RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Supramolecular solvent-based dispersive liquid-liquid microextraction of copper from water and hair samples

Funda Aydin [a], Erkan Yilmaz [b], Mustafa Soylak [b]*

[a] Yuzuncu Yil University, Faculty of Pharmacy, Department of Basic Sciences, 65080 Van, Turkey,

[b] Erciyes University, Faculty of Sciences, Department of Chemistry, 38039- Kayseri-Turkey

ABSTRACT

A supramolecular solvent based dispersive liquid-liquid microextraction (SM-DLLME) procedure has been established for separation and preconcentration of Cu(II) in before their determination by microsampling flame atomic absorption spectrometry. The proposed method has involved the use of supramolecular solvent that have been occurred reverse micelles of decanol dispersed in tetrahydrofuran. Cu(II)-pyrolidine-dithiocarbamate complex was formed to increase the interactions with supramolecular phase at pH 6. After supramolecular solvent was added to the medium, the formation of micelles in the nano and molecular size was performed in an ultrasonic bath. The solution was centrifuged and the metal complex formed was extracted into the supramolecular solvent phase. Some analytical parameters that important in the experimental were examined in details. The detection limit (LOD), the quantification limit (LOQ) and the relative standard deviation (RSD) of the developed method were found as 0.11 µg L^{-1} and 0.34 µg L^{-1} and 2.2 %, respectively. The preconcentration factor was 60. Addition/ recovery studies were also performed in water and human hair samples. The accuracy of proposed method was assessed to analyzed certified reference materials. The procedure was applied to determination of copper in water and hair samples.

Key words: Supramolecular solvent, dispersive liquid–liquid microextraction, ammonium pyrolidinedithiocarbamate, Copper, Microsampling-FAAS

*Corresponding author, Fax number: +903524374933, E-mail: soylak@erciyes.edu.tr

1. Introduction

Heavy metals are widespread used in all areas. They are found substantially around the world because of the industrial and agricultural activities.[1] Heavy metals enter our bodies with drinking water, food and air. Some trace levels of heavy metals such as copper are necessary to maintain the metabolism of the human body. Living organisms need this metal for the proper functioning of organs and metabolic processes. However, copper may also be toxic, when taken in too high dose. It can damage an organism.[2]

Meanwhile, the broad applications of technologies such as electrical and electronic, construction, transportation, paint and chemical industry increases the prevalence of copper as a pollutant. A large amount of copper can cause important environmental problems. Copper ions are present in some surface and ground waters due to the misuse of industrial wastes. This widespread use of copper affects human healthy adversely.[3] Many pollution problems related with heavy metals such as ecological and health problems are raising.[4] Many international organizations have set a permissible limit level for metals related to drinking water. For example, the World Health Organization and Council of the European Union have accepted a maximum allowable limit of 2 mg/L for copper in drinking water.[5-6] The determination of toxic heavy metal ions from various matrices at trace level is very important. Due to low concentration of metal and effects of the matrix, the determination of ultra-trace levels in real samples is difficult. Hence, a separation and preconcentration method is necessary for the environmental samples.[7]

Some analytical techniques for preconcentration and separation of metal ions at trace levels such as liquid-liquid or liquid solid extraction techniques have the disadvantage of the use of large amount of organic solvent which are toxic and pollutants for the environment.[8-12] Because of these disadvantages of classical techniques, microextraction techniques which are simple, miniaturized and consume less chemical solvents are widely used in recent years. Single-drop microextraction (SDME),[13-14] solid-phase microextraction (SPME),[15] dispersive liquid–liquid microextraction (DLLME),[16] hollow fiber liquid-phase microextraction (HF-LPME),[17] solidified floating organic drop microextraction (SFODME)[18-19] and supramolecular solvent-based microextraction (SM-SBM)[20-25] are some of microextraction techniques.

