



## Carrier element-free coprecipitation with 3-phenyl-4-o-hydroxybenzylidenamino-4,5-dihydro-1,2,4-triazole-5-one for separation/preconcentration of Cr(III), Fe(III), Pb(II) and Zn(II) from aqueous solutions

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### ABSTRACT

A separation/preconcentration procedure, based on the coprecipitation of Cr<sup>3+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> ions using a new organic coprecipitant, 3-phenyl-4-o-hydroxybenzylidenamino-4,5-dihydro-1,2,4-triazole-5-one (POHBAT) without adding any carrier element has been developed. The method, thus, has been called carrier element-free coprecipitation (CEFC). The resultant concentrated elements were determined by flame atomic absorption spectrometric determinations. The influences of some analytical parameters including pH of the solution, amount of the coprecipitant, standing time, centrifugation rate and time, sample volume and diverse ions were investigated on the quantitative recoveries of analyte ions. The validation of the present preconcentration procedure was performed by the analysis of two certified reference materials. The recoveries of understudy analytes were found in the range of 93–98%, while the detection limits were calculated in the range of 0.3–2.0 µg L<sup>-1</sup>. The precision of the method evaluated as relative standard deviation (R.S.D.), was in the range of 3–7% depend on the analytes. The proposed method was successfully applied to environmental samples for the determination of the analytes.

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### 1. Introduction

Heavy metals, in environment are one of the major sources of pollution. Small amounts of these elements are common in our environment and actually necessary for good health but large amounts of them may cause acute and chronic toxicity. Heavy metals toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, damage the blood composition, lung, kidneys, liver and other vital organs [1,2]. Because of these reasons determination of metal ion concentrations in environmental samples is one of the most important fields of the analytical chemistry [3,4].

Flame atomic absorption spectrometry (FAAS) is an important method for determination of trace heavy metals, due to its low costs and easy instrument usage [5,6]. Two main limitations in FAAS determinations of trace heavy metal ions are lower levels of analyte ions than the detection limits of FAAS and positive or negative

influences of concomitants ions on the signal of the analytes [7,8]. In order to solve these problems, various separation/preconcentration procedures, including solvent extraction [9,10], adsorption [11,12], cloud point extraction [13], membrane filtration [14,15], coprecipitation [16,17], ion exchange [18], solid phase extraction (SPE) [19,20], electroanalytical techniques [21,22], etc. can be used.

Coprecipitation is widely applied in the analysis of water and food samples for heavy metals because it has some advantages including, simple, short analysis time, high preconcentration factor, low consumption of organic solvent, and several analyte ions can be separated and preconcentrated from the matrix. Various coprecipitation procedures including use of organic and inorganic coprecipitants have been developed, and are well documented [23,24]. Minami et al. have been proposed a preconcentration procedure based on the coprecipitation of copper, chromium and lead by an inorganic coprecipitant, terbium hydroxide [25]. Efendioglu et al. have also used an organic coprecipitant, 4-methylpiperidinedithiocarbamate with carrier element bismuth, in order to coprecipitate cadmium, chromium and lead [26].

In the present work, we established a new coprecipitation method, which has been called carrier element-free coprecipitation

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(CEFC) [27], by using an organic coprecipitant, 3-phenyl-4-o-hydroxybenzylidenamino-4,5-dihydro-1,2,4-triazole-5-one (POHBAT) without adding any carrier element for the separation and preconcentration of  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  ions. Also some of the researchers have not used a carrier element in coprecipitation studies but they have used an organic compound as a chelating agent to form a complex with trace metal ions in aqueous solution and then the chelates formed was accumulated on a collector [28]. In one of our study, we have performed an insoluble form (in water) of organic compound, used as a coprecipitating agent, and adsorbed the heavy metals on the precipitate [29]. It is a great advantage due to there is no contamination and interference risk for analytes from a carrier element. The influences of analytical parameters such as amount of coprecipitant, sample volume, diverse ions, etc. were investigated. The proposed method was applied to several environmental samples for determination of trace metal contents.

## 2. Experimental

### 2.1. Apparatus

A Unicam model AA-929 atomic absorption spectrometer (Solar System ATI, Unicam Analytical Technology Inc., England) equipped with 10 cm of air/acetylene-burner head, and having a deuterium background correction was used for the determination of metal ion concentration. All instruments settings were those recommended in the manufacturer's manual book. The pH measurements were made on Hanna pH-211 digital (HANNA instruments/Romania) pH meter with glass electrode. A centrifuge MSE Mistral 2000 (Lab Extreme, Inc./USA) was employed for the centrifugation of solutions. Milestones Ethos D closed vessel microwave system (Milestone Inc./Italy) (maximum pressure 1450 psi, maximum temperature 300 °C) was operated for digestion of the solid samples.

