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Determination of some trace metal ions in various samples by FAAS after separation/preconcentration by copper(II)-BPHA coprecipitation method

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Abstract A separation/preconcentration procedure based on the coprecipitation of Pb(II), Fe(III), Co(II), Cr(III) and Zn (II) ions with copper(II)-N-benzoyl-N-phenyl-hydroxylamine complex (Cu-BPHA) has been developed. The analytical variables including pH, amount of BPHA, amount of copper (II) as carrier element, and sample volume were investigated for the quantitative recoveries of the elements. No interfering effects were observed from the concomitant ions when present in real samples. The recoveries of the analyte ions were in the range of 95–100%. The detection limits (3 s) for Pb(II), Co(II), Fe(III), Cr(III) and Zn(II) ions were found to be 2.3, 0.7, 0.7, 0.3 and 0.4 $\mu g\ L^{-1}$, respectively. The validation of the procedure was performed by the analysis of CRM (SRM NIST-1547 peach leaves and LGC6019 river water) standard reference materials. The method was applied to the determination of the analytes in real samples including natural waters, hair, urine, soil, sediment and peritoneal fluids samples etc., and good results were obtained (relative standard deviations <4%, recoveries >95%).

Keywords Coprecipitation · BPHA · Preconcentration · FAAS · Trace elements

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Introduction

Heavy metal species in the biotic environment pose not only severe carcinogenic and non-carcinogenic risks to humans, but also potential ecological risks [1]. Therefore, it is important to determine trace elements in environmental samples from the viewpoint of environmental management and/or protection from hazardous infection as well as comprehension of the distribution of trace elements in the environment [2].

Preconcentration of traces of heavy metals is often required prior to the instrumental determination to lower the detection limits and to improve the precision and accuracy of analytical results [3]. Efficient and selective separation of metal ions is gaining more importance because of the increasing demand for high purity products and also for environmental concerns. There are various separation methods such as precipitation, solvent extraction [4], cloud point extraction [5], membrane filtration [6], solid phase extraction [7], ion-exchange [8], solvent sublation [9], electrodeposition [10] are widely used to solve these problems.

The coprecipitation method is useful for the preconcentration of trace metal ions [11] and is one of the most useful ways for the preconcentration/separation of trace elements from sample matrix, and the variety of coprecipitants have been studied [12–14]. This preconcentration purpose is characterised by the formation of insoluble compounds. The coprecipitation is adopted when direct precipitation can not separate the desired metallic species due to its low concentration in sample solution. The coprecipitation phenomenon can be associated with metal adsorption on the precipitate surface or due to metal incorporation onto the precipitate structures. Inorganic or organic substances can be considered as coprecipitation agents. The organic agents usually chosen are those able to originate neutral chelates with metallic

species [15]. The carrier element is precipitated to coprecipitate trace elements in sample solutions. The precipitate is separated by using a decantation, short-time centrifugation, and so on; in this process, a part of the precipitate might be lost together along with a portion of the coprecipitated trace elements [2]. The coprecipitation method has an advantage that many elements other than alkali and alkaline earth elements are preconcentrated quite effectively under the same experimental conditions [16]. Concentration factors by coprecipitation using organic complex agents and a carrier ion reach 5,000–30,000 [17].

Many metal ions from water samples have been preconcentrated by coprecipitation with hydroxides of iron (III) [18], indium(III) [19–21], scandium(III) [11], gallium (III) [16], terbium(III) [22] and zirconium [23]. As a carrier element, metals like copper and zinc are popular, because of their limited negative effects for environment. Organic coprecipitants, generally dithiocarbamates of bismuth [24], nickel [25] and copper[26], cobalt [27] have been widely used as efficient collectors of trace elements.

N-Benzoyl-N-phenyl-hydroxylamine (BPHA), a cupferron analogous, is used extensively as an organic precipitant and solvent extractant since it reacts with several metals to form stable chelates that are soluble in organic solvents [28]. It is well known for its excellent thermal stability and can keep unchanged even in strong acid [29, 30]. BPHA and its analogs have been successfully employed as a spectrophotometric, gravimetric, and extracting reagents [31].

