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## A facile and sensitive coprecipitation method coupled with flame atomic absorption spectrometry for quantification of Cu(II) ions in complex matrices

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**Abstract:** In the present investigation, the application of an organic coprecipitant, 2-[5,6-dichloro-2-(2-bromobenzyl)-1H-benzimidazole-1-yl]acetohydrazide (DIBBA), for separation and preconcentration of Cu(II) ions in fruit and water samples through a new carrier element free coprecipitation (CEFC) method was researched for the first time. Flame atomic absorption spectrometer (FAAS) was used for the analyses of Cu(II) ions. The main effective experimental factors such as solution pH, DIBBA quantity, waiting time, centrifuge speed and duration and volume of sample on the recovery efficiency of Cu(II) ions were explored in detail. Under the optimized conditions the preconcentration factor (*PF*), relative standard deviation (*RSD*), and limits of detection (*LOD*) was achieved as 50, 3.4 % and 0.44  $\mu\text{g L}^{-1}$ , respectively. No interference effects were detected by virtue of the presence of various foreign ions. Satisfactory recoveries (in the range of 94.4 to 103.0 %) in the environmental sample matrix were acquired. After being validated the recommended selective, low cost, simple and rapid CEFC method by spike/recovery tests, it was properly implemented for the low levels detection of Cu(II) ions in sour cherry, mulberry, apple, and peach as fruit samples and stream and sea water samples without any significant matrix effects.

**Keywords:** copper; fruit analyse; heavy metal; preconcentration; separation; water analyses.

### INTRODUCTION

Heavy metal pollution owing to both anthropogenic activities and natural sources is one of the most substantial issues to be considered due to their num-

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erous adverse effects on all living organisms and ecosystem.<sup>1</sup> Heavy metals, which are not degradable in nature and are permanent inorganic pollutants, mostly reach the human body with food and water.<sup>2</sup> As a result of scientific researches, behavioural disorders due to mental and neurological effects, irregularities in neurotransmitter production and their functions have been observed in people exposed to heavy metals.<sup>3</sup> In addition, serious disorders such as disabilities and failure of some organs to function have emerged, depending on the type and concentration of heavy metals exposed. Although a number of heavy metals such as Zn, Se, Mn and Cu are indispensable at certain levels for the human body to maintain their metabolism, they provoke toxic effects if taken at high concentrations.<sup>4</sup> Long-term exposure to copper causes nose, mouth and eye irritation, stomach aches and headaches, diarrhoea and vomiting. High intake of copper can also trigger liver damage and even induce death.<sup>5,6</sup> The maximum admissible Cu(II) ions levels specified by the World Health Organization (WHO) in drinking water is 2.0 mg L<sup>-1</sup>.<sup>7</sup> In this respect, the development of accurate, precise, and selective methods to determine trace amounts of metal ions in environmental samples is a quite popular research area.<sup>8</sup>

Trace heavy metals can be determined using multitudinous analysis methods including flame atomic absorption spectrometry (FAAS)<sup>9</sup>, inductively coupled plasma atomic emission spectrometry (ICP-AES),<sup>10</sup> UV-Vis spectrometry<sup>11</sup> and X-ray fluorescence spectrometry (XRFS).<sup>12</sup> FAAS is among the most prevalently applied methods in recent years in terms of its practicality, cheapness and short analysis time. Two types of critical problems are generally encountered during the quantitation of trace metals in environmental samples by aforementioned methods. One of these problems is the interference effect of the complicated matrix and the other is that the lower levels of trace element than the detection limit of the utilized instrument.<sup>13</sup> In order to eliminate these drawbacks, it is indispensable to implement a traditional separation and preconcentration method such as solid phase extraction,<sup>14</sup> cloud point extraction,<sup>15</sup> liquid-liquid extraction<sup>16</sup> and coprecipitation<sup>8</sup> before the analyses step. Among these, coprecipitation is a powerful alternative due to its low cost, simplicity and rapidity, less usage of chemical reagents and obtaining high preconcentration factors in the method.<sup>2</sup>

The coprecipitation technique is based on the accumulation of metal ions on water-insoluble precipitates of various organic or inorganic characters.<sup>17</sup> In general, in the coprecipitation method two types of reagents are used: *i*) inorganic coprecipitants such as hydroxides and sulphides;<sup>18-23</sup> *ii*) organic coprecipitants such as some chelates or chelating ligands.<sup>1,9</sup> However, in both cases, the carrier element, which is added to the medium in excessive amounts for precipitate formation, may have interference effects during the analysis step. In CEFC method, which has been introduced to the literature as a new method in recent years, an organic compound soluble in an organic solvent but insoluble in water

is used as a coprecipitating agent, while a carrier element is not required for precipitate formation.<sup>8,24,25</sup> Hereby, the pollution risk induced by the carrier element is eliminated. Besides, the method is environmentally friendly as it requires the use of less chemical reagents.