Supramolecular solvent-based microextraction techniques have been used for organic and inorganic determinations.[26-28] Supramolecular solvents (SUPRAS) are nano-structured liquids that consisting of assemblies of amphiphiles dispersed in a continuous phase.[29-30] SUPRAS made up of reverse micelles aggregates of alkanols, that spontaneously form in tetrahydrofuran (THF) /water solution through self-assembly processes. These solvents consist of aqueous cavities surrounded by the polar groups of alkanols with the hydrocarbon chains dissolved in THF. The size of the aqueous cavities can be tailored by controlling the THF/water ratio in the bulk solution where alkanols self-assemble. THF plays double role, not only acts as a disperser solvent but also causes self-assembly of decanol. Alkanol-based SUPRAS provide an effective method for isolating and preconcentrating of hydrophobic complex of metals with ligand and organic compounds. These solvents have different interactions with this kind of structure. SUPRAS involve both dispersion and hydrogen bond interactions. This nanostructured liquid provides excellent reaction media for the extraction process.[31] Supramolecular based methods which are developed as an alternative to organic solvents have been widely used as a friendly solvent for extraction of hydrophobic compounds from environmental waters. This method allows us to obtain short extraction time; easy sample preparation and large quantities of toxic substances don’t be used.

The aim of this work was to develop a suitable microextraction method by using supramolecular solvent which was rapid, easy and low cost for separation and preconcentration of copper.

2. Experimental

2.1. Reagents and Solutions

All chemicals used were analytical reagent grade and all aqueous solutions were prepared with ultrapure water. Millipore water purification device (18.2 MΩ cm) was used. 1000 ppm Cu^{2+} solution as a stock solution was prepared from $Cu(NO_3)_2.3H_2O$. Working solutions were prepared by appropriate dilution of the stock solution. % 0.1 (w/v) APDC (ammonium pyrrolidinedithiocarbamate) obtained from Sigma-Aldrich was prepared with using ethanol. Ammonium acetate/acetic acid solution was used as a buffer to adjust pH of sample solutions to pH 6. 1-Decanol and THF that purchased from Merck were used as extraction solvents. These solutions were added to the solutions by mixing 150 µL of 1-decanol and 600 µL of THF for each microextraction. 30 % (v/v) H_2O_2 and 65 % HNO_3 (Merck) were used for digestion of human hair sample. TMDA-51.3 and TMDA-64.2 (Water-Trace Elements) and NCS ZC 8100 2b Human Hair certified reference material was used for validation of the procedure.

2.2. Apparatus

Flame atomic absorption spectrometer (Perkin-Elmer Model 3110) with air–acetylene, and copper hollow cathode lamp was used. The instrumental parameters were adjusted as follows: wavelength 324.8 nm, slit width: 0.7 nm and lamp current: 15.0 mA. A home-made micro-sampling introduction system that was made Teflon was connected to FAAS nebulizer. During the analysis, a 100 micro liters of sample was injected through the space where is the middle of the Teflon, by micropipette.[32]

Brand mark micropipette was used to transfer reagents and injection. Measurements were made considering the peak heights. The pH meter model Sartorius PT-10 with combined glass electrode was utilized for pH adjustment. An ultrasonic water bath (Sonorex) was used to acquire a good cloudy solution. The Centrifuge ROTINA 38 centrifuge equipped with an angle rotor (8 x 50 mL, 5000 rpm) from Hettich was used for separating supramolecular solvent phase from the aqueous phase.

2.3. Supramolecular solvent based dispersive liquid–liquid microextraction procedure

Schematic presentation of the presented procedure is given in Figure 1. Studies of method was carried out with 10 mL model solutions containing 0.10 µg of Cu(II). 10 mL of solution containing copper was placed in a 50 mL conical centrifuge tube. Whereupon, 2.5 ml of acetate buffer solution was added to adjust of sample pH (6.0) using diluted NaOH and HCl solutions. Then, 0.5 mg of ammonium pyrrolidine dithiocarbamate was added. After waiting for approximately 5 minutes for the complex formation, extractor solvent consisting of tetrahydrofuran (600 µL) and 1-decanol (150 µL) was injected rapidly into the sample. The mixture was sonicated for 5 minutes and a cloudy solution was obtained. During this time, supramolecular solvent spontaneously formed into the bulk solution. This solution was centrifuged at 4000 rpm for 10 minutes. Then, supramolecular solvent phases that has low density separated fully from the aqueous phase and formed a solvent solution in the upper phase. The lower water phase was taken up with a pipette and discarded. The volume of supramolecular solvent (about 120-150 µL) was completed to 500 µL with methanol. Then, 100 µl of the solution was injected to micro-sampling introduction system connected to FAAS nebulizer. The measurements carried out using the microinjection system were performed in a continuous aspiration mode. The same procedure was applied for the blank solutions.