In the presented work, simple and rapid coprecipitation procedure by using Cu(II)-BPHA precipitate was used as a new coprecipitation technique in order to preconcentrate Pb (II), Fe(III), Co(II), Cr(III) and Zn(II) ions in environmental samples prior to their flame atomic absorption spectrometric (FAAS) determinations. According to our literature knowledge, there is no study on the coprecipitation of trace elements by using copper(II)-BPHA system. We have investigated a new coprecipitation procedure for trace elements for FAAS determination and found that copper (II)-BPHA system has a good collecting ability for this purpose. Also, Cu(II)-BPHA is a convenient coprecipitant to handle, because it can be dissolved in about 500 µL of conc. nitric acid without heating, which is required for the dissolution of the precipitate.

Experimental

Instrument

A Perkin-Elmer AAnalyst 800 Model atomic absorption spectrometer with deuterium background corrector was used for the determination. All measurements were carried out in an air/aceylene flame. The operating parameters for working elements were set as recommended by the manufacturer as given in Table S1 (Supplementary Material). A pH meter Consort C533 model with glass-electrode was employed for measuring pH values in the aqueous phase. An ALC PK 120 model centrifuge was used to centrifuge of solutions. For the digestion of hair samples, a Cem Mars XP-1500 model microwave oven was used.

Reagents and solutions

All the reagents used were of analytical reagent grade. Double distilled deionized water was used throughout the experiments. Laboratory glassware was kept overnight in a dilute HNO_3 solution (1:1) and then rinsed with deionized water. The BPHA solution (0.5%, w/v) was prepared daily in ethanol.

Standard stock solutions of the analytes, 1,000 mg L^{-1}, were prepared by dissolving appropriate amounts of their nitrate salts in 2% (w/v) nitric acid. Working standard solutions were prepared fresh daily by stepwise dilution of the stock solutions with double distilled deionized water. The calibration curve was established using the standard solutions prepared in 1 mol L^{-1} HNO_3 by dilution of the stock solutions.

Phosphate buffer solutions were prepared by mixing of appropriate volumes of 1 mol L^{-1} H_3PO_4 and NaH_2PO_4 solutions for pH 2.0 and 3.0, and of 1 mol L^{-1} NaH_2PO_4 and Na_2HPO_4 solutions for pH values of 5.0, 6.0 and 7.0. Acetate buffer solutions were prepared by mixing appropriate volumes of 1 mol L^{-1} CH_3COOH and CH_3COONa solutions for pH 4.0. Ammonium buffer solutions were prepared by mixing of appropriate amounts of 3 mol L^{-1} NH_3 and 3 mol L^{-1} HCl solutions for pH values of 8.0, 9.0 and 10.0.

Analytical procedure

The copper-BPHA coprecipitation method was tested with model solutions prior to its application to real samples. Twenty five millilitres portion of an aqueous solution containing 20 µg of Cr(III), Fe(III) and Pb(II), 10 µg of Co(II) and 2 µg of Zn(II) was placed in a centrifuge tube. The pH of solution was adjusted to 9.0 with ammonia/ ammonium chloride buffer solution. Then 250 µL of 1,000 mg L^{-1} copper(II) as a carrier element was added to this solution. The 0.5 mL of 0.5% (w/v) BPHA solution was poured into the tube. After the formation of the precipitate, the solution was centrifuged at 3,500 rpm for 10 min. The supernatant was removed. The precipitate remained adhering to the tube was dissolved with 500 µL of concentrated HNO_3. Then the final volume was completed to 10 mL with double distilled deionized water. The analytes in the final solution were determined by FAAS.

Analyses of standard reference materials

A 100-mg amount of the standard reference material (NIST-1547 peach leaves) sample was dissolved with the mixture of 4 mL of concentrated HNO_3 and 2 mL of concentrated H_2O_2 on a hot plate. After completing the dissolution process, all the sample solutions were clear. The volume of the samples was diluted to approximately 25 mL using distilled deionized water. These sample solutions were analysed by using the proposed preconcentration procedure described above. The final measurement volume of the sample solutions was 5 mL.

The second certified reference material was the LGC6019 River water sample. The pH's of the samples were adjusted to 9.0 with ammonia/ammonium chloride buffer solution. Then the separation/preconcentration procedure given above was applied to these sample solutions. The concentration of the investigated analyte ions in the final solution was determined by FAAS.

