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DETERMINATION OF COPPER(II) IN NATURAL WATERS BY EXTRACTION USING N-O-VANILLIDINE-2-AMINO-P-CRESOL AND FLAME ATOMIC ABSORPTION SPECTROMETRY

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□ *A simple and accurate solvent extraction method was developed for the separation and preconcentration of trace levels of copper(II) in water using N-o-vanillidine-2-amino-p-cresol prior to its determination using flame atomic absorption spectrometry. Analytical parameters such as the pH of the aqueous phase, extraction time, concentration of the reagent, concentration of the nitric acid back extraction agent, volumes of aqueous phase and back extraction agent, and concomitant ions on the extraction yield of the copper(II) were investigated and optimized. Under the optimal conditions, the detection limit (3σ) was $0.61 \mu\text{g L}^{-1}$ for a 25 mL blank solution, yielding a preconcentration factor of 12.5. The method was successfully applied to the determination of copper(II) in tap water, river water, and seawater. The accuracy of the method was verified by analyzing two certified reference materials and spiked water samples. The results obtained were in agreement with the certified values and the recoveries for spiked water samples were between 98 and 112%.*

Keywords copper, flame atomic absorption spectrometry, N-o-vanillidine-2-amino-p-cresol (OVAC), preconcentration, separation, solvent extraction

INTRODUCTION

The determination of heavy metals in the environment is of great interest, since their effects on the ecosystem and human health depend on their dose and toxicity. Copper is one of the most widespread heavy metal contaminants in the environment. It is an economically important element that is found in only trace quantities in the Earth's crust. Copper is required as a trace nutrient for both plants and animals but in excess can show toxic effects. High concentrations of copper in the human body can cause stomach and intestinal distress.^[1] Several industries, for example, dye, paper, petroleum, metal plating, and copper-ammonium

rayon, release copper into the environment. High copper concentrations in soils cause delays in flowering and fruiting and low seed set. It is also extremely toxic to aquatic organisms even at low concentrations. Copper contamination in soil and water systems can eventually impact human health through the food chain.^[2] The European Commission has fixed a limit of 2.0 mg L^{-1} for copper in drinking water whereas the limit is set to 1.3 mg L^{-1} in the USA; similar to that in Canada (1.0 mg L^{-1}).^[3,4] The World Health Organization gives the permissible limit of copper in drinking waters as 1.0 mg L^{-1} .^[5] Therefore, it is crucial to develop simple, rapid, and efficient analytical methods for monitoring copper at trace levels in environmental and biological samples.

A variety of methods including electrothermal atomic absorption spectrometry (ETAAS),^[6,7] inductively coupled plasma-optical emission spectrometry (ICP-OES),^[8–10] inductively coupled plasma-mass spectrometry (ICP-MS),^[11,12] and FAAS^[13–15] have been developed for the determination of copper in various sample matrices. Of these, FAAS is one of the most widely used because of its low cost, ease of operation, high sample throughput, and good selectivity. However, it has limited use at low concentrations because its instrumental detection limits are relatively poor.^[16–18] Copper concentration levels in water are fairly low and interferences arising from the sample matrix, especially for sea water, cannot always be eliminated. Matrix separation and analyte preconcentration procedures are often necessary before the determination of copper ions in real samples with complex matrices. Concomitant ions present in highly saline samples may also cause interferences and burner clogging. This would lead to excessive signal drift and poor precision. Preconcentration–matrix separation techniques have been used to overcome these limitations.^[19,20]

Techniques such as co-precipitation,^[21,22] solid-phase extraction,^[23–26] cloud point extraction,^[13,27,28] and solvent extraction^[29–32] are widely used for the separation and preconcentration of trace elements. The large distribution ratios possible in solvent extraction systems enable the determination of substances present at otherwise non-detectable concentrations. A judicious choice of extractant may lead to a preconcentration factor of several orders of magnitude being obtained. Even when the analyte is detectable in the original sample, preconcentration using solvent extraction permits the use of smaller samples, simplification of the procedure, and increased accuracy of analysis. Often, both separation and preconcentration are required, and an advantage of solvent extraction is that both can be obtained simultaneously.^[29,30] Recovery of metals by solvent extraction is achieved by contacting the aqueous phase with an organic phase that contains a metal selective chelating agent dissolved in a diluent. Reagents such as crown ethers, Schiff bases, oximes, amines, and several phosphine oxides have been used as chelating agents.^[33] Schiff bases, which have

good metal complexing capabilities, have also been used as ligands in metal complexes for recent analytical applications.^[33–35]

