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Ultra-Trace Determination of Copper and Silver in Environmental Samples by Using Ionic Liquid-Based Single Drop Microextraction-Electrothermal Atomic Absorption Spectrometry

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Abstract: A sensitive, selective and effective ionic liquid-based single drop microextraction technique was developed by using ionic liquid, 1-hexyl-3-methylimidazolium hexafluorophosphate, C_6MIMPF_6, coupled with electrothermal atomic absorption spectrometry (ETAAS) for the determination of copper and silver in environmental samples. Dithizone was used as chelating agent. Several factors that influence the microextraction efficiency and ETAAS signal, such as pH, dithizone concentration, extraction time, amounts of ionic liquid, stirring rate, pyrolysis and atomization temperature were investigated and the microextraction conditions were established. In the optimum experimental conditions, the detection limits (3 s) of the method were 4 and 8 ng L^{-1} and corresponding relative standard deviations (0.1 µg L^{-1}, n = 6) were 4.2% and 4.8% for Ag and Cu, respectively. The developed method was validated by analysis of a certified reference material and applied to the determination of silver and copper.

Keywords: Ionic liquids, Single-drop microextraction, Electrothermal atomic absorption spectrometry, Silver, Copper, Preconcentration

INTRODUCTION

The determination of trace metal concentration in environmental and biological samples is increasingly getting important in contamination monitoring studies. In spite of great improvements in the sensitivity and selectivity of modern instrumental analysis such as ICP-MS, ICP-AES and electrothermal atomic absorption spectrometry (ETAAS), difficulties still lie in the analysis of trace heavy metals, due to both their low abundance levels in the samples and the high complexity of the sample matrices1-4. In order to achieve accurate, reliable, and sensitive results, preconcentration and separation are needed when the concentrations of analyte metal ions in the original material or the prepared solution are too low to be determined directly by ETAAS 5. Various classical methods including solvent extraction 6-8, solid phase extraction9-22 and precipitation23, 24 have been used for this purpose. However, most of these techniques have some disadvantages such as the requirement for large amount of toxic solvents, time consuming nature of the procedures and probability of sample contamination. Attempts to overcome these drawbacks have led to the development of novel methodologies, which main advantages are speed and negligible volume of toxic solvent used.

One group of these methodologies is liquid-phase microextraction (LPME) techniques 25-27. Single drop microextraction (SDME) is a mode of LPME with several advantages like noticeable reduction in the amount of organic solvent used, simplicity, cost-effectiveness, and high analytical

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frequency. Moreover, SDME combines extraction, preconcentration, and sample introduction in one step 28, 29. In recent years, some reports on the use of SDME for preconcentration of metal ions prior to detection by ETAAS or ETV-ICP-MS have been reported 30-36. In most of these procedures, however, very toxic solvents such as benzene, toluene, or chloroform have been used as extraction phase.

Room temperature ionic liquids (RTILs) are salts resulting from combination of organic cations with various anions, which are liquid over a wide temperature range including room temperature. They have recently attracted special interest as environmentally-friendly solvents to replace traditional volatile organic solvents in various area of chemistry. Many researchers for developing green processes have used RTILs based on alkyl imidazolium hexafluorophosphate. However, it should be noted that these compounds may be potentially toxic due to the instability of the PF_6^- anion towards hydrolysis in contact with moisture, which results in forming some volatile species including HF and POF_3 37. RTILs have some unique physicochemical properties such as negligible vapor pressure, non-flammability as well as good extractability for various organic compounds and metal ions, which make them very useful for LLE and LPME38-41.

The attempts of our group have currently been focused on the application of RTILs in SDME of metal ions with direct injection into the graphite furnace 42, 43. We have improved the sensitivity of this technique by increasing the volume of suspended drop by attaching a plastic tube to the tip of syringe needle and creating grooves in the inner surface of the tube. In the present work, the ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate, C_6MIMPF_6, was employed as a solvent for improving SDME of silver and copper as dithizone complex. The extracted complexes were directly injected into the graphite furnace.