Analysis of peritoneal dialysis fluids

The coprecipitation method was employed for the separation/preconcentration of trace elements in peritoneal dialysis fluid from a hospital at Erciyes University. The electrolyte composition of the peritoneal fluid concentrate (Dianeal 137, Baxter) used in this study was as follows: NaCl 15.7 g L^{-1}, sodium lactate 3.9 g L^{-1}, $CaCl_2.2H_2O$ 257 mg L^{-1}, $MgCl_2.6H_2O$ 152 mg L^{-1}, and glucose without water: 13.9 g L^{-1}.

The analysis of peritoneal dialysis concentrate was carried out after dilution 1:4 with the distilled deionized water. First, it was neutralised and then buffered to pH 9.0 with ammonia/ammonium chloride buffer solution. This sample solution was analysed by using the proposed procedure described above.

Water samples

The presented method was applied to the different natural water samples for the preconcentration/separation of the analyte ions. The water samples were collected from different regions of Turkey. The water samples were stored in polyethylene bottles (pre-washed before with detergent, doubly distilled deionized water, dilute HNO_3 and doubly distilled deionized water, respectively) and acidified to pH about 2.0 with 5 mL of concentrated nitric acid per liter of the sample and were subsequently stored at 4 °C in a refrigerator. The water samples were filtered through a cellulose membrane filter with a pore size of 0.45 μm. Prior to trace metal analysis, the acidified water samples were neutralised, and then the proposed procedure was applied to the samples. The initial volume of the water samples was

750 mL, and the final volume was 5 mL. The levels of the investigated analyte ions in the final solutions were determined by FAAS.

Application to real samples

A 1.0-g aliquots of each of soil and sediment samples were digested with 15 mL of aqua regia and then heated until obtaining a clear solution. After the mixture was evaporated almost to dryness, 10 mL of aqua regia was again added to the residue. Then the mixture was again evaporated to dryness. After the evaporation, 5 mL of double distilled deionized water was added to the residue and then dissolved. The resulting solution was filtered through a cellulose filter paper. The residue on the filter paper was washed with 1–2 mL of 1 mol L^{-1} HNO_3. The filtrate was diluted to 25 mL of double distilled deionized water. Then the proposed procedure given above was applied to this sample solution. A blank digest was carried out in the same way.

For the microwave digestion of hair samples, to a 0.25-g aliquot of hair sample in a digestion vessel 10 mL of concentrated HNO_3 was added. The working conditions of the microwave digestion system were as follows; ramp time: 20 min, pressure: 150 psi, temperature: 210 °C, hold time: 10 min, power: 1,200 W (100%), cool down time: 15 min. After the digestion completed, the proposed preconcentration procedure was applied to the hair sample solution.

Urine samples were digested as follows: An aliquot of 10 mL of urine sample was treated with a mixture of 5 mL of concentrated H_2O_2 and 2.5 mL of concentrated HNO_3 on a hot plate at 80 °C. The system was moderately heated up to the disappearance of the amber color. Then, the sample was evaporated almost to dryness. Thereafter, fresh portions of 2.5 mL of concentrated HNO_3 were added to the dark residue and again heated to dryness [32]. Then the proposed procedure was applied to the resulting sample solutions. A blank digest was carried out in the same way.

Results and discussion

The optimised conditions for the preconcentration/separation procedure were established using 25 mL of deionised water containing 2–20 μg of each element and submitting these solutions to the preconcentration procedure.

Effects of pH on the coprecipitation

For the quantitative coprecipitation efficiency of the analyte ions, the working pH of the media is one of the best important factors. The influences of pH on the recoveries of the analytes for the copper-BPHA precipitate system were studied in the pH range of 2.0–10.0 by using model

solutions containing the analyte ions. The pH values were adjusted by using the related buffer solutions given before. The results are shown in Fig. 1. The recoveries of all the analyte ions were not quantitative, except for iron(III), at acidic pH values. Therefore, the pH 9.0 was selected as working pH for the subsequent studies, and at this pH the ammonia/ammonium chloride buffer system shows a good buffering capacity. Quantitative recovery values (>95%) were obtained at pH 9.0 for the working metals ions.

Effect of the amount of BPHA

The effects of amount of BPHA reagent on the recoveries (%) of the analyte ions were investigated. The results are given in Fig. 2. When the experiments were performed without BPHA at pH 9.0, the recovery values were not quantitative for the studying metal ions. The recoveries of the analyte ions increased with the increasing amounts of BPHA. These results show that for the quantitative recoveries of the studied metal ions, BPHA is necessary. For all the subsequent works 500 µL of 0.5% (w/v) BPHA solution was used.

