Acetohydrazide Derivative for Selective Separation and Preconcentration of Cu(II) Ions by Coprecipitation Method Without Using a Carrier Element

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ABSTRACT A simple and rapid procedure based on the combination of carrier element free coprecipitation (CEFC) and flame atomic absorption spectrometric (FAAS) determinations has been developed for selective separation and preconcentration of Cu(II) ions in some environmental solid (Turkish and import coffee) and liquid (sea and stream waters) samples. In this method, acetohydrazide derivative was used as an organic coprecipitant without adding any carrier element for coprecipitation of Cu(II) ions. The preconcentration factor was found to be 50, the limit of detection (LOD) was $0.31\,\mu g\,L^{-1}$, while the relative standard deviation (RSD) was found to be 1.6% for Cu(II) ions.

KEYWORDS acetohydrazide derivative, carrier element free coprecipitation, copper, flame atomic absorption spectrometry

INTRODUCTION

Although copper is considered as an essential micronutrient that plays an important role in carbohydrate and lipid metabolism, long-term exposure to copper of $40\,\mu g\,L^{-1}$, may cause acute gastrointestinal effects, including stomachaches, dizziness, vomiting, and diarrhea, and high uptake of copper may cause liver and kidney damage and even death.[1–3] Hence, the accurate and precise determination of Cu(II) ions in environmental samples is one of the main fields in analytical chemistry, in terms of taking the necessary precautions in consumption of food and water samples.[4] Although the atomic absorption spectrometer (AAS) is a widely used instrumental technique for the determination of trace heavy metal ions, some problems, including lower analyte levels than the limit of quantitation of the instrument and interfering effects of the matrix ions, limit the direct determination of analyte ions by using AAS and most other instrumental techniques.[5] To overcome these problems, some separation and preconcentration techniques such as ion exchange,[6] solvent extraction,[7] cloud point extraction,[8] solid phase extraction,[9,10] membrane filtration,[11]

and electroanalytical techniques[12] have been used prior to the analysis step. Apart from these, the coprecipitation technique also has an important place because of its advantages, including simplicity, rapidity, ability to attain a high preconcentration factor, low consumption of organic solvents, and that several analyte ions can be preconcentrated and separated from the matrix simultaneously by using various organic or inorganic coprecipitants.[13]

The coprecipitation method can be applied through the usage of three procedures. First, some metal hydroxides, such as aluminum,[14] lanthanum,[15] erbium,[16] and dysprosium,[17] can be used as inorganic coprecipitants. Second, the organic coprecipitants such as dibenzyldithiocarbamate,[18] 9-phenyl-3-fluorone,[19] and rubeanic acid[20] can be used for the collection of trace metal ions. However, for the formation of a precipitate together with organic coprecipitants, the addition of a large amount of carrier elements such as Cu, Bi, Ni, and Co is necessary. The last procedure is carrier element free coprecipitation (CEFC), in which for the formation of the coprecipitating agent, only an organic ligand is used, without the addition of a carrier element. The CEFC method has great advantages for separation and preconcentration of heavy metals because there is no contamination and background adsorption risk for metal ions from a carrier element.[21–25]

In the present study, we applied the CEFC method for selective separation and preconcentration of Cu(II) ions from aqueous solutions by using an acetohydrazide derivative ligand, 2-{4-[2-(1H-Indol-3-yl)ethyl]-3-(4-chlorobenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl} N′-(2-hydroxyphenilmethylidene) acetohydrazide (ITAH), as an organic coprecipitant without any carrier element. The selectivity of ITAH toward the quantitative recoveries of different metal ions (Cu(II), Pb(II), Cd(II), Mn(II), Co(II), Cr(III), Cr(VI), V(V), Fe(III), Ni(II), Zn(II), Al(III), Mo(VI), Pd(II), Pt(IV), Au(III), Se(IV)) was checked in the pH range of 2–10. The quantitative recovery values were obtained only for Cu(II) ions, in the presence of other metal ions at pH 5. The influences of the various analytical parameters such as the effects of pH, quantity of ITAH, standing time, centrifugation rate and time, and sample volume were investigated in detail upon the recoveries of the Cu(II) ions. After being validated, the method was applied to determine Cu(II) ions in several solid and liquid environmental samples.