N-o-vanillidine-2-amino-p-cresol (OVAC) is a chelating ligand containing two hydroxyl oxygen atoms and one imine nitrogen atom donor site. This chelating agent produces complexes with the copper ion in a very short time (1 min). Fast and efficient extraction of copper from natural waters is very important for analytical and environmental aspects because the extraction process enables a matrix free preconcentration of copper. A new procedure was developed for the separation and preconcentration of copper using solvent extraction with the reagent OVAC as the complexing reagent. After optimization of the experimental variables and determination of analytical features, the procedure was applied to the determination of copper in tap, river, and seawater samples. The developed method was verified using certified reference materials.

EXPERIMENTAL

Instrumentation

A PerkinElmer model AAnalyst 200 (Shelton, CT, USA) flame atomic absorption spectrometer equipped with deuterium background correction was used for determining the concentration of Cu(II) in the aqueous phase after the back extraction. A copper hollow cathode lamp was the radiation source operating at a wavelength of 324.75 nm and lamp current of 30 mA. All measurements were obtained using an air-acetylene flame at flow rates of 10 and 2.5 L min⁻¹, respectively. A Hanna Instruments Model 221 (Cluj-Napoca, Romania) digital pH-meter with a combined glass electrode was used for all pH measurements.

Reagents and Solutions

All chemicals used in this article were of analytical reagent grade and were used without further purification. Nitric acid, acetic acid, and chloroform were obtained from Riedel-de Haen (Sigma-Aldrich, St. Louis, MO, USA) and ethanol and sodium acetate from Sigma-Aldrich (St. Louis, MO, USA). O-vanillin and 2-amino-*p*-cresol were purchased from Fluka (Gillingham, Dorset, UK). Ultrapure water of 18.2 MΩ cm resistivity, obtained from a Purelab Option-Q water purification system (Elga Labwater, Lane End, UK), was used throughout. The laboratory glassware used was kept in 10% (v/v) nitric acid overnight and rinsed with ultrapure water before use. A stock standard containing 1000 mg Cu(II) L⁻¹ was prepared by dissolving appropriate amounts of Cu(NO₃)₂ · 3H₂O (Riedel-de Haen) in 1% HNO₃.

Calibration standards were prepared daily from the stock by appropriate dilution with ultrapure water. A buffer solution (1.0 M at pH 4.0) was prepared using pure acetic acid and sodium acetate. The solution of OVAC (2.0×10^{-3} M) was prepared daily by dissolving appropriate amounts of the reagent in chloroform immediately before use. The certified reference materials QCS-19 (High purity standards, Charleston, USA) and riverine water (SRLS-5; National Research Council, Ottawa, Canada) were used in this study.

N-o-vanillidine-2-amino-p-cresol (OVAC) was synthesized according to the procedure given in the literature.^[36]

Extraction Procedure

The method was tested using model solutions before its application to various samples. For this purpose, 10 mL of aqueous solutions containing 10 μ g of Cu(II) ions in appropriate buffer were shaken with 5 mL chloroform solution of the OVAC (2.0×10^{-6} – 2.0×10^{-3} M) on a mechanical shaker at room temperature (22°C) for 10 min. After extraction of the aqueous phase, the two phases were allowed to separate, and the organic phase was transferred into another separatory funnel. To this organic phase, 2–5 mL of 1.0 M HNO₃ solution were added and the mixture was mechanically shaken at 22°C for 20 min. The amount of copper back-extracted into the aqueous phase after stripping the organic phase was determined by FAAS.

Preconcentration Procedure

The effect of the sample volume on the recovery of the analyte was tested. Therefore, 10, 25, 50, and 100 mL of sample solutions containing 4 μ g Cu(II) ions in pH 4.0 buffer were extracted into 5 mL of 2.0×10^{-3} M OVAC in chloroform. Copper was stripped from the organic phase with 2 mL of 1.0 M HNO₃ solution. The effect of the sample volume (50 and 100 mL) on the recovery of the analyte was studied using 10 mL (for 50 mL sample volume) and 20 mL (for 100 mL sample volume) of 2×10^{-3} M OVAC.