MATERIALS AND METHODS

Apparatus

A Shimadzu (Kyoto, Japan) Model AA-670G atomic absorption spectrometer equipped with a GFA-4A graphite furnace atomizer and deuterium lamp background correction was employed. Deuterium lamp background correction was employed to correct for the non-specific absorbance. Silver and copper hollow cathode lamps (Hamamatsu photonics K.K., Japan) were used as the radiation sources. The operating conditions of the hollow cathode lamps were those recommended by the manufacturer. Pyrolytically coated graphite tubes were used throughout. Argon 99.999% (Roham gas Co. Tehran, Iran), with 1.5 L min^{-1} flow rate, was used as a protective and purge gas. The detailed graphite furnace temperature program used for the determination of Ag and Cu are shown in Table 1.

Table 1. Optimum operating conditions for SDME-ETAAS of silver and copper

	Ag	**Cu**
Wavelength (nm)	328.1	324.8
Lamp current (mA)	6	6
Spectral bandpass (nm)	0.5	0.5
Background Correction	Deuterium	Deuterium
Drying temperature (ºC)	120 (ramp 20 s)	120 (ramp 20 s)
Prolysis temperature (ºC)	950 (hold 40 s)	1000 (hold 40 s)
Atomization temperature (ºC)	1800 (hold 4s, gas stop)	2400 (hold 4s, gas stop)
Cleaning temperature (ºC)	3000 (hold 2 s)	3000 (hold 2 s)
Argon purge gas flow rate (L min^{-1})	1.5	1.5
Determination mode	Peak height	Peak height

A 10-µL microsyringe (Hamilton) was employed to introduce 8 µL of ionic liquid extracting phase to the solution and to inject it into the graphite furnace. However, It is not possible to suspend a microdrop of C_6MIMPF_6 from the tip of a bare needle because it is easily released. In order to avoid this problem, a grooved plastic tube was attached to the tip of microsyringe as described in detail elsewhere43. An electronic analytical balance (Libror, AEL-200, shimadzu) was used for weighting the solid materials. An IKA (Germany) magnetic stirrer model RH D KT/C was used for stirring the solutions.

Standard solutions and Reagents

All chemicals used were of analytical-reagent grade and all solutions were prepared with doubly distilled water (obtained from Ghazi Serum Co., Tabriz, Iran).

A stock standard solution of silver and copper was prepared by dissolving an appropriate amount of $AgNO_3$ and Cu $(NO_3)_2$ (Merck) into a 100 mLflask and diluting to the mark with acidic (HNO_3) distilled water. The working solutions of silver and copper were made by suitable dilution of the stock solution with doubly distilled water. 0.0012 mol L^{-1} solutions of dithizone (Merck) were prepared in ethanol. A 0.1% (w/v) chemical modifier solution was prepared by diluting $Pd(NO_3)_2$ stock solution (10 g L^{-1}, Merck).

Sample preparation

Water samples including river, lake, underground, and subterranean canal waters were collected from local sources (Tabriz and Tasooj). After sampling, they were filtered through Rund filter paper (blue band, no. 300210) to remove suspended particulate matter. Aliquots of 3 mL from each sample solution were used for the analysis.

A standard reference material, NIST SRM 1643e (Trace Elements in Water) was used for validation of the method. Suitable aliquot of this sample was diluted 25 fold and 3.0 mL of this solution was subjected to the analysis according to the recommended procedures.

SDME procedure

3.0 mL of sample was added into a 5-mL capacity vial with a septum and a magnetic bar. Then 70 µL 0.0012 mol L^{-1} dithizone solution was added. The vial was placed on a magnetic stirrer with a stirring rate of 1000 rpm. A 8-µL volume of C_6MIMPF_6 was drawn into the microsyringe and the syringe was fixed above the vial with a clamp. After introducing the needle through the septum, the needle tip was immersed into the sample solution and the microdrop was exposed. The microdrop was left for 12 min under constant stirring, and then it was aspirated back into the microsyringe and injected manually into the graphite furnace. Ten microliter of palladium modifier (0.1 %) was injected into the furnace. Then, the temperature program in Table 1 was followed. Calibration was performed using aqueous calibration solutions submitted to the same SDME procedure described above.

