



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



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## 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.

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## 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 cholesterol 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 separation 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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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 methylenediacetohydrazid (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 ( $1000 \text{ mg L}^{-1}$ ) in  $0.5 \text{ M HNO}_3$  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  $10\% \text{ (v/v) HNO}_3$  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-211 model 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<sup>®</sup> 611UV). Milestones Ethos D (Milestone 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,  $25.0 \text{ mL}$  portion of a solutions containing of  $20.0 \mu\text{g Cr(III)}$ ,  $25.0 \mu\text{g Pb(II)}$  and  $15.0 \mu\text{g Cu(II)}$  and  $1.0 \text{ mL}$  of coprecipitating agent ( $0.1\% \text{ w/v}$ ) were added to a beaker. The pH of the solutions was adjusted to 7.0 by using diluted NaOH and/or  $\text{HNO}_3$  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  $0.5 \text{ mL}$  of concentrated  $\text{HNO}_3$ . Finally, the

volume was completed to  $5.0 \text{ mL}$  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  $0.45 \mu\text{m}$  cellulose nitrate with membrane, then their pH values were adjusted to 7.0. Then  $1.0 \text{ mL}$  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  $5.0 \text{ mL}$  with distilled water and levels of the analytes were determined by FAAS.

The digestion of black tea ( $0.750 \text{ mg}$ ) and tobacco ( $0.750 \text{ mg}$ ) was carried out using  $4.0 \text{ mL}$  of  $\text{HNO}_3$ , and  $2.0 \text{ mL}$  of  $\text{H}_2\text{O}_2$  and the digestion of CRM-SA-C Sandy Soil C Standard material ( $0.500 \text{ mg}$ ) was carried out with  $1.5 \text{ mL}$  of  $\text{HNO}_3$ ,  $4.5 \text{ mL}$  of  $\text{HCl}$ ,  $1.0 \text{ mL}$  of  $\text{HF}$  and  $2.0 \text{ mL}$  of  $\text{H}_2\text{O}_2$  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  $5.0 \text{ mL}$  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,  $0.1\% \text{ w/v}$ ) 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  $1.0 \text{ mg}$  of ICOTMA. All experiments were performed by using  $1.0 \text{ mg}$  ( $1.0 \text{ mL}$  of  $0.1\% \text{ (w/v)}$ ) of ICOTMA amount at optimal pH value.

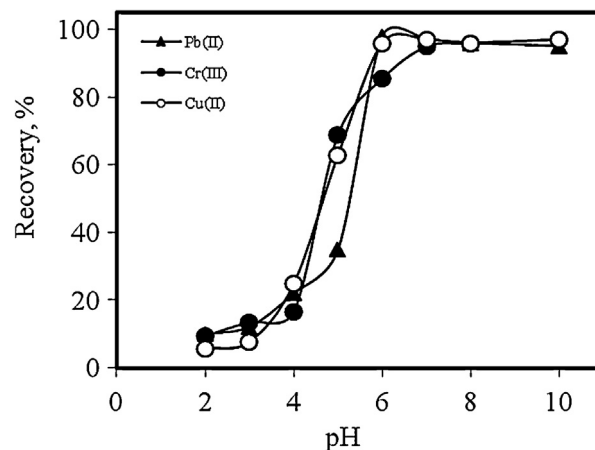


Fig. 1. Effect of pH on the recoveries of analyte ions (N: 3, sample volume:  $50 \text{ mL}$ , quantity of ICOTMA:  $1.0 \text{ mg}$  ( $1.0 \text{ mL}$   $0.1\% \text{ (w/v)}$ ), standing time: 10 min, centrifugation rate: 3500 rpm, centrifugation time: 10 min).

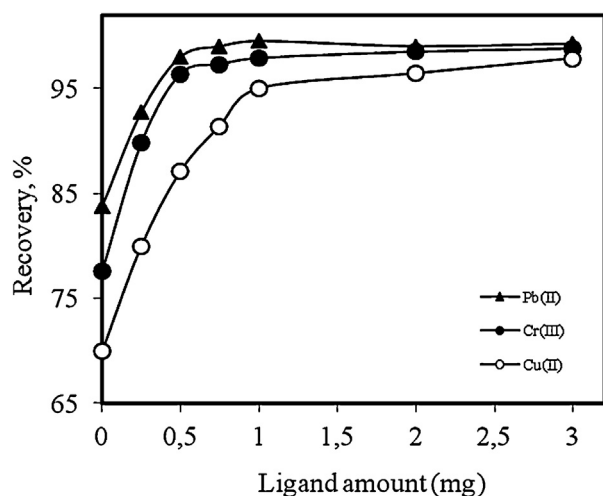


Fig. 2. Effect of ICOTMA amount on the recoveries of analyte ions (N: 3, pH: 7.0, sample volume: 50 mL).