EXPERIMENTAL

Apparatus and Reagents

The analyses of Cu(II) and other metal ions, used for checking the selectivity of ITAH, were performed by a Unicam AA-929 model flame atomic absorption spectrometer (Solar System ATI Unicam Analytical Technology Inc., Cambridge, UK). The instrumental parameters were those recommended by the manufacturer. The pH measurements were made on a Hanna pH-211 (HANNA Instruments, Romania) digital pH meter with glass electrode. Sigma 3-16P (Sigma Laborzentrifugen GmbH, Germany) model centrifuge was used to centrifuge solutions. Digestion of the solid samples was carried out by using a Milestone Ethos D (Milestone Inc., Italy) closed-vessel microwave system (maximum pressure 1450 psi, maximum temperature 300°C).

All of the chemicals used in this work were analytical grade from Merck (Darmstadt, Germany) or Fluka (Buchs, Switzerland). Distilled/deionized water (Millipore Milli-Q system) was used for all dilutions. Laboratory glassware was kept overnight in a 10% (v/v) HNO$_3$ solution and then rinsed with distilled/deionized water. The working solution of Cu(II) ions was prepared by diluting a stock solution of 1000 mg L^{-1} of the given element supplied by Sigma and Aldrich. ITAH (Scheme 1) was synthesized according to the literature.[26] For separation and preconcentration experiments, 0.2% (w/v) ITAH solution was prepared in the mixture of dimethyl sulfoxide (Merck) and ethanol (Merck) (1:4). The certified reference materials, drinking water standard (CRM-TMDW-500), and sandy soil standard (CRM-SA-C) used in the experimental studies were
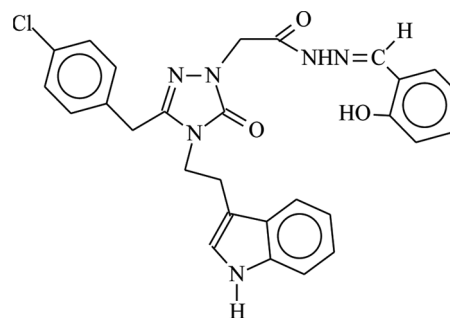
SCHEME 1 Chemical structure of ITAH.

obtained from High-Purity Standard Inc. Also, all of the metal salts used in the evaluation of matrix interferences were obtained from Merck.

Preconcentration Studies

Two milliliters of ITAH solution (0.2% (w/v)) was added into 50 mL of aqueous solution containing 12.5 μg of Cu(II) ions. The pH of the solution was adjusted to 5.0 by using dilute HCl or NaOH solutions. The tube was shaken slowly for several seconds and allowed to stand for 30 min. Then, the solution was centrifuged at 2000 rpm for 5 min. The supernatant was removed and the precipitate left adhering to the tube was dissolved with 1.0 mL of conc. HNO_3. The volume was completed to 5.0 mL by the addition of distilled water. The levels of Cu(II) ions were determined by FAAS.

Analysis of Real Samples

As real water samples, sea water (Black Sea, Trabzon/Turkey) and stream water (Şana Stream, Trabzon/Turkey) were collected and filtered through a cellulose membrane filter of 0.45 μm pore size. The samples were stored in polyethylene bottles and acidified with 1% (v/v) nitric acid and were subsequently stored at 4°C in a refrigerator. Before the analysis, the pH of the samples was adjusted to 5.0. Then the procedure given in the "Preconcentration Studies" was applied.

Prior to determination of Cu(II) ions in solid samples, Turkish coffee, a type of import coffee, and a certified reference material, CRM-SA-C Sandy Soil C, were digested with the microwave digestion system. For that purpose, 1.000 g of Turkish coffee and import coffee and 0.100 g of CRM-SA-C Sandy Soil C were weighed into Teflon vessels, separately; 6 mL of HNO_3 and 2 mL of H_2O_2 for coffee samples, and 4.5 mL of HCl, 1.5 mL of HNO_3, 1 mL of HF, and 2 mL of H_2O_2 for CRM-SA-C Sandy Soil C standard were added into the vessels. Digestion conditions for the microwave system were applied as (45 bar) 6 min for 250 W, 6 min for 400 W, 6 min for 650 W, 6 min for 250 W, vent: 3 min. After microwave digestion, the sample volume was made up to 50 mL with distilled water. Blanks were prepared in the same way as the sample but omitting the sample. The preconcentration procedure given in the

"Preconcentration Studies" was applied to the samples. The final volume was 5 mL.