Amount of copper as carrier element

The influences of amount of copper(II) as carrier element on the recoveries of the analyte ions were also investigated. Without copper, the recoveries for the analyte ions were below 60%. Quantitative recovery values (>95%) for the analyte ions were obtained for 0.25 mg of copper(II). All the further works were performed with 250 µL of 1,000 mg L^{-1} of copper(II) solution. The results are given in Fig. 3.

Effect of standing time

Firstly, the effects of the rate of centrifugation were examined in the range of 1,500–3,500 rpm under the optimal experimental conditions with model solutions. All
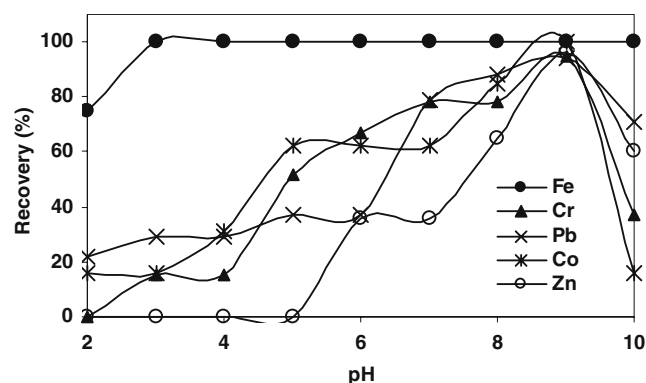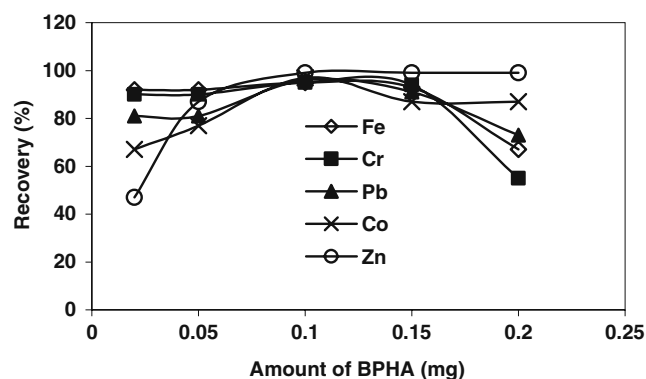

Fig. 2 Effect of the amount of BPHA ($N=3$)

the analytes were recovered quantitatively at the centrifugation rate of 3,500 rpm. The influences of the standing time on the recoveries of the analyte ions were investigated in the range of 5–40 min at 3,500 rpm. Quantitative recoveries (>95%) were obtained for all the analytes for 10 min of standing time and for the centrifugation rate of 3,500 rpm.

Dissolution of the precipitate

For the dissolution of the copper(II)-BPHA precipitate, several common concentrated mineral acids were examined, i.e., HNO_3 and HCl. As a result, it was found that the copper(II)-BPHA precipitate has been easily dissolved in 500 µL of concentrated nitric acid. Then the resulting clear solution was diluted to 5 mL with distilled water.

Effect of sample volume

The influences of the sample volume on the coprecipitation efficiencies of the analytes were examined. The analyte ions were quantitatively recovered for the sample
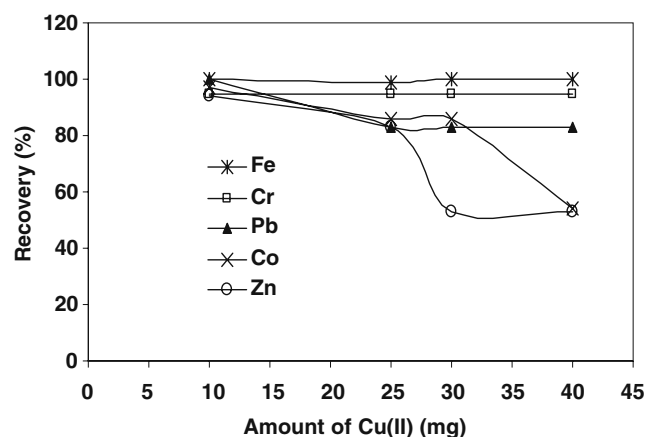

Fig. 1 Influences of pH on the recoveries of the analyte ions ($N=3$)