### 3.3. Effect of sample volume

In order to obtain high preconcentration factor, sample volume is one of the key factor [37–40]. The effect of sample volume on the recovery of Pb(II), Cr(III) and Cu(II) ions were investigated in the sample volume range of 50–1000 mL containing 20.0  $\mu\text{g}$  Cr(III), 25.0  $\mu\text{g}$  Pb(II) and 15.0  $\mu\text{g}$  Cu(II) ions. The recovery values of the analyte ions decreased when increasing the volume of the sample solution. As can be seen in Fig. 3, the recovery values were not quantitative above 250 mL of sample volume. Thus, the optimum sample volume was determined as 250 mL for the quantitative determination of Pb(II), Cr(III) and Cu(II) ions at pH 7.0. The enrichment factor of the analyzed ions obtained as 50 when the final volume was 5.0 mL.

### 3.4. Influences of foreign ions

The effect of foreign ions is a notable parameter for quantitative recoveries of metal ions from real samples [41–45]. Analyte ions exist in real samples together with different matrix ions. The influences of some cations and anions were researched on the recoveries of Pb(II), Cr(III) and Cu(II) ions at pH 7.0. High concentrations of some cations and anions, also some transition metals have not interfered effect on the FAAS determination of the analyte ions (Table 1). Consequently, the CEFC method could be performed to the real samples involving high content of foreign ions at tolerable concentration levels.

Table 1

Influences of some foreign ions on the recoveries of analyte ions (N: 3, pH: 7.0, 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.

| Ions                                    | Added as                          | Conc. ( $\text{mg L}^{-1}$ ) | Recovery, (%) |             |             |
|---|-----------------------------------|------------------------------|---------------|-------------|-------------|
|   |                                   |                              | Pb(II)        | Cr(III)     | Cu(II)      |
| Na <sup>+</sup>                         | NaCl                              | 5000                         | 92.2 ± 0.8    | 96.8 ± 2.4  | 97.6 ± 3.4  |
| K <sup>+</sup>                          | KCl                               | 1000                         | 97.4 ± 2.0    | 96.1 ± 4.3  | 96.9 ± 1.5  |
| Ca <sup>2+</sup>                        | CaCl <sub>2</sub>                 | 1000                         | 99.3 ± 1.0    | 91.1 ± 3.2  | 99.3 ± 1.0  |
| Mg <sup>2+</sup>                        | Mg(NO <sub>3</sub> ) <sub>2</sub> | 1000                         | 100.6 ± 2.5   | 93.0 ± 3.4  | 100.7 ± 2.0 |
| NH <sub>4</sub> <sup>+</sup>            | NH <sub>4</sub> NO <sub>3</sub>   | 1000                         | 92.3 ± 3.5    | 97.0 ± 0.9  | 92.1 ± 1.5  |
| NO <sub>3</sub> <sup>-</sup>            | NaNO <sub>3</sub>                 | 5000                         | 93.5 ± 1.8    | 97.1 ± 0.6  | 94.7 ± 0.5  |
| CO <sub>3</sub> <sup>2-</sup>           | Na <sub>2</sub> CO <sub>3</sub>   | 1000                         | 97.1 ± 1.6    | 101.4 ± 1.5 | 97.6 ± 2.4  |
| SO <sub>4</sub> <sup>2-</sup>           | Na <sub>2</sub> SO <sub>4</sub>   | 1000                         | 94.2 ± 3.7    | 95.5 ± 3.0  | 94.5 ± 3.9  |
| PO <sub>4</sub> <sup>3-</sup>           | Na <sub>3</sub> PO <sub>4</sub>   | 1000                         | 100.1 ± 1.8   | 104.7 ± 2.4 | 95.2 ± 2.0  |
| Ni(II), Al(III), Cd(II), Zn(II), Mn(II) | <sup>b</sup>                      | 25                           | 95.4 ± 2.9    | 91.5 ± 0.9  | 93.4 ± 2.4  |
| Mixed <sup>a</sup>                      |                                   |                              | 102.2 ± 3.1   | 96.1 ± 2.1  | 95.7 ± 2.9  |

<sup>a</sup> 7349  $\text{mg L}^{-1}$  Na<sup>+</sup>, 8389  $\text{mg L}^{-1}$  Cl<sup>-</sup>, 7291  $\text{mg L}^{-1}$  NO<sub>3</sub><sup>-</sup>, 250  $\text{mg L}^{-1}$  K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, 10  $\text{mg L}^{-1}$  Ni(II), Al(III), Cd(II), Zn(II), Mn(II).