RESULTS AND DISCUSSION

Optimization Parameters

The pH value of an aqueous solution may alter the charge of the precipitate and it also can affect the chemistry of the metals present in the working media. The influences of solution pH on the recoveries of Cu(II), Pb(II), Cd(II), Mn(II), Co(II), Cr(III), Cr(VI), V(V), Fe(III), Ni(II), Zn(II), Al(III), Mo(VI), Pd(II), Pt(IV), Au(III), and Se(IV) ions were investigated in the pH range of 2.0–10.0. At pH 5.0, only Cu(II) ions were quantitatively recovered by using the present coprecipitation procedure. Hence, it can be said that the developed separation and preconcentration method based on the CEFC by using ITAH is selective for only Cu(II) ions. Figure 1 depicts the recovery values of Cu(II) ions in the pH range of 2–10. As can be seen, after pH 5.0 Cu(II) ions were quantitatively recovered, all further works were performed at pH 5.0.

The influences of the amount of ITAH on the quantitative coprecipitation of Cu(II) ions were evaluated in the ITAH amount range of 0.0–6.0 mg (Fig. 2). Under optimum conditions, the recoveries of Cu(II) ions were below 5% without adding ITAH. These results indicated that for the formation of a precipitate that collects the Cu(II) ions quantitatively, ITAH is necessary. The recovery values of Cu(II) ions increased with increasing the amount of ITAH from
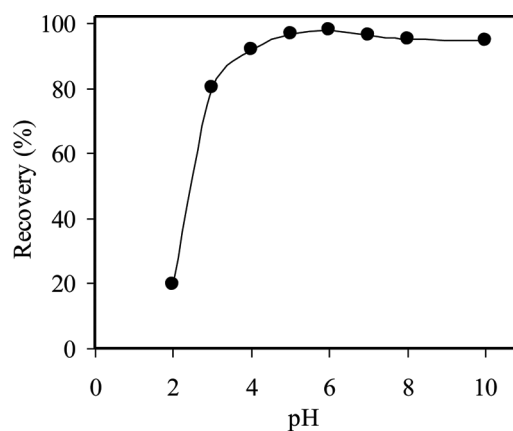
FIGURE 1   Effect of pH on the recovery of Cu(II) ions (*N*: 3, sample volume: 50 mL, quantity of ITAH: 2.0 mL (0.2% (w/v)), standing time: 30 min, centrifugation rate: 2000 rpm, centrifugation time: 5 min).
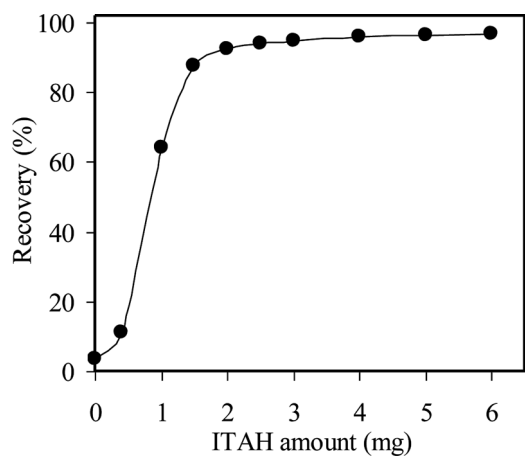
FIGURE 2 Effect of ITAH amount on the recovery of Cu(II) ions (*N*: 3, sample pH: 5.0, sample volume: 50 mL).

0.4 to 4.0 mg. Because the further increase in the ITAH amount did not significantly affect the recovery values, for all other experiments, 4.0 mg (2.0 mL of 0.2% (w/v)) of ITAH was used.

The quality of the precipitate that forms in aqueous medium may also be influenced by the standing time and centrifugation time and rate. Hence, the coprecipitation experiments were performed in the standing time range of 0–120 min (Fig. 3a), centrifugation rate range of 1000–3500 rpm (Fig. 3b), and centrifugation time range of 1–30 min (Fig. 3c). The optimum standing time and centrifugation time and rate for the quantitative recoveries of Cu(II) ions were determined as 30 min, 5 min, and 2000 rpm, respectively.