RESULTS AND DISCUSSION

Optimization of ETAAS conditions

The selection of an appropriate pyrolysis temperature is very important for removing as much the matrix as possible while preventing the pyrolysis loss of the analyte prior to atomization step. Preliminary experiments indicated that the temperature program suggested by the manufacturer was not efficient in this method. Therefore, the effects of pyrolysis and atomization temperatures and the holding time on the determination of Ag and Cu were investigated. Moreover, it was found that the use of a chemical modifier to reduce matrix interferences and to increase analytical signal is indispensable. Pd $(NO_3)_2$ was used as a common chemical modifier. Figure 1 shows the pyrolysis curves of silver and copper in the presence of this modifier. It can be seen that the pyrolysis temperature reached a maximum at 950 ºC and 1000 ˚C for Ag and Cu respectively.

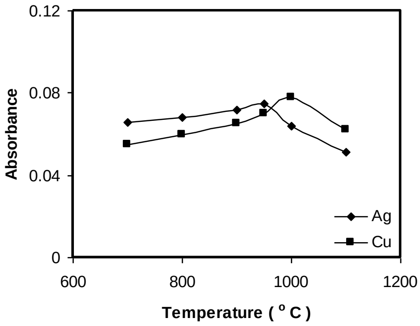

Figure 1. pyrolysis curve (atomization temperatures, 1800 ºC and 2400 ºC for Ag and Cu respectively; pyrolysis time, 40 s).

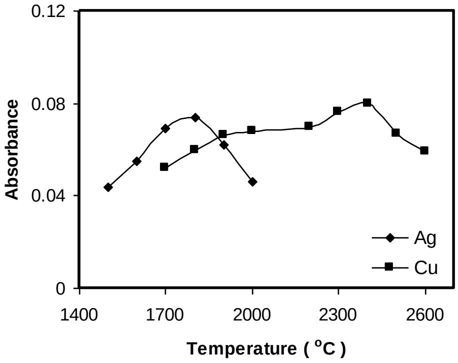

Figure 2. atomization curve (pyrolysis temperature, 950 ºC and 1000 ºC for Ag and Cu respectively; atomization time, 4 s) for the single drop microextraction of 0.1 µg L^{-1}Ag and Cu. Other conditions are given in Table 1.

The effect of pyrolysis time on the absorbance of Ag and Cu was also investigated. The results revealed that the absorbance signals of both elements enhanced with increasing pyrolysis time up to 40 s and no appreciable improvements were obtained for longer times. As a result, a pyrolysis time of 40 s was chosen.

Using the chosen pyrolysis temperatures and times, the effect of the atomization temperature on analytical signals of Ag and Cu was studied. It was found that the signal intensity of Ag and Cu increased with the increase of atomization temperature. The maximum signal intensities of Ag and Cu were obtained at 1800 ◦C and 2400 ◦C, respectively and the results are shown in Figure 2. The results showed that the atomization time had little effect on atomic signals. Therefore, the recommended times by the manufacturer were used as shown in Table 1.

Optimization of microextraction conditions

Extraction of metal ions requires a chelating agent to form an appropriate complex with these ions. In this work dithizone was used as a common chelating agent for the extraction of silver and copper. The effect of dithizone concentration on the extraction efficiency of silver and copper was also investigated and the results are shown in Figure 3.

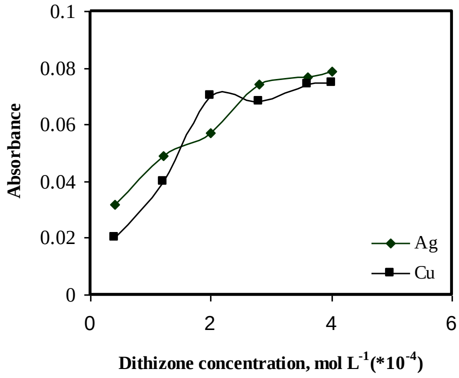

Figure 3. Effect of dithizone concentration on the absorbance of Ag and Cu. Conditions: Ag and Cu, 0.1µg L^{-1}; dithizone, 2.8×10^{-5} mol L^{-1}; stirring rate, 1000 rpm; extraction time, 12 and 15 min for Ag and Cu respectinely ; microdrop volume, 8 µL. Other conditions are as Figure 2.

The absorbance signal increased with increasing dithizone concentration up to about 2.8×10^{-5} mol L^{-1}. Above this concentration the absorbance remained unchanged. Therefore, 2.8×10^{-5} mol L^{-1} of dithizone was selected as the optimum value.

Since concentration of sulfuric acid greatly influences the Ag-dithizone complex formation, its effect was studied in the range of 0.01-0.3 mol L^{-1}. The results are illustrated in Figure 4.