<sup>b</sup> Ions were added as their nitrate salts.

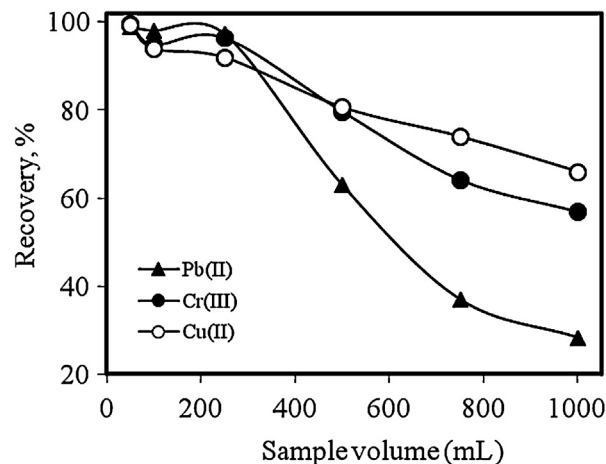


Fig. 3. Effect of sample volumes amount on the recoveries of analyte ions (N: 3, pH: 7.0).

### 3.5. Effect of standing time and centrifugation rate and time

The influences of standing time, centrifugation time and rate on the recoveries of the analyte ions were examined. The influences of centrifugation time on the quantitative recoveries of Pb(II), Cr(III) and Cu(II) ions were investigated in the range of 5–30 min. The quantitative value for the examined ions was obtained after 10 min of centrifugation time. Then the experiments were performed in the standing time range of 0–30 min and centrifugation rate range of 1000–3500 rpm at optimal conditions. The quantitative recoveries were obtained for all the analyte ions after 3500 rpm of centrifugation rate and 10 min of standing time. All other studies were performed at 10 min of centrifugation time, 10 min of standing time and 3500 rpm of centrifugation rate.

### 3.6. Analytical figure of merit

The relative standard deviations (RSD) which reflect the precision of the method were found to be 4.1% for Cr(III), 2.8% for Cu(II) and 3.6% for Pb(II) ions by repeating the method for 10 times by using model solutions containing 20.0  $\mu\text{g}$  of Cr(III), 25.0  $\mu\text{g}$  of Pb(II) and 15.0  $\mu\text{g}$  of Cu(II) ions. The limit of detections (LOD), defined as the concentration that gives a signal equivalent to three times the standard deviation of 10 replicate measurements of the blank samples, were found to be 0.86, 2.06 and 0.56  $\mu\text{g L}^{-1}$ , for Pb(II), Cr(III) and Cu(II) ions, respectively.

**Table 2**

Spiked recoveries of analyte ions from water samples (N:3, pH:7.0, sample volume: 50 mL, quantity of ICOTMA: 1.0 mg, final volume: 5.0 mL).

| Analyte | Added ( $\mu\text{g}$ ) | Stream water            |              | Sea water               |              |
|---------|-------------------------|-------------------------|--------------|-------------------------|--------------|
|         |                         | Found ( $\mu\text{g}$ ) | Recovery (%) | Found ( $\mu\text{g}$ ) | Recovery (%) |
| Pb(II)  | 0                       | BDL <sup>a</sup>        | –            | BDL                     | –            |
|         | 20                      | 18.9 $\pm$ 0.4          | 94.5         | 19.1 $\pm$ 0.4          | 95.5         |
|         | 40                      | 38.7 $\pm$ 0.6          | 96.8         | 38.7 $\pm$ 1.6          | 96.8         |
| Cr(III) | 0                       | BDL                     | –            | BDL                     | –            |
|         | 16                      | 15.3 $\pm$ 0.9          | 95.6         | 15.4 $\pm$ 0.7          | 96.2         |
|         | 32                      | 30.3 $\pm$ 1.5          | 94.7         | 31.5 $\pm$ 1.1          | 98.4         |
| Cu(II)  | 0                       | BDL                     | –            | BDL                     | –            |
|         | 6                       | 6.0 $\pm$ 0.4           | 100.0        | 5.7 $\pm$ 0.2           | 95.0         |
|         | 12                      | 11.5 $\pm$ 0.6          | 95.8         | 11.8 $\pm$ 0.5          | 98.3         |

<sup>a</sup> Below detection limit.

### 3.7. Analysis of real samples

The developed method was applied to water samples (sea and stream water) and solid samples (black tea and tobacco). The precision tests of the recommended procedure were performed with standard additions. The different amounts of analyte ions were added in 50 mL of sea and stream water and 0.750 g of tobacco and black tea and then, the CEFC was applied to the solutions. The results for water samples are given in Table 2 and the results for tobacco and black tea samples were given in Table 3. There are good agreements between added and found levels of analytes for all samples.