The purpose of the presented research is to develop a new CEFC method by applying an organic coprecipitant, 2-[5,6-dichloro-2-(2-bromobenzyl)-1*H*-benzimidazole-1-yl]acetohydrazide (DIBBA), which was employed for the first time for the selective determination of Cu(II) ions in fruit (sour cherry, mulberry, apple and peach) and water (stream and sea water) samples. Actually, in the first stage of the study, the usability of DIBBA was investigated in the separation and preconcentration of different heavy metals such as Ni(II), Mn(II), Cd(II), Pb(II) and Cr(III) ions from environmental samples by coprecipitation method, apart from Cu(II) ions. However, quantitative recovery values were obtained only for Cu(II) ions. Therefore the experimental conditions affecting the Cu(II) ions recovery efficiency including sample pH, DIBBA amount, waiting time, centrifuge speed and duration and sample volume were evaluated and optimized. The method validation was performed via spike tests and then the applicability of the method was evaluated by the analysis of Cu(II) ions in the fruit and water samples.

## EXPERIMENTAL

### *Chemicals and instruments*

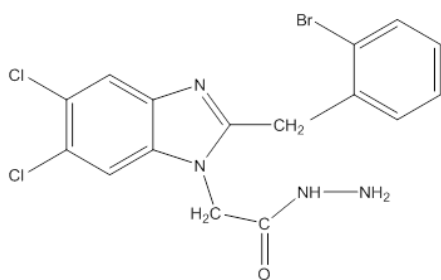
Perkin Elmer AAnalyst 400 model flame atomic absorption spectrophotometer (FAAS) equipped with hollow cathode lamp was employed to determine Cu(II) levels in the solutions. Ground interference was eliminated with deuterium lamp. Analyses were performed at the primary wavelength (324.8 nm) of the copper element. In addition, the following instruments were employed during the experiments; Nuve NF 200 model centrifuge for separating the precipitates from the solution, Hanna pH-211 digital pH meter with glass electrode for adjusting the pH of the solutions, and Milestone Ethos D closed vessel microwave solubilisation system with a maximum pressure and temperature of 10 MPa and 300 °C, respectively for digestion of fruit samples.

All of the reagents including HNO<sub>3</sub>, NaOH, ethyl alcohol, dimethyl sulfoxide (DMSO), NaCl, NH<sub>4</sub>NO<sub>3</sub>, KCl, H(AuCl<sub>4</sub>), CaCl<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, Mn(NO<sub>3</sub>)<sub>2</sub>, NaNO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub> and Cr(NO<sub>3</sub>)<sub>3</sub> used at different stages of the experimental studies were of analytical reagent grade and were purchased from Fluka (Buchs, Switzerland) or Merck (Darmstadt, Germany). The stock solution of copper at a concentration of 1000 mg L<sup>-1</sup>, prepared in 0.5 vol. % HNO<sub>3</sub>, was diluted daily for the preparation of standard and working solutions. Milli-Q system was utilized to obtain the distilled/deionized water used throughout the experiments. The synthesis of the coprecipitating agent, DIBBA, was performed by the procedure expressed in the literature.<sup>26</sup> The chemical structure of DIBBA was given in Scheme 1. To prepare 100 mL of 0.2 % DIBBA solution, 0.2 g of DIBBA was weighed and dissolved in a mixture of 100 mL of ethyl alcohol and DMSO (1:1) by heating at 80 °C.

### *General procedure of the developed coprecipitation method*

Two mL of DIBBA (0.2 %) were added to 15.0 mL of model solutions containing 5.0 µg of Cu(II) ions in centrifuge tubes. The solutions' pH value was arranged to 8.0 using diluted

HNO<sub>3</sub> or NaOH solutions. For the formation of the precipitate, these solutions were waited for 5 min. At the end of this waiting period, the mixture was centrifuged at 2500 rpm for 3 min and the supernatant was decanted. The precipitate remaining at the bottom of the tube was dissolved by using 1.0 mL of concentrated HNO<sub>3</sub>. The volume was completed to 2.0 mL with distilled water, and then Cu(II) ions levels were determined in the final solution by FAAS.