Application to Real Samples

The optimized method was applied to the determination of copper in the certified reference materials SLRS-5 riverine water and QCS-19. The pH of SLRS-5 (10 mL) was adjusted to 4.0 with acetic acid/sodium acetate buffer solution. The QCS-19, which contains 100 mg L⁻¹ of 19 elements, was diluted to 4 μ g L⁻¹ using 0.08 M, pH 4.0 acetic acid/sodium acetate buffer solution. The analytical procedure described above was then

applied to the two sample types. Aliquots (25 mL) of the diluted QCS-19 were used for analysis. The final measurement volumes were 2 mL. The student's t-test was applied to the results of the method and certified values.

The method was also applied to tap water from Balıkesir University, river water from Büyük Bostancı River, and seawater from the Aegean Sea near the Edremit Coast. The river water and seawater samples were passed through a cellulose membrane filter with a 0.45 μm pore size, acidified to pH 2 with nitric acid, and stored in pre-cleaned polyethylene bottles. Tap water samples were taken and analyzed without pretreatment. The water samples (25 mL) were adjusted to pH 4.0 using acetic acid/sodium acetate buffer and 10% (w/v) sodium hydroxide solution before analysis. The final measurement volume was 2 mL.

RESULTS AND DISCUSSION

Optimization of the Experimental Variables

To obtain highly sensitive, accurate, and reproducible results, analytical parameters including the pH of the aqueous phase, the concentration of the OVAC reagent, extraction time, concentration of back extraction agent, and volumes of aqueous phase and back extraction agent, were optimized. A univariate optimization procedure was undertaken. All the experiments were performed in triplicate. Optimal conditions were defined as those in which the maximum recovery for Cu(II) was obtained.

The selectivity of an extraction can often be controlled by careful pH adjustment since binding of metal ions to the chelate compounds during solvent extraction is dependent on the pH of the medium. The effect of pH (between 3.0 and 8.0) on the extraction of 10 mL of 1 mg L^{-1} Cu(II) solution into chloroform containing OVAC were examined using the procedure given above. Figure 1 shows that quantitative extraction rates were obtained between pH values of 4.0 and 7.0. The maximum recovery (95%) was obtained at pH 4.0 so this trend might be caused by the effect of different aqua complexes of copper formed at different pH in water. Therefore, pH 4.0 was selected for the subsequent experiments because other possible concomitant ions as well as copper have less chance of producing hydroxide precipitates at acidic pH.

In general, mass transfer is a time-dependent process and the maximum absorbance signal is attained when the system is at equilibrium. However, as long as extraction conditions are reproducible, complete equilibrium does not need to be reached to obtain accurate and precise analysis; although a decrease in preconcentration factor/sensitivity may result. The effect of extraction time on the solvent extraction of 10 mL of 1 mg L^{-1} Cu(II) solution was examined over the range of 1–50 min using

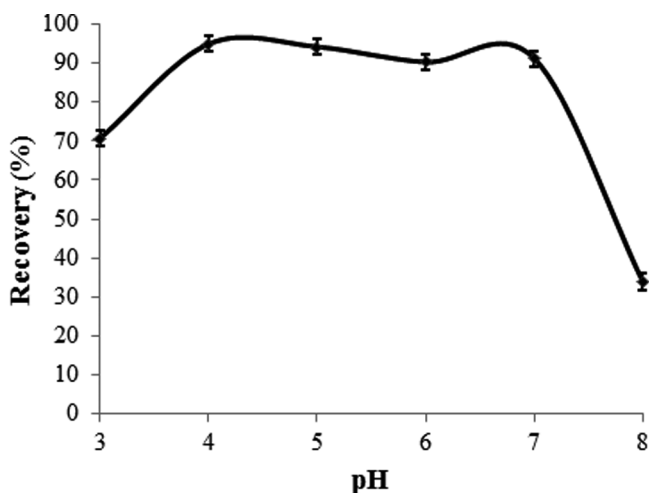


FIGURE 1 Effect of pH on the extraction of copper, $n = 3$.

the above procedure. Quantitative recoveries were obtained to obtain reproducible results even after only 1 min. This result showed that the extraction process of copper using OVAC reached equilibrium very rapidly and that is one of the main advantages of this procedure. However, an extraction time of 10 min was selected in all subsequent studies to guarantee completion of the process even when high volumes of samples were used.

The concentration of chelating agent used in the solvent extraction is a critical factor. The effect of concentration of OVAC between 2.0×10^{-6} and 1.0×10^{-2} M on the extraction of $10 \mu\text{g}$ of copper in 10 mL of aqueous solutions was investigated. Figure 2 shows that quantitative recoveries (93–95%) were obtained over an OVAC concentration range of 1.4×10^{-3} – 1.0×10^{-2} M. Low concentrations of OVAC are therefore sufficient to obtain quantitative extraction of copper. This is another advantage of the procedure since less consumption of the ligand would make the method cheaper to use in routine analyses. Subsequent studies were performed using an OVAC concentration of 2.0×10^{-3} M.