The accuracy of method was examined by the determination of Pb, Cr and Cu using a certified reference material (CRM-C-Sandy Soil C) (Table 4). There is a good concordance between the obtained and certified values. The results from the method could be successfully applied for separation and preconcentration with the ICOTMA on the quantitative recovery of the analytes from water and food samples.

The present method was applied to natural water and food samples. The results are given in Table 5. The levels of lead, chromium and copper in liquid and solid samples were found at  $\mu\text{g L}^{-1}$  and  $\mu\text{g g}^{-1}$ , respectively.

**Table 3**

Spiked recoveries of analyte ions from solid samples (N:3, pH:7.0, quantity of ICOTMA: 1.0 mg, quantity of tobacco and black tea: 0.75 g, final volume: 5.0 mL).

| Analyte | Added ( $\mu\text{g}$ ) | Black tea               |              | Tobacco                 |              |
|---------|-------------------------|-------------------------|--------------|-------------------------|--------------|
|         |                         | Found ( $\mu\text{g}$ ) | Recovery (%) | Found ( $\mu\text{g}$ ) | Recovery (%) |
| Pb(II)  | 0                       | BDL                     | –            | BDL                     | –            |
|         | 20                      | 19.4 $\pm$ 0.6          | 97.0         | 19.2 $\pm$ 0.6          | 96.0         |
|         | 40                      | 38.9 $\pm$ 1.3          | 97.2         | 37.5 $\pm$ 1.1          | 93.8         |
| Cr(III) | 0                       | 1.7 $\pm$ 0.03          | –            | 2.2 $\pm$ 0.03          | –            |
|         | 16                      | 17.5 $\pm$ 0.13         | 98.8         | 17.1 $\pm$ 0.9          | 93.1         |
|         | 32                      | 32.2 $\pm$ 1.3          | 95.3         | 32.7 $\pm$ 1.5          | 95.3         |
| Cu(II)  | 0                       | 2.9 $\pm$ 0.05          | –            | 3.0 $\pm$ 0.04          | –            |
|         | 6                       | 8.6 $\pm$ 0.2           | 95.0         | 8.7 $\pm$ 0.1           | 95.0         |
|         | 12                      | 13.9 $\pm$ 0.9          | 91.7         | 13.8 $\pm$ 0.4          | 90.0         |

**Table 4**

Application of the present method to the standard reference material (N: 3, quantity of CRM-SA-C Sandy Soil C: 0.1 g, final volume: 5.0 mL).

| Element | Certified value ( $\mu\text{g g}^{-1}$ ) | Found value ( $\mu\text{g g}^{-1}$ ) |
|---------|--|--------------------------------------|
| Pb      | 120 $\pm$ 8                              | 113 $\pm$ 5                          |
| Cr      | 54.1 $\pm$ 4.2                           | 52.0 $\pm$ 3.2                       |
| Cu      | 63.6 $\pm$ 4.0                           | 62.5 $\pm$ 2.1                       |

**Table 5**

Analyte levels in real solid/liquid samples after being applied the presented coprecipitation procedure (N: 3, sample volumes: 250 mL, quantity of tobacco and black tea: 0.75 g, final volumes: 5.0 mL).

| Element | Liquid samples ( $\mu\text{g L}^{-1}$ ) |                | Solid samples ( $\mu\text{g g}^{-1}$ ) |                  |
|---------|---|----------------|--|------------------|
|         | Sea water                               | Stream water   | Black tea                              | Tobacco          |
| Pb      | 14.2 $\pm$ 0.5                          | 19.2 $\pm$ 0.9 | BDL <sup>a</sup>                       | BDL <sup>a</sup> |
| Cr      | BDL                                     | 24.1 $\pm$ 0.4 | 2.3 $\pm$ 0.04                         | 3.0 $\pm$ 0.04   |
| Cu      | 8.8 $\pm$ 0.2                           | 36.9 $\pm$ 1.0 | 3.8 $\pm$ 0.06                         | 4.0 $\pm$ 0.05   |

<sup>a</sup> Below the detection limit.

## 4. Conclusion

In order to determine the levels of lead, chromium and copper in environmental samples, a simple, rapid, and low cost separation and preconcentration method based on CEFC was developed. In accordance with this purpose for the occurrence of the precipitate only an organic ligand, ICOTMA, was used without needing a carrier element. Therefore, the contamination risk for the analyte ions from a carrier element was eliminated. After being optimized the experimental parameters and validated the method, it was applied to determine lead, chromium and copper in tobacco, black tea, stream and sea water samples.

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