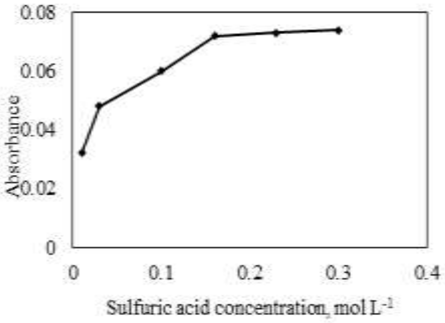

Figure 4. Effect of sulfuric acid concentration on the absorbance of Ag. Other conditions are as Figure 3.

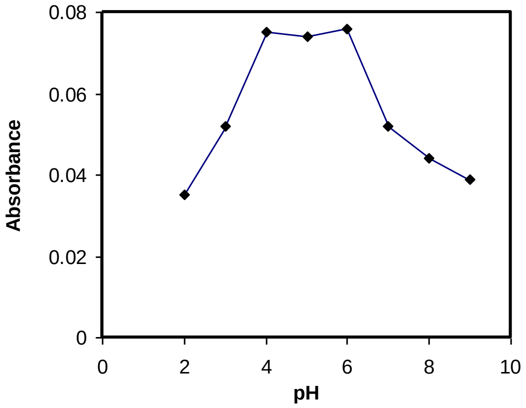

Figure 5. Effect of pH on the absorbance of Cu. Other conditions are as Figure 3.

The absorbance signal for silver was reached a maximum in 0.16 mol L^{-1} sulfuric acid solution and remained constant for higher acid concentrations. The effect of pH on the formation and extraction of Cu- dithizone was studied within the pH range of 2–9. The results are illustrated in Figure 5. The absorbance signal for copper is relatively constant in the pH range of 4–6 and diminishes at higher pH values. Therefore, a pH value of 5 was selected for further study. This pH was adjusted by using 1.0 M HCl and NaOH.

One of the important factors in SDME, which affects the extraction efficiency, is the volume of the microdrop. In general, the extraction efficiency is increased with increasing the volume of organic phase. However, increasing the drop volume in SDME usually results in the release of the microdrop. It has been shown that the stability of the organic drop depends on upward floating force, downward gravity and adhesion forces[44]. In our case since the density of ionic liquid phase is greater than that of aqueous solution, the balance between gravity and adhesion force determines the stability of microdrop at the tip of needle. Thus, in order to enhance the adhesion force of the microdrop, a plastic tube was attached to the tip of syringe needle and furthermore, the inner surface of the tube was made rough by grooving. In this way, larger volumes of IL can be suspended at tip of needle and also higher stirring rates can be tolerated. The effect of C_6MIMPF_6 drop size on the absorbance signals of silver and copper, which was investigated in the range of 1-9 µL, is depicted in Figure 6. As can be seen, the signals enhanced considerably with the increasing of the microdrop volume. Since the 9-µL microdrop is relatively unstable and may be released from the tip of the syringe needle, 8 µL was selected as appropriate drop size.

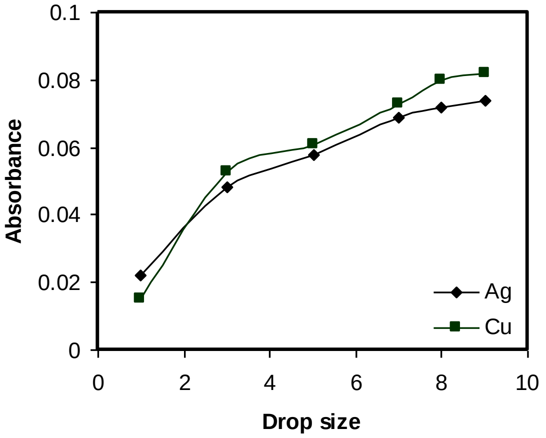

Figure 6. Effect of microdrop volume on the absorbance of Ag and Cu. Dithizone, 2.8×10^{-5} mol L^{-1}other conditions are as Fig. 3.

Another main parameter in SDME is stirring rate which affects the speed of extraction. The observed rate constant for SDME according to Jeannot and Cantwell45 is inversely dependent on the thickness of the interfacial layer surrounding the solvent droplet, which in turn, can be controlled by stirring rate. The effect of sample stirring on the absorbance signal of silver and copper are shown in Figure 7, which indicates that agitation of the sample greatly improves extraction efficiency.