Nitric acid concentrations (0.1–1.0 M) were tested for the back-extraction of Cu(II) ions from the organic phase into the aqueous phase. The copper concentrations were 1.0 mg L^{-1} in 10 mL aqueous solutions on the extraction stage of these experiments. The stripping efficiency was quantitative (92–95%) for all concentrations of nitric acid solution. 1.0 M HNO_3 was chosen as the stripping agent for all subsequent studies since a higher concentration of the back extractant may enable lower volumes of it to be used, yielding a higher preconcentration factor. For this purpose, the effect of the volume of 1.0 M HNO_3 solution on the back-extraction of

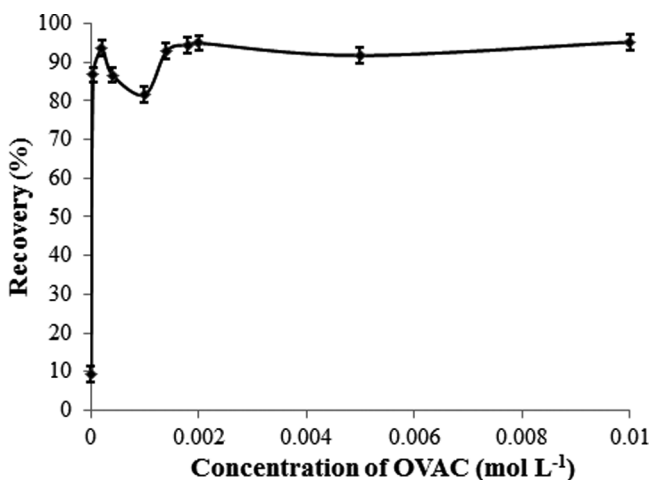


FIGURE 2 Effect of the concentration of the OVAC on the extraction of 1.0 mg L^{-1} of Cu(II) in 10 mL of aqueous solutions, $n = 3$.

Cu(II) ions from the organic phase to the aqueous phase was examined over the range of 1 and 5 mL. Back-extraction efficiency was quantitative (92–94%) over the range 2–5 mL. Therefore, 2 mL of 1.0 M HNO_3 solution was used for all further experiments. A low volume of back extractant is very important in preconcentration experiments because this will enable higher preconcentration factors to be obtained. The effect of back extraction time using 2 mL of 1.0 M HNO_3 solution was examined over the range of 1–20 min using the procedure given above. Quantitative recoveries and reproducible results were obtained after 10 min (Figure 3). This result showed that the

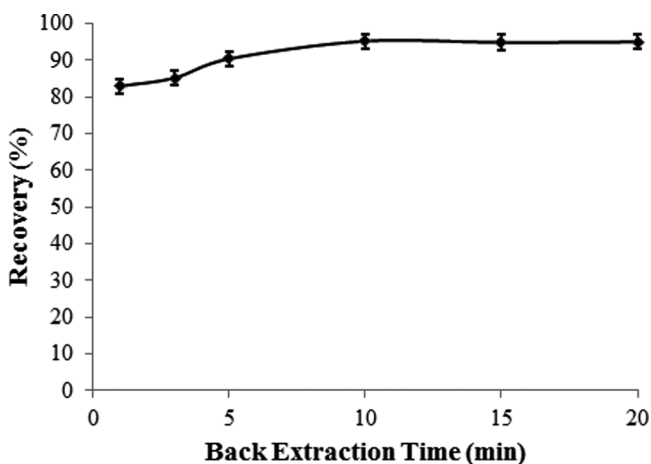


FIGURE 3 Effect of back-extraction time on the extraction of Cu(II), $n = 3$.

back extraction process of copper using 2 mL of 1.0 M HNO₃ reached equilibrium relatively rapidly. However, an extraction time of 20 min was selected to guarantee complete back extraction for all subsequent studies.