Fig. 3 Influences of amount of copper(II) on the coprecipitation efficiency of the analyte ions ($N=3$)

Table 1 Recovery tests for Pb (II), Co(II), Fe(III), Cr(III) and Zn(II) ions in different samples, (N=3)

Element	Added (µg)	Sea water		Hair	
		Found (µg)	Recovery (%)	Found (µg)	Recovery (%)
Pb	–	2.30±0.07[a]	–	2.0±0.2	–
	5	7.21±0.09	98	6.8±0.4	96
	10	12.4±0.9	101	11.7±0.6	97
Co	–	0.90±0.02	–	–[b]	
	5	5.82±0.09	98	4.9±0.6	98
	10	11.0±0.1	101	9.9±0.9	99
Fe	–	4.7±1.1	–	–	
	5	9.5±0.9	96	4.8±0.2	96
	10	15.0±1.1	103	9.7±0.6	97
Cr	–	0.53±0.06	–	0.72±0.04	–
	5	5.3±0.8	96	5.5±0.1	96
	10	10.3±0.9	98	10.3±0.9	96
Zn	–	36.5±3.1	–	128±4	–
	25	62.6±2.8	104	153±4	101
	50	86.2±3.9	99	180±5	104

[a] Confidence limits at 95% confidence level (mean ± t·s /√N)

[b] Below the detection limit

volumes in the range of 25–750 mL. The copper-BPHA precipitate including the analyte ions was successfully dissolved in 500 µL of concentrated nitric acid. The final volume was completed to 5 mL with double distilled deionized water. The recoveries (%) were quantitative for all the metal ions. The preconcentration factor is calculated as the ratio of the highest sample volume (750 mL) to the final measurement volume (5 mL). So, the preconcentration factor was 150. The results are given in Fig. S1 (Supplementary Material).

Matrix effects

As pointed out in "Introduction" section, one of the main problems in atomic absorption spectrometric determination of metals is matrix interferences originated from the sample. For this purpose, the influences of the some ions and substances were investigated. The results are given in Table S2 (Supplementary Material). The tolerance limit of foreign ions and/or materials was taken as the value which caused an error of not more than ±5% in the absorbance

measurements. Therefore, all of the investigated foreign ions and/or subtances have no serious interfering effect on the recommended coprecipitation procedure. The recoveries were generally satisfactory and changed from 91 to 103%.

Analytical performance

The limit of detection (LOD) of the proposed method for the determination of investigated elements were studied under the optimum experimental conditions by applying the procedure for blank solutions. The detection limits was established by analyzing 20 blank solutions (3 s). The detection limits of Pb(II), Co(II), Fe(III), Cr(III) and Zn(II) were found to be 2.3, 0.7, 0.7, 0.3 and 0.4 µg L^{-1}, respectively. The relative standard deviations of the proposed method for the analyte ions were <4%. A common misconception is that the LOD is the smallest concentration that can be measured. Instead, quantitation is generally agreed to begin at a concentration equal to 10 standard deviations of the blank. This is called the limit of quantitation (LOQ) or limit of determination. Therefore,

Table 2 Results of analysis of the standard reference materials using the presented procedure (N=3)

Element	LGC6019 river water (µgL^{-1})		NIST-1547 peach leaves (µgg^{-1})	
	Certified value	Found	Certified value	Found
Pb	5.2±0.3	5.1±0.3[b]	0.87±0.03	0.85±0.08
Co	–[a]	–	–	–
Fe	287±7	285±3	218±14	220±3
Cr	0.78±0.2	0.81±0.1	–	–
Zn	59.7±2.5	58.3±2.0	17.9±0.4	18.8±1.2

[a] Below the detection limit

[b] Confidence limits at 95% confidence level (mean ± t·s /√N)

Table 3 The application of the presented method to the real samples (N=4)

Sample	Pb	Co	Fe	Cr	Zn
Concentration ($\mu g \ L^{-1}$)					
Urine	2.5 ± 0.7^a	$-^b$	–	3.0 ± 0.3	–
Peritoneal fluid	–	–	–	–	–
Concentration ($\mu g \ g^{-1}$)					
Hair samples	2.0 ± 0.2	–	–	0.70 ± 0.04	128 ± 4
Soil	12.1 ± 0.9	15.2 ± 1.1	515 ± 3	15.7 ± 1.7	9.4 ± 2.5
Sediment	7.1 ± 0.6	3.5 ± 0.8	834 ± 4	20.4 ± 2.3	211 ± 3

[a] Confidence limits at 95% confidence level (mean $\pm$ t·s /$\sqrt{N}$)

[b] Below the detection limit

LOQ is equal to about 3.3 LOD [33]. So, LOQ values for Pb(II), Co(II), Fe(III), Cr(III) and Zn(II) ions were found to be 7.7, 2.3, 2.3, 1.0 and 1.3 $\mu g \ L^{-1}$, respectively.