2.4. Applications

Tap, well, sea and underground water were collected from various regions of Turkey were used. These samples were filtered through membrane filters with 0.45 µm pores. Then, developed microextraction technique was applied to all water samples.

A human hair sample was taken from men using a stainless steel scissors. All glassware and plastic equipments were immersed in hydrochloric acid to avoid contamination. Then all equipments were washed with deionised water and dried. The hair sample was washed with acetone, deionised water.[33] This procedure was performed again in order to thoroughly remove contaminants adhered. Then, the hair sample was dried and was ready to apply the methods developed. 10 mg of human hair sample was carefully weighted into beaker. 5 mL concentrated HNO_3 (65 %) and 10 mL H_2O_2 (30 %) were added on hair sample. Watch glass was placed over the beaker and digested at 100 ^{0}C. Mixtures were evaporated on the hot plate until to dryness and 5 mL concentrated HNO_3 /10 mL H_2O_2 were added again and were evaporated until to dryness. Distilled water was added to the residue by using micropipette and was transferred to a 50 mL conical-bottom glass centrifuge tube. Final volume of the solution was completed to 5 mL. After the pH of samples was adjusted to 6.0 using diluted sodium hydroxide and hydrochloric acid developed microextraction method was applied to the human hair sample.

3. Results and Discussion

3.1 Effects of the pH

In the extraction operations, the optimum pH determination of the sample solution is very important to form complexes of trace metal ions with a suitable complexing agent and to pass to the extraction phase from the water phase.[34] So, the effect of pH on the recovery of Cu(II) was studied in the range of 2.0-8.0. The results of Figure 2 are that, the recovery % of pH increased after the pH 4. The results were obtained quantitatively in the range of pH 4-7 and the results fall down after the pH 8. Therefore, pH 6 was selected as suitable pH and experiments which later would be done at pH 6.

3.2 Influences of the amount of APDC

SM-DLLME depends on formation of hydrophobic complex between the analytes and the chelating agent.[35,36] To increase the extraction efficiency, the effects of the recovery of the amount ligand which added to the solution in the studied pH was examined by adding in the range 0.1 to 1.5 mg APDC (0.1 %). The results obtained are depicted in Figure 3. Results reveal that; 0.5 mg and greater than 0.5 mg of chelating agent was suitable to obtain quantitative recovery %. When the amount of chelating agent was less than the 0.5 mg, the recoveries founded were not quantitative. 0.5 mg ligand amount was enough to convert all copper to metal complex. Therefore, the amount of ligand was chosen as 0.5 mg to achieve quantitative recoveries (>95%) and this amount of ligand was selected for later studies.

3.3 Type and amount of supramolecular solvent

The influence of supramolecular extraction solvent composition was examined on the microextraction of copper. To obtain the formation of the suitable cloudy solution, different extraction solvent including 1-decanol, undecanol and decanoic acid were tested with THF.

THF both acts as a dispenser solvent and causes self-assembly of decanol that can compose of reversed micelles.[21] The recoveries of copper with decanoic acid-THF, undecanol-THF and 1-decanol-THF were 78 ± 3 %, 85 ± 3% and 98 ± 2%, respectively. The quantitative recovery (>95%9 was obtained with 1-decanol-THF. Therefore, 1-decanol was used to form supramolecular solvent together with THF.

The amount of 1-decanol-THF greatly influences both the volume of extractant yielded and the extraction efficiency in the cloudy solution. Hence, firstly the volume of 1-decanol was studied at the range of 50-250 µL. The results are depicted in Figure 4. The recovery % of Cu(II) was found to be quantitative, when the volume of 1-decanol is above 100 µL. Above 200 µL, the recoveries were decreased. Hence, the volume of 1-decanol was determined as 150 µL as an optimum extraction solvent to obtain quantitative extraction of Cu-APDC complex.

