu\text{g g}^{-1}$) | Recovery (%) |
| Pb(II) | 120 ± 8.0 | 112.6 ± 4.8 | 93.8 ± 9.3 |
| Cu(II) | 63.6 ± 4.0 | 59.4 ± 3.7 | 93.4 ± 5.4 |

Table 5. Analyte levels in real solid/liquid samples after the presented coprecipitation procedure was applied (N : 3, pH: 7.0, MITA amount: 1.5 mg, sample volumes: 250 mL, sample quantities: 0.750 g of waste tea and tobacco, final volumes: 2.0 mL).

| | Liquid samples ($\mu\text{g L}^{-1}$) | |
|--------------|---|------------------|
| | Pb(II) | Cu(II) |
| Seawater | BDL | 11.67 ± 0.91 |
| Stream water | BDL | 12.74 ± 0.79 |
| | Solid samples ($\mu\text{g g}^{-1}$) | |
| | Pb(II) | Cu(II) |
| Tobacco | BDL | 1.95 ± 0.22 |
| Waste tea | BDL | 7.19 ± 0.40 |

BDL: Below detection limit

3. Experimental

3.1. Apparatus and reagents

PerkinElmer AAnalyst 400 model flame atomic absorption spectrometer was utilized to determine the analyte ions concentrations in aqueous solutions. All measurements were performed in an air/acetylene flame with a 10-cm-long burner head. A Hanna pH-211 digital (Hanna Instruments, Romania) pH meter with a glass electrode was used for pH adjustment. A Sigma 3-16P (Sigma Laborzentrifugen GmbH, Germany) model centrifuge was used for centrifugation of solutions. A Milestones Ethos D closed vessel microwave system (Milestone Inc., Italy) was utilized for digestion of the solid samples.

All of the chemicals used in this work were analytical grade and purchased from Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland). Distilled/deionized water (Millipore Milli-Q system) was used throughout the experiments. The standard and working solutions of Pb(II) and Cu(II) ions were prepared by the dilution of 1000 mg L^{-1} stock solutions of the given elements purchased from Sigma and Aldrich. Dilute HNO_3 (Merck) and NaOH (Merck) solutions were used for pH adjustments. Coprecipitating agent, 2-{3-(4-methylbenzyl)-4-[2-(1H-indol-3-yl)ethyl]-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl} -N³ (phenylmethylene) acetohydrazide (MITA), was synthesized³⁷ in the organic chemistry research laboratory at Karadeniz Technical University's Chemistry Department (Figure 4). In addition, 0.1% (w/v) MITA solution was prepared in dimethyl sulfoxide and ethanol (1:4) mixture. The certified reference material, sandy soil standard (CRM-SA-C Sandy Soil C), was procured from High-Purity Standard Inc.

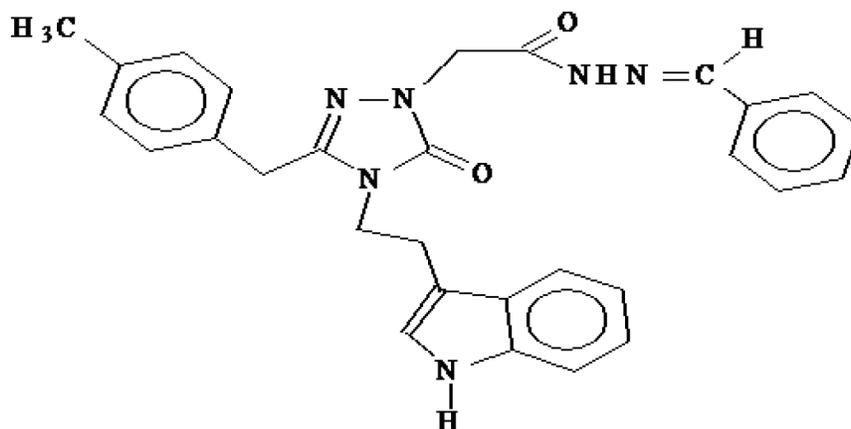


Figure 4. Chemical structure of MITA.