The sample volume is a key factor in obtaining a high preconcentration factor. The effect of the sample volume on the recovery of the analyte was studied by varying the sample volumes from 10–100 mL containing the same amount of analyte ion. Therefore, 10, 25, 50, and 100 mL of sample solutions containing 4 µg Cu (II) ions in pH 4.0 buffer were extracted into 5 mL of 2.0×10^{-3} M OVAC in chloroform. Copper was stripped from the organic phase using 2 mL of 1.0 M HNO₃ solution. The results in Table 1 show that the recoveries of the copper ions were unaffected up to a sample volume of 25 mL with an extraction efficiency of 93% being achieved at an aqueous to organic phase ratio of 5:1. A preconcentration factor of 12.5 was, therefore, achieved using 25 mL of sample and 5 mL of 2.0×10^{-3} M OVAC reagent in chloroform. Further increases in aqueous to organic phase ratio resulted in decreased extraction. This may be due to a decrease in the interaction between the organic phase containing OVAC and aqueous phase containing Cu(II). To test this theory, the effect of the sample volume (50 and 100 mL) on the recovery of the analyte was studied using 10 mL (for 50 mL sample volume) and 20 mL (for 100 mL sample volume) of the 2.0×10^{-3} M OVAC reagent. The results shown in Table 1 demonstrate that quantitative recovery was obtained for a 50 mL sample volume. Therefore, a preconcentration factor of 25 can be achieved when using 50 mL of the sample and 10 mL of 2.0×10^{-3} M OVAC in chloroform. It should be noted that double the volume of chloroform was used to improve the preconcentration factor. Since it is an environmental hazard, 5 mL of chloroform was selected as the optimal volume of organic phase even though it gives a lower preconcentration factor.

Effect of Matrix Ions

An interference study was undertaken in which model solutions containing concomitant ions were used to determine their effects on the

TABLE 1 Effect of volumes of aqueous phase and organic phase on the recovery of copper (n = 3)

Aqueous sample volume (mL)	Organic phase volume (mL)	Back extraction volume (mL)	Recovery (%)
10	5	2	94.3 ± 0.9
25	5	2	93.4 ± 1.2
50	5	2	81.6 ± 1.4
100	5	2	55.5 ± 1.8
50	10	2	91.1 ± 0.9
100	20	2	85.7 ± 1.5

extraction efficiency of Cu. The potential interference effects from several elements were determined individually to make the study more complete. Solutions (10 mL) containing 10 µg Cu(II) and various amounts of individual interfering ions were treated according to the recommended procedure. The tolerance limit is defined as the ion concentration causing a relative error smaller than $\pm 5\%$ relative to the signal of the analyte alone.

TABLE 2 Comparative data from recent studies on preconcentration of copper

Method	Technique	Sample	Detection limit ($\mu\text{g L}^{-1}$)	Preconcentration factor	Reference
Solvent extraction	FAAS	Tap water, river water, and seawater samples	0.61	12.5	This work
Cloud point extraction	FAAS	Water, serum, and hair samples	0.94	25	[14]
Solid phase extraction	FAAS	Water samples and multivitamin/multielement supplements	0.9	100	[16]
Coprecipitation	FAAS	Natural water and soil samples	1.36	10	[22]
Cloud point extraction	Spectrofluorimetric	Water samples and parenteral solutions	0.29	10	[28]
Cloud point extraction	Spectrophotometric	Food and water samples	5.0	22	[37]
Membrane filtration	FAAS	Food, water, and geological samples	1.2	60	[38]
Organic drop microextraction	FAAS	Water, food, and rock samples	4.1	13	[39]
Solvent extraction	High-performance liquid chromatography	River water	3.0	–	[40]
Solvent extraction	FAAS	Water, hair, and food samples	0.8	20	[41]
Cloud point extraction	FAAS	Vegetable, liver, meat, and water samples	0.6	30	[42]
Solid phase extraction	FAAS	Water samples	0.2	100	[43]
Solid phase extraction	FAAS	Food samples	1.2	100	[44]
Solid phase extraction	FAAS	Water samples	12	10	[45]

TABLE 3 Results for the certified reference materials

Reference material	Certified value ($\mu\text{g L}^{-1}$)	Found value ^a ($\mu\text{g L}^{-1}$)	Recovery (%)	R.S.D (%)	$ x - \mu ^b$	$\frac{t_s}{\sqrt{N}}^c$
QCS-19 High purity standard	4.0	4.2 ± 0.2	104	4.8	0.2	0.3
SLRS-5 River water	17.4 ± 1.3	16.7 ± 0.7	96	4.2	0.7	1.1

^aMean value ± standard deviation based on four replicate determinations.

^bx: experimental mean value, μ : certified value.