To examine the effect of the volume of THF, a series of microextraction solvents that had different volume of THF (in the range of 200-1000 µL) and in a fixed amount of 1-decanol (150 µL) were prepared. The optimum volume of THF was determined to ensure better micelle formation, better dispersion and to recovery Cu (II) quantitatively. Te recovery of Cu(II) was not quantitative up to 600 µL of THF (Fig. 5). Above this volume, the recoveries were sufficient to obtain quantitative results. Therefore, 600 µl of THF was selected with 1-decanol as supramolecular solvent and this volume was used in subsequent studies.

Quantitative extraction efficiency for copper(II) with presentedmicroextraction system was obtained when the 1-decanol/THF volume ratio was 0.250. The recoveries of copper(II) were not quantitative at other volume ratio of decanol/THF. This point is agree with the literatures. [22-24]

3.4 Effects of ultrasonic mixing time and centrifuge time

After 1-decanol-THF was injected to the model solution medium, model solutions were kept in an ultrasonic bath between 2-10 minutes and were investigated the recoveries. Depending on the ultrasonication time, the recovery of analytes increased linearly up to 5 min. This ultrasonic bath time (5 min.) was adequate for obtaining maximum recovery %. So, this time was selected as optimal for subsequent studies.

Centrifugation time used for extraction is an important experimental parameter in terms of separating of the extraction phase exactly from the water phase. That's why; the influence of centrifugation time was studied with model solutions at 4000 rpm (3500 rcf) between 2-10 minutes. Because of the best separation was achieved in 10 minutes, the centrifugation of sample solution carried out at 10 minutes in following microextraction studies.

3.5 Sample volume

Various experiments were carried out by using different sample volume between 10-50 mL for investigating of the effect of sample volume on the recovery of analyte. Other experimental conditions were kept constant. Copper recovery was found quantitatively (≥ 95%) up to 30 ml, after 30 mL sample volume results decreased. Subsequently, we can study up to 30 mL by this developed method. As a result, preconcentration factor is calculated 60 (the first volume: 30, the final volume: 0.5 mL).

3.6 Effects of matrix components

Because of the matrix effect, trace heavy metals can't be determined directly with FAAS. [37- 43] Therefore, model solutions containing interference ions (alkali, alkaline earth and other ion and metals) that can be found in real samples were prepared to examine the influence of matrix effect on the microextraction of Cu(II). General procedure was applied to these solutions containing 0.5 µg of copper in 10 ml and different amount of foreign ions. The tolerance values were defined as the amount of interference ions. Table 1 shows the results of the interference ions. As can be seen Table 1, matrix ions has no important interference effect on the determination of Cu(II) up to the amount of obtained maximum values.

3.7 Analytical performance

To obtain the calibration curves, five standard solutions were used in the supramolecular solvent. Several analytical parameters such as enhancement factor (EF), limit of detection (LOD), limit of quantification (LOQ) and repeatability were obtained from applying developed method. Calibration curve equation was found as A= 0.00394 + 0.054C (A: The absorbance of the solution, C: Determined Cu concentration of the solution). The correlation coefficient (R^2) was 0.995. Limit of detection (LOD) and limit of quantification (LOD) were determined by using blank solutions. LOD was calculated by using of the ratio value of three times standard deviation of absorbance of ten blank to the slope of the calibration curve (3s/m) was 0.11 µg L^{-1}. LOQ was calculated by using of the ratio value of ten times standard deviation of absorbance of ten blank to the slope of the calibration curve (10s/m) was 0.34 µg L^{-1}. Relative standard deviation (RSD) % was calculated to determine of the precision of the method by using ten model solutions which had 25 µg L^{-1} of copper (II) and this result was founded as 2.2 %. The enhancement factor (EF) calculated as the ratio of the slope of calibration curve of copper(II) after preconcentration to that of prior preconcentration was found as 60.3.

3.8 Accuracy and application of the method

In order to test the reliability of this method, the addition- recovery studies were applied to samples of water and hair. Different amounts of copper were added for water and hair samples. The recoveries obtained after the addition of known amounts of copper to the real samples can be seen at the Table 2 and 3. The recoveries ranged between 95-102 %, for water and hair samples. According to the results, the copper recoveries consisted with the addition copper amounts.