3.2. Procedure of the method

The performance of the presented CEFC method was evaluated by using artificial model solutions prior to separation and preconcentration of the analyte ions from real samples. For that purpose, 1.5 mL of MITA solution prepared in dimethyl sulfoxide and ethanol mixture (0.1%, w/v) were added to 50 mL of aqueous solution containing 10.0 μg of Pb(II) and 3.0 μg of Cu(II) ions. After that, pH of the solution was adjusted to 7.0 using diluted HNO_3 and NaOH solutions. After 10 min of standing time, the solution was centrifuged at 2000 rpm for 10 min. The precipitate that remained adhering to the tube was dissolved with 1.0 mL of conc. HNO_3 without heating. The final solution volume was completed to 2.0 mL with distilled/deionized water, and then the levels of analyte ions were determined by FAAS.

3.3. Analysis of real samples

The separation and preconcentration method was carried out to determine the levels of Cu(II) and Pb(II) ions in seawater (Black Sea, Trabzon, Turkey), stream water (Şana Stream, Trabzon, Turkey), waste tea, and tobacco samples. For that purpose, the water samples were filtered through a cellulose membrane filter of 0.45- μm pore size. After acidification with 1% (v/v) nitric acid solution, they were stored at 4 °C in polyethylene bottles. The waste tea and tobacco samples and CRM-SA-C Sandy Soil C were digested in a closed microwave digestion system. Then 0.750 g of waste tea and tobacco samples and 0.250 g of CRM-SA-C Sandy Soil C were placed in Teflon vessels, separately. Next 6.0 mL of HNO_3 and 2.0 mL of H_2O_2 for waste tea and tobacco samples and 4.5 mL of HCl, 1.5 mL of HNO_3 , 1 mL of HF, and 2 mL of H_2O_2 for CRM-SA-C Sandy Soil C standard were added to the vessels. Digestion conditions for the samples were according to the literature.²⁸ The volumes of the obtained clear solutions were made up to 50 mL with distilled/deionized water. A blank digest was carried out in the same way. Finally, the explained procedure was applied to the solutions after the pH values were adjusted to 7.0.

4. Conclusion

A separation and preconcentration technique based on CEFC was developed in order to determine the Pb(II) and Cu(II) levels accurately in sea and stream waters as liquid samples and waste tea and tobacco samples as solid samples. 2-[3-(4-Methylbenzyl)-4-[2-(1H-indol-3-yl)ethyl]-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl]-N'(phenylmethylene)acetohydrazide (MITA) was utilized as an organic coprecipitant without using a carrier

Table 6. Comparison of the presented method with some recent studies on coprecipitation reported in the literature.

| Analytes | Organic coprecipitating agent | Carrier element | pH | PF | LOD ($\mu\text{g L}^{-1}$) | RSD (%) | Ref. |
|--|-------------------------------------|-----------------|------|-----|--|-------------------------|-----------|
| Cd(II), Cu(II) | MEFMAT | - | 6.8 | 50 | 0.45, 1.49 | 2.0, 3.2 | 30 |
| Pb(II), Cr(III), Cu(II) | ICOTMA | - | 7.0 | 50 | 0.86, 2.06, 0.56 | 3.6, 4.1, 2.8 | 31 |
| Cd(II), Cr(III), Co(II), Cu(II), Fe(III), Pb(II), Mn(II) | CTAB | - | 10.0 | 10 | 0.61, 16.8, 12.7, 1.36, 2.08, 4.30, 0.22 | < 5 | 32 |
| Cr(III), Cu(II), Fe(III), Pb(II), Zn(II) | APSAL | - | 7.0 | 100 | 0.2, 0.5, 0.8, 1.2, 0.7 | < 5 | 33 |
| Cu(II) | ITAH | - | 5.0 | 50 | 0.31 | 1.6 | 34 |
| Ni(II), Cu(II) | ICOTPA | - | 7.5 | 125 | 0.27, 0.58 | < 4 | 35 |
| Co(II), Cu(II), Ni(II) | IMOTPA | - | 6.5 | 100 | 0.40, 0.16, 0.17 | 2.7, 1.9, 2.4 | 36 |
| Cu(II), Ni(II) | BUMECTAC | Mo(VI) | 1.3 | 40 | 0.43, 0.70 | 3.6, 3.9 | 38 |
| Pb(II), Cd(II), Zn(II), Co(II) | Diethyldithiocarbamate | Mo(VI) | 4.5 | 150 | 2.2, 0.1, 0.2, 0.6 | < 5 | 39 |
| Cd(II), Cu(II), Ni(II), Pb(II), Zn(II) | 8-Hydroxyquinoline | La(III) | 8.0 | 60 | 0.31, 2.9, 1.4, 3.2, 1.2 | < 3 | 40 |
| Co(II), Pb(II), Cu(II), Fe(III), Zn(II) | 2-Nitroso-1-naphthol-4-sulfonicacid | Ni(II) | 8.0 | 25 | 1.05, 2.67, 1.30, 1.38, 0.50 | 4.5, 5.7, 3.8, 6.1, 7.5 | 41 |
| Co(II), Cu(II), Fe(III), Pb(II), Mn(II) | QAN | Ni(II) | 9.0 | 100 | 0.83, 0.23, 0.04, 0.03, 0.06 | < 3.5 | 42 |
| Pb(II), Cd(II), Cr(III), Ni(II), Mn(II) | Dibenzylidithiocarbamate | Cu(II) | 9.0 | 50 | 0.87, 0.34, 0.75, 0.06, 0.45 | < 10 | 43 |
| Pb(II), Cu(II) | MITA | - | 7.0 | 125 | 1.32, 0.47 | 3.25, 2.96 | This work |