### 2.2. Reagents and solutions

All the chemicals used in this work were analytical grade of Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland), unless otherwise. Distilled/deionized water was used all experiments. The single element stock solutions of the metal ions ( $1000 \text{ mg L}^{-1}$ ) in 0.5 M  $\text{HNO}_3$  obtained from Merck and Fluka were used. Metal working solutions at  $\text{mg L}^{-1}$  level were prepared daily by diluting the stock solutions. Standard reference materials, CRM-TMDW-500 Drinking Water and IAEA-336 Lichen were obtained from High-Purity Standards Inc. and from IAEA Laboratory Seibersdorf, respectively.

In this study, POHBAT used as a coprecipitating agent was synthesized in the organic chemistry research laboratory (Karadeniz Technical University, Faculty of Arts and Science, Chemistry Department). The detailed information of its synthesis was given in the literature [30]. The NaOH and  $\text{HNO}_3$  solutions were used for adjusting the pH of the solutions. The glassware used was soaked in 10% (v/v) nitric acid solution for 1 day before use then cleaned repeatedly with distilled/deionized water. For storage of water samples, polypropylene bottles (5 L) were used prior to analysis.

### 2.3. Model working

Prior to preconcentration of the analyte ions from real samples, the performance of the present CEFC method should be tested by using artificial model solutions. For that purpose, 1 mL of coprecipitating agent solution prepared in ethyl alcohol (0.1% w/v) were added into a 50 mL of aqueous solution containing 25  $\mu\text{g}$  of  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ , 10  $\mu\text{g}$  of  $\text{Zn}^{2+}$  and 50  $\mu\text{g}$  of  $\text{Pb}^{2+}$  ions. pH of the solution was

adjusted to 7. After standing for 10 min, the solution was centrifuged at 3000 rpm for 20 min. The supernatant was removed. The precipitate remained adhering to the tube was dissolved with 1.0 mL of conc.  $\text{HNO}_3$ . Final volume was completed 5.0 mL with distilled/deionized water, and then the content was analyzed by FAAS for determination of analyte ions.

### 2.4. Analysis of real samples

The preconcentration procedure was applied for determination of chromium, iron, lead and zinc in the following samples; baby food, dried eggplant and drug as real solid samples, stream and sea water as real liquid samples. The method was also applied to standard reference materials (CRM-TMDW-500 Drinking Water and IAEA-336 Lichen Standard).

The solid samples were digested with a closed microwave digestion system for obtaining clear solutions prior to preconcentration of the analyte ions with the present coprecipitation method. For that purpose, triplicate samples of 0.25 g of CRM (IAEA-336), 0.5 g of baby food and dried eggplant, while 0.01 g of drug samples were weighed into teflon vessels separately. HCl,  $\text{HNO}_3$ , HF,  $\text{H}_2\text{O}_2$  in ratio of (4.5:1.5:2:1 mL) were added to CRM of lichen, while  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  in ratio of (6:2 mL) to baby food, drug and dried eggplant samples. The contents of the vessels were digested by microwave irradiation at 30 bar pressure. Digestion conditions for the samples were applied according to the literature [31]. Then the volume of the solutions was diluted to 50 mL with deionized water and the proposed preconcentration procedure was applied to the final solutions. A blank digest was carried out in the same way. The level of the analyte ions in the samples were determined by FAAS after the final volume of the solutions was made 5.0 mL with distilled water.

Triplicate 25 mL of certified reference material of drinking water CRM-TMDW-500 were taken to determine the levels of the investigated analyte ions. From the other real water samples, 750 mL of sea water (from Black Sea-Trabzon-Turkey) and stream water (from Buyukdere-Rize) for analysis of Cr, Fe and Zn, 250 mL of sea water and stream water for analysis of Pb were collected in polyethylene bottles. The samples were filtered through a cellulose membrane of pore size 0.45  $\mu\text{m}$  prior to trace metal analysis, the pH of the samples was adjusted to 7, and proposed procedure given above was applied to all the samples. The final volume of the solutions diluted to 5.0 mL with distilled/deionized water. The levels of the studied analyte ions in the final solutions were determined by FAAS.