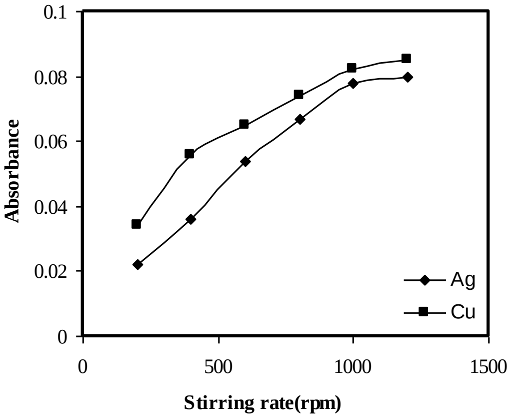

Figure 7. Effect of stirring rate on the absorbance of Ag and Cu. Drop volume, 8 µL, other conditions are as Figure 3.

It should be mentioned that inserting plastic tube with rough inner surface allows using higher stirring rate. However, a steep increase in the stirring rate may lead to the release of the microdrop from the tip of the syringe needle. Increasing stirring rate can also cause a reduction of C_6MIMPF_6 microdrop volume because of enhancing its dissolution. As a compromise between drop stability and higher diffusion of the analyte, a stirring rate of 1000 rpm was selected in this work.

Finally, the effect of extraction time has been studied by varying the exposure time of the microdrop to the aqueous solution from 2 to 18 min and the results are shown in Figure 8. As could be seen, the analytical signals increase quickly with the extraction time until 12 and 15 min for Ag and Cu, respectively. No significant increase was obtained with additional extraction time. Therefore, 12 and 15 min were chosen in the following studies.

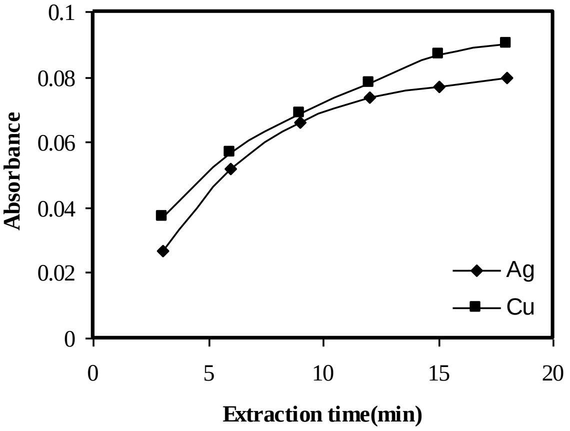

Figure 8. Effect of extraction time on the absorbance of Ag and Cu.

Analytical figures of merit

Under the optimized temperature program and extraction conditions, calibration graphs for Ag and Cu were constructed by preconcentrating a series of standard solutions (with volumes of 3mL) for each analyte. Calibration graph exhibited linearity over the range of 0.01– 0.5 μg L^{-1} for Ag and 0.04–2.0 μg L^{-1} for Cu. The analytical characteristics of the methods are summarized in Table 2. Comparison of analytical features of this method with those of some other preconcentration-ETAAS techniques (Table 2) indicates that the enhancement factor and LOD of the proposed method are better than or comparable with the most of other methods.

Table 2: Analytical characteristics of the proposed method for determination of Ag and Cu.

Parameter	**Ag**	**Cu**
Slope (±SD)	0.712(±0.0024)	0.722(±0.0034)
Intercept (±SD)	0.009(±0.0044)	0.004(±0.0021)
Number of points	9	9
Correlation coefficient (R^2)	0.9980	0.9979
Enhancement factor[a]	71	84
Limit of detection (μg L^{-1})	0.004	0.008
RSD% (n = 6)	4.2	4.8

a Calculated as the slope ratio of the calibration graphs obtained with preconcentration of 3mL solution and without preconcentration.