PF: Preconcentration factor, LOD: Limit of detection, RSD: Relative standard deviation, MEFMAT: 2-[[4-(4-fluorophenyl)-5-sulphanyl-4H-1,2,4-triazol-3-yl]methyl]-4-[[[(4-fluorophenyl) methyl]amino] 5-(4-methylphenyl)-2,4-dihydro-3H-1,2,4-triazol-3-one, ICOTMA: 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 acetohydrazide, CTAB: N-cetyl N,N,N trimethyl ammonium bromide, APSAL: 4-(2-hydroxybenzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one, ITAH: 2-[[4-[2-(1H-Indol-3-yl)ethyl]-3-(4-chlorobenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl] N'-(2-hydroxyphenylmethylidene) acetohydrazide, ICOTPA: 2-[[4-[2-(1H-Indol-3-yl)ethyl]-3-(4-chlorobenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl] -N'-(pyrrol-2-ylmethylidene)acetohydrazide, IMOTPA: 2-[[4-[2-(1H-indol-3-yl)ethyl]-3-(4-methylbenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl] -N'-(pyridim-2-yl methylidene)acetohydrazide, BUMECTAC: di-tert-butyl[methylenebis[5-(chlorobenzyl)-4H-1,2,4-triazol-3,4-diy]]] biscarbamate, QAN: 2-[[E)-(8-hydroxy-2- methylquinolin-5-yl) diazenyl] benzoic acid, MITA: 2-[[3-(4-Methylbenzyl)-4-[2-(1H-indol-3-yl)ethyl]-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl] -N'-(phenylmethylene) acetohydrazide.

element, and thus the interference risk caused by carrier elements for Pb(II) and Cu(II) ions during the FAAS analyses was eliminated. On the other hand, there is no interference from MITA since it is an organic compound and decomposes easily by flame and HNO₃. As stated in “3.2. Procedure of the method” the metal retained coprecipitant was dissolved with 1.0 mL of conc. HNO₃ without heating, which made the process easier and shortened the time. Namely the time required for the completion of the process was just 35 min. Hence it can be considered that the proposed CEFC method is simple, rapid, and low cost. On the other hand, some parameters including pH of the solutions, preconcentration factor, LOD, and RSD of the presented CEFC method were compared with those of other coprecipitation methods^{30–36,38–43} and are summarized in Table 6. There is no need to use a carrier element to form a precipitate and this may be considered one of the main advantages of the proposed method. The optimum pH value (7.0) is also an advantage in the separation and preconcentration of analyte ions from natural water samples without chemically pretreating the samples. Furthermore, the method has relatively high preconcentration factors and low LOD and RSD values compared with other coprecipitation methods reported in Table 6. As a result, under optimized experimental conditions the developed CEFC procedure has been used successfully to determine Pb(II) and Cu(II) levels in the environmental samples.

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