In order to evaluate the validity and applicability of the developed method, the method that based on SM-DLLME method was applied under optimum conditions with TMDA-51.3 and TMDA-64.2 water–trace element and NCS ZC 8100 2b human hair certified reference materials (CRMs). The results are shown in Table 4. The recoveries % ranged between 95-100 %. The copper results were obtained close to the certified value.

The developed microextraction method was applied to the determination of copper in hair and water samples given in Table 5.

3.9 Comparison between proposed method and other extraction methods

A comparison of the SM-DLLME method and some of the published extraction methods for preconcentration and determination of Cu(II) was observed in Table 6. As it can be seen, the performed method are comparable with other reported methods that flame atomic spectrometry were applied as detection methods. The values of LOD, relative standard deviation and enhancement factor is generally good except for a few exceptions.[44-51] The presented method can be used to determination of trace level of copper in real samples.

4. Conclusions

Supramolecular-solvent based dispersive liquid liquid microextraction method based on the formation of reverse micelles of decanol dispersed in THF/water has great advantages in many aspects to determine the copper accurately by using microsampling FAAS. The application of SUPRAS method is quite simple and rapid. A single extraction is sufficient and don’t need another extraction procedures. The separation and preconcentration of copper and ready for sample analysis procedures take approximately 35-40 minute. The method is an environmentally friendly method, because it doesn’t require too much organic solvent. The amount of THF (600 µL) and 1-decanol (150 µL) used to create SUPRAS phase is very low. Because the extraction solvent doesn’t need to be evaporated, the direct extraction solvent analysis (in microliters level) can be done to analyze the copper. Besides, a large amount of sample volume doesn’t require and very small sample volume (500 µL) can be analyzed with FAAS in this method. Also, the selectivity of method is good, no interference effect in the presence of a matrix component was observed. Due to such advantages, the developed method is a practical and reliable method to determine copper from environmental water samples and human hair.

References

1 A. Duran, M. Soylak, S.A. Tuncel, *J.Hazard.Mater.*, 2008, **155,** 114-120.

2 S. L. Belli, A. Zirino, *Anal. Chem.,* 1993, **65,** 2583–2589.

3 V. K. Gupta, M. L.Yola, N. Atar, Z. Ustundag, A.O. Solak, *Electrochim. Acta,* 2013, **112,** 541– 548.

4 M. Ghaedi, K. Niknam, K. Taheri, H. Hosseinian, M. Soylak, *Food Chem. Toxicol.,* 2010, **48,** 891-897.

5 World Health Organization. (2008). Drinking Water Quality: Third Edition incorporating the First and Second Addenda, Volume 1: Recommendations. Geneva.

6 Council of the European Union. (1998). Council Directive 98/83/EC on the Quality of Water Intended for Human Consumption.