^ct: statistical value (For 3 degrees of freedom, the critical value of t at the 95% confidence level is 3.18); s: standard deviation; N: number of independent determinations.

Results demonstrated that 100 mg L⁻¹ Al(III), Cd(II), Cr(III), Fe(III), Mn(II), Ni(II), Zn(II), Ba(II), Mg(II), Ca(II), Co(II), and Pb(II) had no significant effect on the extraction and determination of Cu(II). The results indicate that this method may easily be applied for the determination of copper in natural water samples.

Analytical Figures of Merit

The analytical performance of the optimized method was evaluated. A calibration curve over the range of 2.0–100 $\mu\text{g L}^{-1}$ Cu(II) was obtained using 25 mL of Cu(II) solutions treated using the optimized conditions. The calibration equation was $A = 0.0029C + 0.0026$ with a correlation coefficient of 0.9999, where A is absorbance and C is the concentration of Cu(II). The limits of detection (LOD) and quantification (LOQ) were calculated after the procedure was applied to the blank solutions. The limits of detection and quantification were defined as 3s/m and 10s/m, where s is standard deviation of fifteen replicate signals and m is the slope of the calibration curve after preconcentration, were 0.61 $\mu\text{g L}^{-1}$ and 2.0 $\mu\text{g L}^{-1}$, respectively.

A comparison with data from other recent studies for the determination of Cu(II) ions in various samples is given in Table 2. The detection limit and preconcentration factor obtained by the present method are better than the majority of the methods given in Table 2.

TABLE 4 Recovery results for copper in water samples

Sample	Measured ^a ($\mu\text{g L}^{-1}$)	RSD ^b (%)	Added ($\mu\text{g L}^{-1}$)	Found ^a ($\mu\text{g L}^{-1}$)	RSD ^b (%)	Recovery (%)
Tap water	6.57 ± 0.19	2.9	2.0	8.70 ± 0.34	3.9	107
River water	1.51 ± 0.21	13.9	4.0	5.44 ± 0.21	3.9	98
Seawater	2.76 ± 0.19	6.9	2.0	5.00 ± 0.34	6.8	112

^aMean value ± standard deviation based on three replicate determinations.

^bR.S.D: Relative standard deviation.

Accuracy of the Method

Two certified reference materials (SLRS-5 riverine water and QCS-19 aqueous standard) were analyzed to evaluate the accuracy of the developed method. Table 4 shows that the results were in good agreement with certified values. The precision was between 4.2 and 4.8% relative standard deviation (RSD). Table 3 indicates that the recoveries for certified reference samples were between 96 and 104%. Application of the student's *t*-test to the results of the proposed method and certified values showed that $|x - \mu|$ differences are smaller than $\frac{ts}{\sqrt{N}}$ for certified samples, indicating that there is no evidence of systematic error in the method.

Application to Water Samples

The method was applied to the determination of Cu(II) in tap water, river water, and seawater. The accuracy of the solvent extraction method was evaluated by using spike/recovery experiments. The results presented in Table 4 demonstrate that quantitative recoveries were obtained (98–112%). The precision for the determination of analyte in the spiked water samples was in the range 3.9–6.8% RSD. The results indicate that the method is capable of matrix-free determination of copper in seawater. The method can therefore be used to analyze seawater. Since the concentrations of the concomitant ions in seawater are much higher than for most other natural waters and the procedure has been confirmed as being independent of matrix effects, the method developed can be applied to the separation and preconcentration of Cu(II) in natural waters.

CONCLUSIONS

Preconcentration and matrix separation using the OVAC reagent combined with detection by FAAS was a reliable method for the determination of Cu(II) in natural water samples. The developed method was simple, sensitive, reliable, and requires only 11 min for the separation and preconcentration of Cu(II). However, 10 min for extraction and 20 min for back extraction giving a total of 30 min were used to analyze samples in this work. The precision and accuracy of the method were satisfactory. The OVAC reagent was a powerful complexing agent for the selective extraction of Cu(II) ions. The stripping of Cu(II) from the organic phase was achieved using 2 mL of 1.0 M HNO₃ solution in one step. The method also had good tolerance towards many interfering ions and was relatively rapid compared with other extraction methods reported in the literature.^[29,30,33,46] It was concluded that the method may be a reliable

alternative for the separation and preconcentration of Cu(II) in natural waters. The method could be used in conjunction with other analytical techniques, such as ICP-OES and ICP-MS. If instrumentation such as these is used, then a much lower detection limit would be obtained.

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