Apart from these optimization parameters, we considered that the analyte amounts may also affect the quantitative recovery values. In order to test the effect of the amount of Cu(II) ions on the recoveries of it, the experiments were performed by varying the Cu(II) amount in the range of 50–500 μg under the optimum conditions. It was seen that, by increasing the Cu(II) amount from 50 to 500 μg, the recovery values decreased from 95% to 58%. This may be related to the insufficient amount of the precipitate for the collection of all the Cu(II) ions on itself.

In order to evaluate the possible application of the presented coprecipitation procedure for the water samples, the effects of sample volume were examined in the range of 50–1000 mL (Fig. 4). Cu(II) ions were quantitatively (>95%) recovered in the sample volume ranges of 50–250 mL. After 250 mL of sample volume, the recoveries decreased slowly so the sample volume was chosen as 250 mL in the appli-
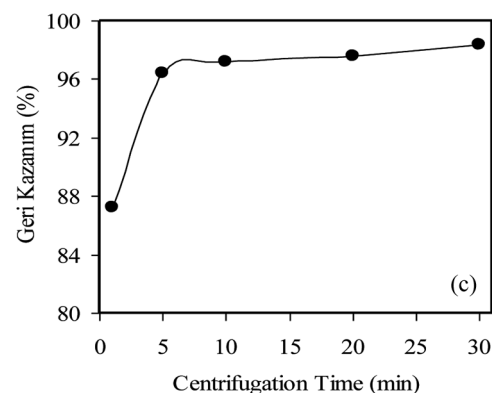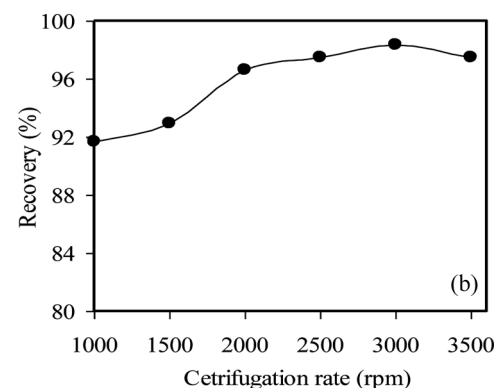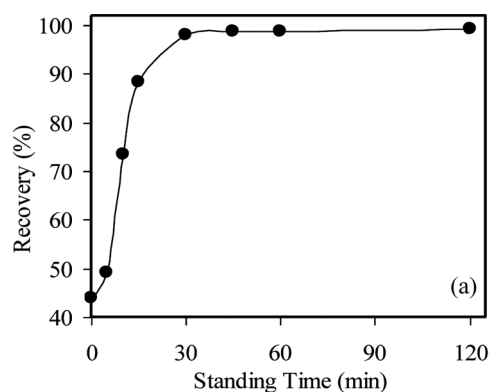
FIGURE 3 (a) Effect of standing time on the Cu(II) recoveries (pH: 5.0, centrifugation rate: 2000 rpm, centrifugation time: 5 min). (b) Effect of centrifugation rate on the Cu(II) recoveries (pH: 5.0, standing time: 30 min, centrifugation time: 5 min). (c) Effect of centrifugation time on the Cu(II) recoveries (pH: 5.0, standing time: 30 min, centrifugation rate: 2000 rpm).

cation of the procedure for sea and stream waters. The preconcentration factor is calculated by the ratio of the highest sample volume and the lowest final volume, and it was found as 50 for Cu(II) ions when the final volume was 5.0 mL.

Effect of Matrix Ions

In determination of analyte ions by FAAS in environmental real samples, the interfering effects
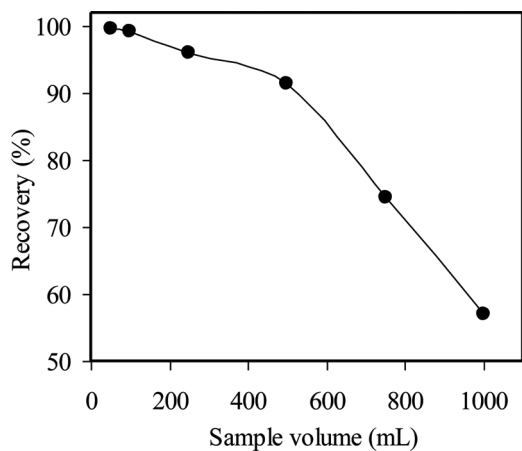
FIGURE 4 Effect of sample volumes on the Cu(II) recoveries (*N*: 3, sample pH: 5.0).