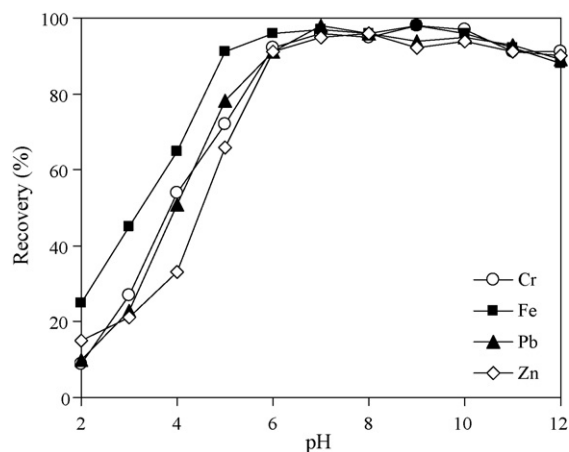


Fig. 1. Effect of pH on the recovery of zinc, chromium, iron and lead from 50 mL of sample solution containing 25  $\mu\text{g}$  of Fe and Cr, 10  $\mu\text{g}$  of Zn, 50  $\mu\text{g}$  of Pb ( $n=3$ , amount of POHBAT: 1.0 mg, final volume: 5.0 mL).

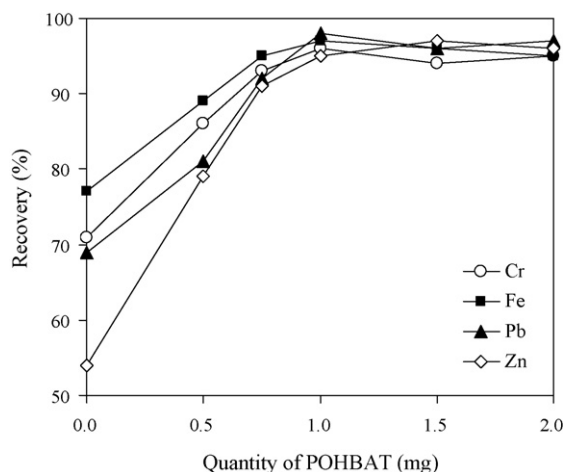


Fig. 2. Influences of POHBAT amount ( $n=3$ ).

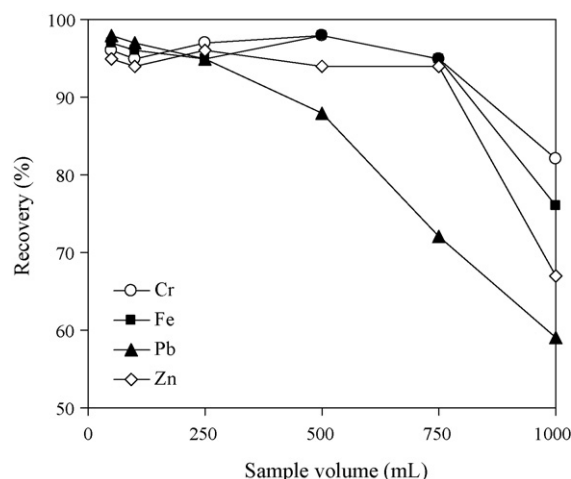


Fig. 3. Effects of sample volume on the recoveries of analytes ( $n=3$ ).

### 3. Results and discussion

#### 3.1. Effect of pH

The influences of pH of the aqueous solution on the recovery values of analytes were investigated at the range of 2–12 because pH is one the most important factor on the quantitative recoveries of analytes. For that purpose, 1 mL of coprecipitating agent were added to test solutions containing analyte ions, then pH of these solutions were adjusted by the addition of NaOH and HNO<sub>3</sub> solutions. After that the coprecipitation procedure given above was applied to these solutions. The results for this study are given in Fig. 1. According to the results, the maximum percent recoveries were in the pH range 7–8 for Zn, 6–10 for Fe, 7–10 for Cr and Pb. pH 7 was selected as working pH for all further works. Because pH 7 is a neutral value, this may be an advantage in the separation and preconcentration of trace metal ions from natural water samples without any chemical pretreatment of the sample [32].