Interference studies

In view of the high selectivity provided by ETAAS, the possible interferences can mostly be attributed to the preconcentration step. In order to demonstrate the selectivity of the developed microextraction method for the determination of *Ag and Cu, solution of 0.5 μg L^{-1} of studied* analyte containing the corresponding interfering ions were prepared and operated according to the recommended procedure. An ion was considered to interfere when its presence produced a variation of more than 5% in the absorbance of the sample. The results are shown in Table 3. All studied ions were found not to affect Ag and Cu signals in the SDME-ETAAS system when they are present in 50-fold excess. Higher concentrations of alkali and alkaline earth metals can be tolerated. As shown later, these results permit the application of the proposed system for interference-free determination of ultra-trace silver and copper in water samples.

Table 3: Tolerance limits of interfering ions in the determination of 0.1µgL^{-1} Ag and Cu.
Foreign ion to analyte ratio..

Coexisting ions	**Foreign ion to analyte ratio**	
	Ag	**Cu**
Na^+, K^+, Ca^{2+}, Mg^{2+}, CO_3^{2-}, Cl^-	60000	50000 [a]
Ba^{2+}, Li^+, CH_3COO^-, CO_3^{2-}, I^-, F^-	10000	15000
Be^{2+}, SO_4^{2-}, NO_3^-	5000	5000
Mn^{2+}, Cr(III), Cr(VI), Al^{3+}	2500	3000
Fe^{2+}, Zn^{2+}, Bi^{+3}, Fe^{3+}	1000	2500
Hg^{2+}, V(V), Cd^{+2}	500	1000
Pb^{2+}, Ni^{2+}, As(III), Pd^{2+}	100	250
Cu^{2+}	50	-
Au^{3+}	50	100
Ag^+	-	100

[a] maximum ratio tested.

Analysis of real samples

In order to verify the accuracy of the proposed procedure, the method was first applied to the determination of silver and copper in a standard reference material, NIST SRM 1643e Trace elements in water. The contents of Ag (1.04 ± 0.03 µg L^{-1}) and Cu (21.88 ± 0.02 µg L^{-1}) determined by the present method agreed well with the certified values (Ag 1.062 ± 0.075 µg L^{-1} and Cu 22.76 ± 0.31 µg L^{-1}). It can be concluded that the proposed method is accurate and free from systematic errors.

The proposed method was also applied to the determination of silver and copper in four natural water samples. Table 4 shows the obtained results. The recovery tests were also performed by spiking the samples with different amounts of silver and copper before any pretreatment. As can be seen recoveries between 96 and 105.4% were obtained, which again confirm the accuracy of the method.

Table 4. Determination of Ag and Cu in real samples and relative recoveries of spiked samples

Samples	**added (μg L^{-1})**	**Found [a] (μg L^{-1})**	**Recovery (%)**
Subterranean canal water [b]			
Ag	–	0.090 ± 0.002	–
	0.10	0.190 ± 0.004	99
	0.20	0.280 ± 0.005	96
Cu	–	0.150 ± 0.008	–
	0.10	0.255 ± 0.002	105
	0.20	0.342 ± 0.007	96
River water [c]			
Ag	–	0.046 ± 0.006	–
	0.10	0.148 ± 0.007	102.2
	0.20	0.247 ± 0.008	100.5
Cu	–	0.120 ± 0.01	–
	0.10	0.221 ± 0.005	101
	0.20	0.317 ± 0.009	98.5
Lake water [d]			
Ag	–	0.054 ± 0.003	–
	0.10	0.150 ± 0.005	96.5
	0.20	0.257 ± 0.009	101.9
Cu	–	0.180 ± 0.002	–
	0.10	0.282 ± 0.009	102
	0.20	0.377 ± 0.001	98.5
Underground water [e]			
Ag	–	0.079 ± 0.007	–
	0.10	0.18 ± 0.01	105.4
	0.20	0.28 ± 0.01	102.6
Cu	–	0.10 ± 0.008	–
	0.10	0.203 ± 0.004	103
	0.20	0.294 ± 0.01	97

[a] Mean of three determinations ± standard deviation
[b] Obtained from Tasooj, Iran.
[c] From Almas river, Iran.
[d] From orumye lake, Iran.
[e] Obtained from Sharafkhaneh, Iran.

CONCLUSION

A novel SDME method based on the use of RTILs as extraction solvent has been described for the determination of Ag and Cu in water samples. The method was proved to be simple, selective, fast and environmentally-friendly. The proposed method in combination with ETAAS can be applied to monitor very low concentrations of Ag and Cu in real water samples with good accuracy and precision.

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