of matrix components, such as alkali, earth alkali ions, and anions at mg L^{-1} levels, are one of the significant problems.[27] Hence, in order to assess the possible analytical applications of the presented procedure, the effects of some foreign ions that are the major components of sea water and stream water were evaluated under the optimal conditions by contacting known amounts of some anions and cations with 12.5 µg of Cu(II) ions. Then the presented CEFC procedure was applied for all the concomitant ions, separately. In most cases the recovery values of Cu(II) ions were higher than 95% (Table 1). Also, it

TABLE 1 Influences of Some Foreign Ions on the Recoveries of Cu(II) Ions (*N*: 3, sample pH: 5.0, sample volume: 50 mL, quantity of ITAH: 2.0 mL (0.2% (w/v)), standing time: 30 min, centrifugation rate: 2000 rpm, centrifugation time: 5 min)

| Ions	Added as	Conc. (mg L^{-1})	Recovery (%)
Na^+	NaCl	5000	99.8 ± 4.3
K^+	KCl	1000	100.9 ± 2.0
Ca^{2+}	$CaCl_2$	1000	101.2 ± 1.0
Mg^{2+}	$Mg(NO_3)_2$	1000	97.2 ± 3.6
CO_3^{2-}	Na_2CO_3	1000	98.1 ± 0.8
NO_3^-	$NaNO_3$	5000	93.0 ± 0.3
PO_4^{3-}	Na_3PO_4	1000	99.1 ± 2.0
SO_4^{2-}	Na_2SO_4	1000	101.0 ± 2.6
Al^{3+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Zn^{2+}	[a]	25	97.5 ± 1.4
Mixed[b]			93.8 ± 1.8

[a]Added as their nitrate salts.
[b]7350 mg L^{-1} Na^+, 8390 mg L^{-1} Cl^-, 6460 mg L^{-1}, NO_3^-, 250 mg L^{-1}, K^+, Ca^{2+}, Mg^{2+}, CO_3^{2-}, PO_4^{3-}, SO_4^{2-}, 10 mg L^{-1} Al^{3+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Zn^{2+}.

is important to notice that some of the transition metals did not interfere with the recoveries of the Cu(II) ions. In the view of these results, it can be concluded that the proposed separation and preconcentration method based on CEFC could be applied to the samples containing high amounts of salts and some transition metal ions.

Analytical Performance of the Method

The reproducibility of the method was evaluated by using model solutions containing 12.5 µg of Cu(II) ions in 50 mL of aqueous solution and the procedure was repeated 10 times under optimum experimental conditions. The relative standard deviation (RSD) of these determinations was found to be 1.6%.

The limit of detection (LOD), defined as the concentration that gives a signal equivalent to three times the standard deviation of 10 replicate measurements of the blank samples, for Cu(II) ions was found to be 0.31 µg L^{-1}. The LOD was calculated by dividing the instrumental detection limit by the preconcentration factor (50).

Method Validation and Application to Real Samples

The validation of the presented CEFC procedure was tested by the standard addition method and analysis of certified reference materials. For the standard addition method, different amounts of Cu(II) ions were spiked in sea and stream waters (Table 2) and Turkish and import coffee samples (Table 3). The recommended CEFC procedure was applied to these samples. The recovery values for the Cu(II) ions were in the range of 91–99%. These values show that

TABLE 2 Spiked Recoveries of Cu(II) Ions From Water Samples (*N*: 3, sample pH: 5.0, sample volume: 50 mL, quantity of ITAH: 4.0 mg, final volume: 5.0 mL)

Added (µg)	Stream water		Sea water	
	Found (µg)	Recovery (%)	Found (µg)	Recovery (%)
0	BDL[a]	—	BDL	—
10.0	9.5 ± 0.1	95	9.9 ± 0.4	99
20.0	18.7 ± 0.8	94	18.3 ± 0.9	92

[a]Below detection limit.