#### 3.2. Influences of coprecipitating agent (POHBAT) amount

The effect of POHBAT amount on the coprecipitation of analytes was examined in the range of 0–2.0 mg. The results are shown in Fig. 2. The recoveries of analyte ions were not quantitative (below 75%) without adding POHBAT under optimum conditions. The recoveries of analyte ions increased with increasing amount of POHBAT. The results show that for the quantitative and simultaneous recoveries of understudy analytes, POHBAT was necessary. Quantitative recoveries for all the analytes were obtained at 0.75 mg

of POHBAT. So for all subsequent works 1.0 mg (1 mL of 0.1% w/v) of POHBAT was used.

#### 3.3. Effects of standing time, centrifugation time and rate

The standing time, centrifugation time and rate for precipitate formation was also optimized because these are the important factors influencing the quality of coprecipitate. For that purpose 1 mL of POHBAT (0.1% w/v in ethyl alcohol) were added into a series of solutions (50 mL) containing analyte ions after pH was adjusted to 7. Then the solutions were kept standing from 0 to 20 min. After 10 min the quantitative recoveries for all analyte ions were obtained. As a result the optimum standing time was determined as 10 min for all the studied elements. This period was long enough for the formation of precipitate and adsorption of trace metal ions on the precipitate.

The effects of the centrifugate rate were examined in the range of 1500–3500 rpm at the optimal conditions. The optimum centrifugation rate was determined as 3000 rpm for all studied metal ions. Also the influences of centrifugation time were investigated. For that purpose the standing periods were tried in the range 5–25 min at 3000 rpm. After 15 min the quantitative recoveries for all metal ions were obtained. So, all the other works were performed at 3000 rpm for 20 min.

#### 3.4. Effect of the sample volume

The sample volume used for the coprecipitation procedure influences the preconcentration factor [33–38], therefore sample

**Table 1**  
Effect of matrix ions over the recoveries ( $n=3$ ,  $V$ : 50 mL).

Ions	Added as	Conc. (mg L <sup>-1</sup> )	Recovery (%)			
			Zn	Fe	Pb	Cr
Na <sup>+</sup>	NaCl	10,000	91 ± 3	95 ± 4	96 ± 5	96 ± 2
K <sup>+</sup>	KNO <sub>3</sub>	1,000	96 ± 4	101 ± 3	98 ± 4	102 ± 6
Ca <sup>2+</sup>	Ca(NO <sub>3</sub> ) <sub>2</sub>	1,000	98 ± 5	96 ± 4	94 ± 3	96 ± 5
Mg <sup>2+</sup>	Mg(NO <sub>3</sub> ) <sub>2</sub>	1,000	93 ± 3	91 ± 4	95 ± 8	93 ± 5
Cl <sup>-</sup>	NaCl	15,000	97 ± 3	101 ± 7	96 ± 4	103 ± 5
PO <sub>4</sub> <sup>3-</sup>	Na <sub>3</sub> PO <sub>4</sub>	1,000	92 ± 4	96 ± 3	93 ± 4	99 ± 3
SO <sub>4</sub> <sup>2-</sup>	Na <sub>2</sub> SO <sub>4</sub>	1,000	97 ± 6	95 ± 3	100 ± 5	96 ± 4
NO <sub>3</sub> <sup>-</sup>	NaNO <sub>3</sub>	5,000	102 ± 8	101 ± 5	103 ± 7	104 ± 8
Al <sup>3+</sup> , Cd <sup>2+</sup> , Cu <sup>2+</sup> , V <sup>5+</sup> , Mn <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup> salts except V <sup>5+</sup> (as V <sub>2</sub> O <sub>5</sub> )	50	100 ± 7	99 ± 5	102 ± 8	102 ± 7
Mixed <sup>a</sup>			94 ± 5	93 ± 4	95 ± 6	98 ± 5

<sup>a</sup> Mixed solution contains 11,000 mg L<sup>-1</sup> of Na<sup>+</sup>, 15,000 mg L<sup>-1</sup> of Cl<sup>-</sup>, 500 mg L<sup>-1</sup> of Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup>, 7000 mg L<sup>-1</sup> of NO<sub>3</sub><sup>-</sup> and 10 mg L<sup>-1</sup> of Al<sup>3+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, V<sup>5+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup> ions.

**Table 2**

Spiked recoveries of the analyte ions from water samples ( $n=3$ , sample volume: 50 mL, final volume: 5.0 mL).