Scheme 1. Chemical structure of DIBBA.

#### *Preparation of water and fruit samples*

The developed CEFC methodology based on DIBBA was carried out to fruit samples (sour cherry, mulberry, apple, and peach) obtained from a local market in Gümüşhane and water (stream and sea waters) samples collected from Trabzon to determine their Cu(II) ions levels.

After being collected the sea and stream water samples in prewashed polyethylene bottles, they were acidified with 1 % nitric acid solution. Cellulose nitrate membrane was used for the filtration of the water samples. The pH of the filtrated samples was adjusted to 8.0 before applying the method.

The fruit samples were dried at 90 °C in an oven for 24 h and then homogenized by grinding in an agate mortar. Then the homogenized samples were digested by a closed vessel microwave digestion system. For this purpose, the fruit samples weighing 0.75 g were placed in Teflon vessels, separately. 2.0 mL of H<sub>2</sub>O<sub>2</sub> and 6.0 mL of HNO<sub>3</sub> were used as digestion reagents. The microwave digestion program was implemented in four sequential steps at a pressure of 4.56 MPa: 1) 6 min to reach 160 °C (power (*P*) = 250 W); 2) 6 min to hold 180 °C (*P* = 400 W); 3) 6 min to reach 220 °C (*P* = 650 W); 4) 6 min to hold 220 °C (*P* = 250 W). After microwave digestion the volume of each sample was made up to 50 mL with distilled water and the Cu(II) ions were preconcentrated performing the suggested procedure.

## RESULTS AND DISCUSSION

#### *Optimization of the experimental parameters*

The pH of the aqueous media is a critical factor in the quantitative recovery of analyte ions, since it directly affects the competition of metal ions and hydronium or hydroxide ions. In addition, the surface charge of the precipitate formed is enormously dependent on the pH value of the aqueous media. The influences of pH on the recovery of Cu(II) ions applying the CEFC method based on DIBBA was scrutinized in the pH range of 2.0–8.0. In these experiments, 4.0 mg of DIBBA was added to 15 mL of solutions at different pH values containing 5.0 µg of Cu(II) ions and the waiting time, centrifuge speed and duration kept as 5 min, 2500 rpm and 3 min, respectively. At pH 2.0, Cu(II) ions recovery value

was 6.9 % and it increased distinctively as the pH increased, reaching 97.3 % at pH 8.0 (Fig. 1). The surface of the precipitate formed at acidic pH values is positively charged due to the excess hydronium ions in the medium. The electrostatic repulsion between the positively charged precipitate surface and the metal cations prevents the retention of the metal cations on the precipitate surface. Therefore, the recovery values were low at acidic pH. On the contrary, as the pH increases, the surface of the precipitate becomes negatively charged due to the hydroxide ions present in the solution. An electrostatic interaction occurs between the precipitate surface and the metal cations which resulted in the increase of recovery values. Cu(II) ions are collected on the precipitate through surface adsorption, inclusion, and occlusions mechanisms. In precipitation by adsorption mechanism, the electrostatic interaction between the precipitate surface and metal ions becomes important. Consequently, the optimum pH was specified as 8.0 for the analyses of Cu(II) ions quantitatively.

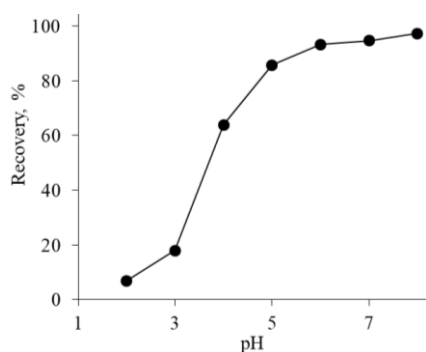


Fig. 1. Effect of pH on the Cu(II) ions recovery.

The impacts of DIBBA quantity on the Cu(II) ions recovery were assessed in the DIBBA amount range of 0.0–6.0 mg (3.0 mL of 0.2 % solution) at the solution pH of 8.0. When the CEFC experiments were carried out without adding any DIBBA to the medium, it is noticed that the recovery value of Cu(II) ions was less than 70 %. The recovery value of Cu(II) ions increased from 82.2 to 97.8 % with the increase of DIBBA amount from 0.5 to 2.0 mg and remained approximately constant with the subsequent increases in DIBBA quantity (Fig. 2). These results demonstrated that DIBBA is indispensable for the determination of Cu(II) ions quantitatively through the proposed CEFC method. The amount of DIBBA was determined as 4.0 mg (2.0 mL of 0.2 % solution) for further studies.