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TABLE 3 Spiked Recoveries of Cu(II) Ions From Solid Samples (*N*: 3, sample pH: 5.0, quantity of ITAH: 4.0 mg, sample quantities: 1.000 g of Turkish and import coffee, final volume: 5.0 mL)

Added (μg)	Import coffee		Turkish coffee	
	Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
0	1.6 ± 0.3	—	4.8 ± 0.4	—
10.0	10.7 ± 0.6	91	14.3 ± 0.3	95
20.0	20.4 ± 0.8	94	23.6 ± 0.7	94

TABLE 4 Application of the Present Method to the Certified Reference Materials (*N*: 3, quantity of ITAH: 4.0 mg)

Element	CRM TMDW-500 drinking water[a]		CRM-SA-C sandy soil[b]	
	Certified value (μg L^{-1})	Found value (μg L^{-1})	Certified value (μg L^{-1})	Found value (μg L^{-1})
Cu(II)	20.0 ± 0.2	20.8 ± 0.5	63.6 ± 4.0	62.5 ± 3.6

[a]Sample volume: 50 mL.
[b]Sample quantity: 0.1 g.

the presented CEFC procedure can be applied for the selective preconcentration of Cu(II) ions in real solid and liquid samples.

The certified reference materials (CRM-TMDW-500 Drinking Water and CRM-SA-C Sandy Soil C) were also used for method validation. The obtained results were in good agreement with the certified values (Table 4).

The method was applied to the determination of Cu(II) ions in sea and stream waters and Turkish and import coffee samples after the accuracy of the method was ensured. After applying the preconcentration procedure to the samples, the obtained results were tabulated in Table 5.

TABLE 5 Analyte Levels in Real Solid/Liquid Samples After Being Applied the Presented Coprecipitation Procedure (*N*: 3, sample volumes: 250 mL, sample quantities: 1.000 g of Turkish and import coffee, final volumes: 5.0 mL)

Element	Liquid samples		Solid samples	
	Sea water (μg L^{-1})	Stream water (μg L^{-1})	Import coffee (μg g^{-1})	Turkish coffee (μg g^{-1})
Cu(II)	6.6 ± 0.5	7.1 ± 0.3	1.6 ± 0.3	4.8 ± 0.4

CONCLUSIONS

For selective, accurate, and precise determination of Cu(II) ions in environmental solid and liquid samples, a CEFC method combined with FAAS has been developed in the present work. We have used ITAH as an organic coprecipitating agent, which provides selective and quantitative collection of Cu(II) ions on itself, besides Pb(II), Cd(II), Mn(II), Co(II), Cr(III), Cr(VI), V(V), Fe(III), Ni(II), Zn(II), Al(III), Mo(VI), Pd(II), Pt(IV), Au(III), and Se(IV) ions, at pH 5.0. In the proposed method, no carrier element has been used; thus, there is no contamination risk for Cu(II) ions from a carrier element. This also enables the usage of fewer chemicals than those of other separation and preconcentration methods. The method has a high preconcentration factor,[16] low RSD,[14,16,17,21,22,28,29] and relatively low LOD values[14,17,21,28,29] when compared the other

TABLE 6 Comparison of the Method With Some Recent Studies on Coprecipitation Reported in Literature

System	PF[a]	LOD (μg L^{-1})	RSD (%)	Ref.
Al(OH)$_3$	125	3.0	2–3	[14]
Er(OH)$_3$	25	0.11	<9	[16]
Dy(OH)$_3$	250	22.0	1–7	[17]
2-{[4-(4-Fluorophenyl)-5-sulphanyl-4H-1,2,4-triazol-3-yl]methyl}-4-{[(4-fluorophenyl)methylene]amino}-5-(4-methylphenyl)-2,4-dihydro-3H-1,2,4-triazol-3-one	50	1.49	2	[21]
3-Benzyl-4-p-nitrobenzylidenamino-4,5-dihydro-1,2,4-triazole-5-on	150	0.3	2	[22]
Diethyldithiocarbamate (DDTC)/Ni(II)	60	0.5	3.0	[28]
4-Methylpiperidinedithiocarbamate/Bi(III)	200	0.5	<10	[29]
2-{4-[2-(1H-Indol-3-yl)ethyl]-3-(4-chlorobenzyl)-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl} N′-(2-hydroxyphenilmethylidene) acetohydrazide	50	0.31	1.6	This work

[a]Preconcentration factor.

methods reported in Table 6. After evaluation of the optimization parameters such as quantity of ITAH, standing time, centrifugation rate and time, and sample volume in detail and validation of the method, it was successfully applied for the determination of Cu(II) ions in various solid and liquid samples with a low detection limit and high accuracy and precision.

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