Element	Added ( $\mu\text{g}$ )	Sea water		Stream water	
		Found ( $\mu\text{g}$ )	Recovery (%)	Added ( $\mu\text{g}$ )	Recovery (%)
Fe	0	ND	–	ND	–
	5	$4.7 \pm 0.2$	94	$5.1 \pm 0.2$	102
	15	$15.2 \pm 0.9$	101	$15.1 \pm 0.8$	101
Zn	0	ND	–	ND	–
	5	$4.9 \pm 0.2$	98	$4.8 \pm 0.3$	96
	10	$9.7 \pm 0.3$	97	$10.1 \pm 0.4$	101
Pb	0	ND	–	ND	–
	10	$9.6 \pm 0.5$	96	$10.3 \pm 0.5$	103
	20	$18.9 \pm 1.1$	95	$19.9 \pm 0.8$	100
Cr	0	ND	–	ND	–
	5	$5.1 \pm 0.2$	102	$5.2 \pm 0.3$	104
	15	$15.3 \pm 0.4$	102	$15.4 \pm 0.6$	103

ND: not detected.

volume range of 50–1000 mL of model solutions were used to examine the coprecipitation efficiencies of the analytes. The results for this study are given in Fig. 3. The results show that the metal recoveries were quantitative up to 250 mL for Pb while 750 mL for Fe, Cr and Zn. The preconcentration factor is calculated by the ratio of the highest sample volume for each analytes to lowest volume. The preconcentration factors were found to be 50 for Pb, 150 for Fe, Cr and Zn when the final volumes were 5.0 mL.

**Table 3**

Spiked recoveries of the analyte ions from solid samples ( $n=3$ , samples quantities: 0.01 g of drug, 0.5 g of dried eggplant and baby food, final volume: 5.0 mL).

Element	Added ( $\mu\text{g}$ )	Baby food		Drug		Dried eggplant	
		Found ( $\mu\text{g}$ )	Recovery (%)	Found ( $\mu\text{g}$ )	Recovery (%)	Found ( $\mu\text{g}$ )	Recovery (%)
Fe	0	$23.6 \pm 1.2$	–	$98.7 \pm 6.1$	–	$75.0 \pm 3.1$	–
	10	$33.0 \pm 1.8$	94	$108.4 \pm 5.1$	97	$84.8 \pm 4.1$	98
	20	$42.6 \pm 2.7$	95	$117.2 \pm 5.7$	93	$95.1 \pm 3.2$	101
Zn	0	$20.5 \pm 1.1$	–	$5.1 \pm 0.3$	–	$7.3 \pm 0.2$	–
	10	$30.7 \pm 1.2$	102	$15.2 \pm 0.7$	101	$16.9 \pm 0.8$	96
	20	$40.1 \pm 2.0$	98	$24.8 \pm 1.3$	99	$27.1 \pm 1.4$	99
Pb	0	ND	–	ND	–	ND	–
	5	$4.7 \pm 0.3$	94	$5.1 \pm 0.3$	102	$5.2 \pm 0.3$	104
	10	$10.1 \pm 0.7$	101	$10.3 \pm 0.3$	103	$10.2 \pm 0.4$	102

**Table 4**

Application of the present method to the standard reference materials ( $n=3$ ).

Element	CRM-TMDW-500 <sup>a</sup> Drinking Water		IAEA-336 <sup>b</sup> Lichen Standard	
	Certified value ( $\mu\text{g L}^{-1}$ )	Found value ( $\mu\text{g L}^{-1}$ )	Certified value ( $\mu\text{g g}^{-1}$ )	Found value ( $\mu\text{g g}^{-1}$ )
Fe	$100.0 \pm 0.5$	$94.8 \pm 4.4$	$430.0 \pm 51.6$	$428.2 \pm 27.2$
Pb	$40.0 \pm 0.2$	$38.5 \pm 1.9$	4.9 <sup>c</sup>	$4.60 \pm 0.31$
Zn	$70.0 \pm 0.4$	$68.4 \pm 3.3$	$30.4 \pm 3.3$	$29.6 \pm 1.7$

<sup>a</sup> Sample volume of drinking water standard was 25 mL and final volume was 5.0 mL.

<sup>b</sup> Quantity of Lichen Standard was 0.25 g and after being digested the standard sample, the presented coprecipitation method was applied. Final volume was 5.0 mL.

<sup>c</sup> Not any certified value reported.

**Table 5**

Analyte levels in real solid/liquid samples after being applied the presented coprecipitation procedure ( $n=3$ , sample volumes: 750 mL for analysis of Cr, Zn and Fe, and 250 mL for analysis of Pb. Sample quantity: 0.50 g of baby food and dried eggplant, 0.01 g of drug sample, final volumes: 5.0 mL).