Since the waiting time, centrifuge speed and duration have considerable influence on the quality of the precipitate formed in the aqueous solution, the impacts of these factors on the recovery of Cu(II) ions were evaluated in detail. For this reason, the coprecipitation analyses were carried out at 1–120 min of waiting time, 1000–5000 rpm of centrifuge speed, and 1–10 min of centrifuge duration. For the quantitative recovery of Cu(II) ions with the CEFC method based on

DIBBA, the optimum waiting time, centrifuge speed and duration were determined as 5 min, 2500 rpm and 3 min, respectively.

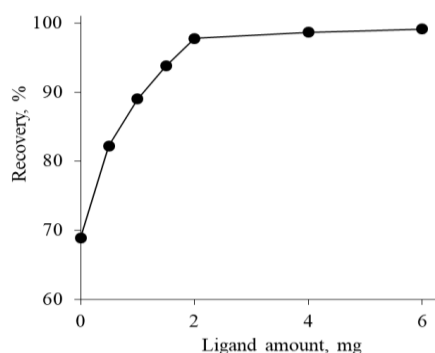


Fig. 2. Influences of DIBBA quantity on the Cu(II) ions recovery.

High preconcentration factors (PF) are required in order to determine the analyte ions present at very low levels in environmental samples with the developed separation and preconcentration methods. The most important factor affecting the PF is the sample volume since the PF is calculated by dividing the optimum sample volume by the final volume. Therefore, the influences of sample volume were assessed at different sample volumes between 100 and 1000 mL. The Cu(II) ions were recovered quantitatively up to 100 mL of sample volume. It is noticed that the recovery values decreased rapidly at volumes higher than 100 mL (Fig. 3). As a result, PF was obtained as 50 when used 100 mL of sample volume and 2 mL of final volume.

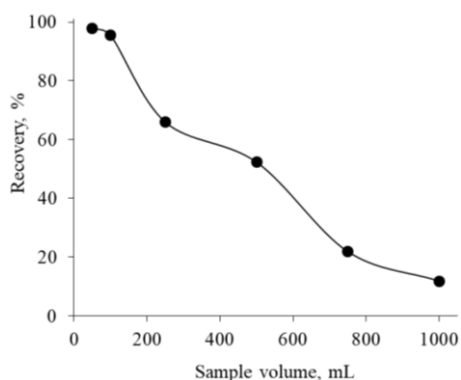


Fig. 3. Sample volume impact on the recovery of Cu(II) ions.

#### *Influences of matrix ions*

Since the proposed process was implemented to analyse the Cu(II) ions in fruit and water samples, the possible disruptive effect of the common coexisting ions on the performance of the process should be investigated. The maximum levels of different anions and cations that can be found together with Cu(II) ions

were chosen and their effects on the recovery efficiency of Cu(II) ions were evaluated. In these tests, certain concentration of coexisting ions were added to the 50 mL of model solution containing 5.0  $\mu\text{g}$  of Cu(II) ions and the developed procedure was carried out. Satisfactory recoveries changing between 92.6 and 100.2 % for Cu(II) ions were obtained (Table I).

TABLE I. Influences of matrix ions on the recovery of Cu(II) ions; \* – nitrate salts were used

Ion	Added as	$c_{\text{Cu(II)}} / \text{mg L}^{-1}$	Recovery, %
Na <sup>+</sup>	NaCl	5000	95.3±3.1
K <sup>+</sup>	KCl	1000	94.7±2.2
Ca <sup>2+</sup>	CaCl <sub>2</sub>	1000	96.3±0.7
Mg <sup>2+</sup>	Mg(NO <sub>3</sub> ) <sub>2</sub>	1000	95.0±2.1
CO <sub>3</sub> <sup>2-</sup>	Na <sub>2</sub> CO <sub>3</sub>	1000	92.6±1.8
NO <sub>3</sub> <sup>-</sup>	NaNO <sub>3</sub>	1000	93.9±2.6
NH <sub>4</sub> <sup>+</sup>	NH <sub>4</sub> NO <sub>3</sub>	1000	94.2±1.5
Au(III), Mn(II), Cr(III), Zn(II)	*	25	97.6±0.7
Mixed <sup>a</sup>	–	–	100.2±1.0