Accuracy of the method

In order to estimate the accuracy of the procedure, different amounts of the studied metal ions were added to sea water and soil samples. The resulting solutions were submitted to the proposed preconcentration/separation procedure. The obtained results are shown in Table 1. A good agreement was obtained between the added and the measured analyte amounts. The recovery values calculated for the added analytes were always higher than 95%, thus confirming the accuracy of the procedure and its independence from the matrix effects. These results confirm the validity of the proposed method.

The method presented here was also checked with the two certified reference materials, LGC6019 river water and NIST-1547 peach leaves, for the determination of Co(II), Pb(II), Fe(III), Cr(III) and Zn(II) ions. The acquired results are given in Table 2. The results were in good agreement with the certified values of the certified reference materials.

Application to real samples

The procedure presented here was applied to various real samples including hair, peritoneal fluids, urine, soil,

sediment and water samples. The results are given in Table 3. Also, the results obtained from the application of the proposed method to the different natural water samples can be seen in Table 4.

Comparison with other coprecipitation methods

Comparative data from some recent papers based on the coprecipitation procedures were summarised in Table S3 (Supplementary Material). The method presented in this study is most promising for the trace elements with a preconcentration factor of 150. The preconcentration factor achieved with presented procedure is superior with respect to the coprecipitation methods given in the literature. The precipitate could be easily dissolved with 500 μL HNO_3. The detection limits for the trace elements were generally lower than those of the methods given in Table S3. Also, the method is relatively rapid as compared with previously reported procedures for the enrichment of traces metal ions.

Conclusion

Coprecipitation with Cu(II)-BPHA system offers a useful multielement preconcentration technique for the environmental samples. The procedure has been successfully applied to the analyte ions with acceptable accuracy and

Table 4 The application of the presented method to the water samples for the determination of the analyte ions ($\mu g \ L^{-1}$, N=4)

Samples	Pb	Co	Fe	Cr	Zn
Tap water	$-^a$	–	2.61 ± 0.02^b	0.62 ± 0.01	9.0 ± 1.3
Sea water	2.5 ± 0.8	0.90 ± 0.03	4.7 ± 1.1	0.51 ± 0.06	36.5 ± 3.8
Wastewater	2.8 ± 0.5	1.3 ± 0.9	42.1 ± 3.2	84.5 ± 3.8	3.4 ± 1.1
Rain water	–	0.90 ± 0.06	10.6 ± 1.8	0.62 ± 0.01	7.5 ± 1.2
Snow	2.4 ± 0.9	–	0.90 ± 0.01	1.02 ± 0.03	2.5 ± 0.1
Lakewater I	2.9 ± 0.1	1.2 ± 0.05	7.6 ± 0.9	0.63 ± 0.01	11.5 ± 1.8
Dam water	–	0.9 ± 0.01	2.80 ± 0.08	0.70 ± 0.01	7.5 ± 1.3
Lakewater II	–	0.9 ± 0.01	3.54 ± 1.2	0.73 ± 0.01	5.0 ± 1.3
Crater water	–	1.30 ± 0.05	5.2 ± 1.3	0.82 ± 0.04	5.0 ± 1.4

[a] Below the detection limit

[b] Confidence limits at 95% confidence level (mean $\pm$ t·s /$\sqrt{N}$)

precision. The time required for the coprecipitation and determination was about 20 min. The coprecipitated analyte ions can be sensitively determined by FAAS without any influence of copper and BPHA.

The coprecipitation method is rapid and has good reproducibility. The usefulness of the method is shown by the control analyses of the standard reference materials. The procedure offers a useful multielement enrichment technique in various samples including water analysis, hair, urine etc. with acceptable accuracy and precision. The detection limits of the analytes are superior compared to those of the preconcentration techniques given in the literature [22, 34].

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