Element	Liquid samples		Solid samples		
	Sea water ( $\mu\text{g L}^{-1}$ )	Stream water ( $\mu\text{g L}^{-1}$ )	Baby food ( $\mu\text{g g}^{-1}$ )	Dried eggplant ( $\mu\text{g g}^{-1}$ )	Drug ( $\mu\text{g g}^{-1}$ )
Fe	$18.9 \pm 0.6$	$666.7 \pm 39.2$	$47.2 \pm 2.4$	$150.0 \pm 6.2$	$9870 \pm 610$
Pb	$5.4 \pm 0.4$	$7.2 \pm 0.2$	ND	ND	ND
Zn	$20.7 \pm 0.7$	$44.0 \pm 2.7$	$41.0 \pm 2.2$	$14.6 \pm 0.4$	$510 \pm 30$
Cr	$2.8 \pm 0.1$	$3.9 \pm 0.2$	–	–	–

### 3.5. Effect of the matrix ions

One of the main problems in the atomic absorption spectrometric determination of the heavy metal ions is interference from matrix [39–45]. Therefore the effect of concomitant ions on the coprecipitation efficiency of the analyte ions was examined. For this, various amounts of interfering ions were added to a solution containing 25  $\mu\text{g}$  of Fe and Cr, 10  $\mu\text{g}$  of Zn, 50  $\mu\text{g}$  of Pb ions and the present procedure was followed. The results show that the presences of interfering anions and cations have no obvious influence on the coprecipitation of the studied metal ions under optimum conditions (Table 1). Also some of the transition metal ions at  $\text{mg L}^{-1}$  levels did not interfered on the recoveries of the analyte ions. The proposed separation/preconcentration method could be applied to the samples containing high salts and some transition metal ions at tolerable levels given in Table 1.

### 3.6. Analytical performance of CEFC method

The analytical performance of the proposed procedure was evaluated by the resulted recoveries of analytes, determined by FAAS. The precision of the method was evaluated as the relative standard deviations obtained after replicated analyzing samples. In presented coprecipitation method, relative standard deviation (R.S.D.) was obtained after analyzing a series of 10 replicates with the preconcentration step. From the results, R.S.D. was between 3 and 7% for four metal ions.

The detection limit, defined as the concentration equivalent to three times the standard deviation of 10 replicate measurements of

blank samples, for Cr, Zn, Pb and Fe were found to be 0.5, 0.3, 2.0 and 0.7  $\mu\text{g L}^{-1}$ , respectively for 50 mL of sample volume concentrated finally to 5.0 mL.

### 3.7. Method validation

In order to evaluate the accuracy of the present CEFC method, different amounts of the investigated metal ions were spiked with 50 mL of sea water, stream water, 0.50 g of baby food and dried eggplant while 0.01 g of drug samples. The coprecipitation procedure given above was applied to the samples. Final volume of the solutions was 5.0 mL. The results were given in Tables 2 and 3. A good agreement was obtained between the added and measured analyte amounts. The results show that the presented separation/coprecipitation method can be applied for the separation and preconcentration of the analyte ions in real samples.

The standard reference materials (CRM-TMDW-500 Drinking Water and IAEA-336 Lichen Standard) were also used for the method validation. Good agreement was obtained between analytical values and certified values (Table 4).

### 3.8. Application to real samples

After being verified the accuracy of the present CEFC method, the coprecipitation procedure was applied to the real solid and liquid samples; baby food, dried eggplant and drug samples as solid samples, stream water from Buyukdere-Rize and seawater from Black Sea-Trabzon as liquid samples. After applying the present preconcentration procedure to the samples, the results were tabulated in Table 5.

## 4. Conclusions

The present CEFC method using POHBAT as a coprecipitating agent offers a useful separation/preconcentration technique for environmental samples. In this study we used an organic coprecipitant. This agent provides effective and quantitative collection of trace metal ions on itself without adding any carrier metal for the formation of insoluble complexes or salts which may cause contamination and interference risk for analytes. The procedure has been successfully applied to the real samples for the determination of Fe, Cr, Zn and Pb levels with acceptable accuracy and precision. The coprecipitated analyte ions can be sensitively determined by atomic absorption spectrometry without any influence of coprecipitant agent. The method is very simple and fast.

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