<sup>a</sup>687 mg L<sup>-1</sup> Na<sup>+</sup>, 1040 mg L<sup>-1</sup> Cl<sup>-</sup>, 960 mg L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>, 100 mg L<sup>-1</sup> K<sup>+</sup>, PO<sub>4</sub><sup>3-</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, CO<sub>3</sub><sup>2-</sup>, Mg<sup>2+</sup>, 10 mg L<sup>-1</sup> Au(III), Mn(II), Cr(III), Zn(II)

The effect of Au(III), Mn(II), Cr(III) and Zn(II) concentrations on the recovery of Cu(II) ions was investigated in the concentration range of 5–25 mg L<sup>-1</sup> and it was seen that the recovery of Cu(II) ions was quantitative in all foreign heavy metal ions concentrations studied. Since Au(III), Mn(II), Cr(III) and Zn(II) concentrations will not be higher than 25 mg L<sup>-1</sup> in the environmental samples to which the method will be applied, only the highest concentration levels of them is given in Table I. These results demonstrated that the foreign ions have a minimal interfering impact on the analyses of Cu(II) ions with the suggested method and it can be concluded that the process can be performed successfully for the coprecipitation of Cu(II) ions in complicated matrices.

#### *Analytical figure of merits*

The substantial analytical features of the developed CEFC method based on DIBBA including *RSD*, *LOD* and limit of quantification (*LOQ*) were acquired under the following optimized experimental conditions; pH: 8.0, DIBBA amount: 2.0 mg, waiting time: 5 min, centrifuge speed: 2500 rpm and centrifuge duration: 3 min. The method precision was evaluated with respect to *RSD*, obtained by practicing the method ten times to model solutions containing 5.0  $\mu\text{g}$  of Cu(II) ions under the given experimental conditions above. Accordingly, the *RSD* was calculated as 3.4 %. The *LOD* was calculated by considering three times the standard deviations obtained by the blank analyses ( $n = 10$ ) and for the *LOQ*, ten times the standard deviation achieved from blank analyses ( $n = 10$ ) was taken into account. The *LOD* and *LOQ* were found to be 0.44 and 1.47  $\mu\text{g L}^{-1}$ , respectively. The comparison of the developed method with other Cu(II) coprecipitation

studies in literature from the point of solution pH, *LOD*, *RSD* and *PF* is given in Table II.

TABLE II. Comparison of the present CEFC system with different Cu(II) ions coprecipitation studies in literature

System	<i>PF</i>	<i>LOD</i> / $\mu\text{g L}^{-1}$	<i>RSD</i> / %	pH	Ref.
La-2,2'-bipyridyl-erythrosine	50	10.3	1.85	4.5	17
APSAL <sup>a</sup>	100	0.5	<5	7.0	24
2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline	25	0.80	8	9.0	27
<i>N</i> -cetyl <i>N,N,N</i> -trimethyl ammonium bromide	10	1.36	<5	10.0	28
ICOTMA <sup>b</sup>	50	0.56	2.8	7.0	29
Zirconium(IV) hydroxide	25	1.55	6.4	8.0	30
Ni <sup>2+</sup> /2-Nitroso-1-naphthol-4-sulfonic acid	25	1.3	3.8	8.0	31
MEFMAT <sup>c</sup>	50	1.49	2.0	6.8	32
Ni(II)-salicylaldehyde	20	1.32	2.5	9.0	33
DIBBA	50	0.44	3.4	8.0	This study

<sup>a</sup>4-(2-hydroxybenzylideneamino)-1,2-dihydro-2,3-dimethyl-1-phenylpyrazol-5-one; <sup>b</sup>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; <sup>c</sup>2-[[4-(4-fluorophenyl)-5-sulphonyl-4H-1,2,4-triazol-3-yl]methyl]-4-[[4-(4-fluorophenyl) methylene]amino]-5-(4-methylphenyl)-2,4-dihydro-3H-1,2,4-triazol-3-one

The fact that the developed CEFC method based on DIBBA has lower *LOD* and *RSD* values and high *PF* value compared to many methods in the literature indicates the superiority and suitability of the process.<sup>17,24,27-33</sup>

#### Analysis of real samples

The spike/recovery test was applied for both fruit and water samples for the validation of the method. The relative recovery (*RR*) values obtained for the water (Table III) and the fruit samples (Table IV) were in the range of 96.3–103.0 % and 94.4–100.6 %, respectively. The good agreement between the added and found values demonstrated the validity of the method and also its applicability with high accuracy without significant matrix effect. Eventually, the suggested methodology was applied smoothly to determine Cu(II) ions levels of several water and fruit samples (Table V).

TABLE III. Recovery of Cu(II) ions from water samples (50 mL of each sample volume and 2.0 mL of final volume); ND – not detected

Quantity of Cu(II) added to the medium, $\mu\text{g}$	Stream water		Sea water	
	Quantity of Cu(II) found, $\mu\text{g}$	Recovery %	Quantity of Cu(II) found, $\mu\text{g}$	Recovery %
0	ND	–	ND	–
20	20.6±0.5	103.0	19.4±0.7	97.0
40	38.5±1.6	96.3	40.1±1.2	100.3



TABLE IV. Cu(II) ions recovery from fruit samples (0.75 g of each fruit sample quantities and 2.0 mL of final volume)

Sample	Quantity of Cu(II), $\mu\text{g}$		Recovery, %
	Added	Found	
Sour cherry	0	2.53 $\pm$ 0.06	–
	20	21.4 $\pm$ 0.5	94.4
Mulberry	0	2.88 $\pm$ 0.08	–
	20	23.0 $\pm$ 0.6	100.6
Apple	0	2.45 $\pm$ 0.06	–
	20	21.7 $\pm$ 0.4	96.3
Peach	0	3.72 $\pm$ 0.12	–
	20	22.8 $\pm$ 0.5	95.4

TABLE V. Cu(II) levels in water ( $\mu\text{g L}^{-1}$ ) and fruit samples ( $\mu\text{g g}^{-1}$ , 100 mL of each sample volume, 0.75 g of each fruit sample quantities, and 2.0 mL of final volume)

Liquid samples			Solid samples		
Sea water	Stream water	Sour Cherry	Mulberry	Apple	Peach
3.38 $\pm$ 0.10	15.10 $\pm$ 0.48	3.37 $\pm$ 0.05	3.84 $\pm$ 0.13	3.27 $\pm$ 0.07	4.96 $\pm$ 0.15

#### CONCLUSION

A new organic coprecipitant, DIBBA, exhibited a great potential for separation and preconcentration of Cu(II) ions by carrier element free coprecipitation (CEFC) method. Until now, DIBBA has not been applied in any other analytical applications. The preconcentration conditions were optimized with respect to pH (8.0), DIBBA amount (4.0 mg), volume of sample (100 mL), waiting time (5 min), centrifuge duration and speed (3 min and 2500 rpm). Short waiting time and centrifuge duration as well as low LOD and RSD values and high preconcentration factor are the notable advantages of the presented method. Since the carrier element was not used for the precipitate formation in the method, the contamination risk originated from the carrier element and the possible interference effect in the determination of the analyte ions were eliminated. In addition, the method allows the use of chemical reagents and harmful solvents at a minimum level and thus it will be beneficial in reducing the environmental pollution. In brief, the obtained results indicated that the proposed sensitive and facile method is a promising alternative for the determination of Cu(II) ions in fruit and water samples.

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## ИЗВОД

ЈЕДНОСТАВНА И ОСЕТЉИВА МЕТОДА КОПРЕЦИПИТАЦИЈЕ У КОМБИНАЦИЈИ СА ПЛАМЕНОМ АТОМСКОМ АПСОРПЦИОНОМ СПЕКТРОМЕТРИЈОМ ЗА КВАНТИФИКАЦИЈУ Cu(II) ЈОНА У СЛОЖЕНИМ МАТРИЦАМА

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У овом истраживању коришћен је 2-[5,6-дихлоро-2-(2-бромобезил)-1H-бензимидазол-1-ил]ацетохидразид (DIBVA), као копреципитациони реагенс, за сепарацију и предконцентрацију Cu(II) јона у узорцима воћа и вода, први пут применом нове методе копреципитације без елемента у носачу. Примењена је пламена атомска апсорпциона спектрометрија за анализу Cu(II) јона. Детаљно су испитивани експериментални услови, који утичу на ефикасност и принос Cu(II) јона, као што су рН, количина DIBVA, време и брзина центрифугирања и запремина узорка. Под оптимлним условима предконцентрациони фактор (PF), релативна стандардна девијација (RSD) и границе детекције (LOD) су износили 50, 3,4% и 0,44 µg L<sup>-1</sup>, редом. Нису детектоване интерференције у присуству страних јона. Постигнут је задовољавајући проценат приноса (94,4–103,0 %) у узорцима из животне средине. После валидације методе, као селективне, економичне, једноставне и брзе, SEFC метода је примењена за детекцију ниских нивоа концентрација Cu(II) јона у узорцима вишања, дудиња, јабука и бресака, као и морске и воде из потока без значајног утицаја матрице.

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