7 F.A. Aydin, M. Soylak, *Talanta,* 2007, **72,** 187-192.

8 M. Soylak, Y. Akkaya, *Trace Elem. Electroly.,* 2002, **19,** 100-104.

9 M. Soylak, A. Uzun, L. Elci, *Trace Elem. Electroly.,* 2002, **19,** 15-19.

10 M. Soylak, S. Saracoglu, L. Elci, *Trace Elem. Electroly.,* 2003, **20,** 160-165.

11 O. Yalcinkaya, O. M. Kalfa, A.R. Turker, *Turk. J. Chem.,* 2010, **34,** 207-217.

12 D. Nasser, J. Nasrin, A. Y. Kumar, *Turk. J. Chem.,* 2008, **32,** 561-570.

13 A. Jain, K. K. Verma, *Anal. Chim. Acta,* 2011, **706,** 37–65.

14 X. Wen, Q. Deng, J. Guo, S. Yang, *Spectrochim. Acta A,* 2011, **79,** 508–512

15 N. Philiswa, J. Nomngongo, N. Catherine, *Spectrochim. Acta B,* 2014, 98, 54–59.

16 M. Soylak, E. Yılmaz, *Desalination,* 2011, **275,** 297–301.

17 H. Jiang, B. Hu, B. Chen, W. Zu, *Spectrochim. Acta B,* 2008, **63,** 770–776.

18 M. R. Moghadam, S. Dadfarnia, A. M. H. Shabani, *J. Hazard. Mater.,* 2011, **186,** 169–174.

19 S. Dadfarnia, A. M. H. Shabani, *Anal. Chim. Acta,* 2010, **658,** 107–119.

20 S. Jafarvand, F. Shemirani, *Sep. Sci.,* 2011, **34,** 455-661.

21 A. Ballesteros-Gomez, S. Rubio, D. Perez-Bendito, *J. Chromatogr.,* 2009, **1216A,** 530–539.

22 S. Jafarvand, F. Shemirani, *Anal. Methods,* 2011, **3,** 1552-1559.

23 A. Moral, M. D. Sicilia, S. Rubio, *J. Chromatogr. A,* 2009, **1216,** 3740–3745.

24 S. Jafarvand, F. Shemirani, *J. Sep. Sci.* 2011, **34,** 455–461.

25 F. Rezaei, Y. Yaminia, M. Moradi, B. Daraei, *Anal. Chim. Acta,* **2013,** 804, 135–142.

26 E. Yilmaz, M. Soylak, *Talanta,* 2014, **126,** 191–195.

27 F. J. López-Jiménez, S. Rubio, D. Pérez-Bendito, *Food Chem.,* 2010, **121,** 763–769.

28 C. Caballo, M.D. Sicilia, S. Rubio, *Anal. Chim. Acta,* 2013, **761,** 102–108.

29 E. M. Costi, M. D. Sicilia, S. Rubio, *J. Chromatogr. A,* 2010, **1217,** 6250–6257.

30 S. Jafarvand, F. Shemirani, *J. Sep. Sci.,* 2011, **34,** 455–46.

31 A Ballesteros-Gomez, S. Rubio, *Anal. Chem.* 2012, **84**, 342-349

32 E. Yılmaz, M. Soylak, *Talanta,* 2014, 126, 191–195.

33 P. Bermejo-Barrera, O. Muniz-Naveiro, A. Moreda-Pineiro, A. Bermejo-Barrera, *Forensic SCI Inter.,* 2000, **107,** 105–120.

34 Naeemullah, M. Tuzen, T. G. Kazi, D. Citak, M. Soylak, *J. Anal. At. Spectrom.,* 2013, **28,** 1441-1445.

35 M. Salahinejad, F. Aflaki, *J. Chem. Health Risks*, 2013, **3,** 55-64.

36 A. Garcia-Prieto, L. Lunar, S. Rubio, D. P´erez-Bendi, *Anal. Chim. Acta,* 2008, **617,** 51–58.

37 A. Gundogdu, D. Ozdes, C. Duran, V.N. Bulut, M. Soylak, H.B. Senturk, *Chem. Eng. J.,* 2009, **153,** 62-69.

38 A.A. Ensafi, M. Jokar, M. Ghiaci, *J. Iran. Chem. Soc.,* 2015, **12,** 457–467.

39 H.B. Senturk, A. Gundogdu, V.N. Bulut, C. Duran, M. Soylak, L. Elci, M. Tufekci, *J. Hazard. Mater.,* 2007, **149,** 317-323.

40 M. Soylak, N.D. Erdogan, *J. Hazard. Mater.,* 2006, **137,** 1035-1041.

41 M.A. Farajzadeh, M. Bahram, B. G. Mehr, J. A. Jöhnsson, *Talanta,* 2008, **75,** 832–840.

42 M. Soylak, L. Elci, *J. Trace Microprobe Techn,* 2000, **18,** 397-403.

43 M. Tuzen, M. Soylak, *J. Hazard. Mater.,* 2009, **162,** 724-729.

44 N. Jalbani, M. Soylak, *Food Chem.,* 2015, **167,** 433–437.

45 K. Shrivas, N. K. Jaiswal, *Food Chem.,* 2013, **141,** 2263–2268.

46 M. Rajabi, S. Asemipour, B. Barfi, M. R. Jamali, M. Behzad, *J. Mol. Liq.,* 2014, **194,** 166–171.

47 C.A. Sahin, I. Tokgöz, *Anal. Chim. Acta,* 2010, **667,** 83–87.

48 M. Soylak, O. Ercan, *J. Hazard. Mater.,* 2009, **168**, 1527–1531.

49 V.A. Lemos, M.S. Santos, G.T. David, M.V. Maciel, M.A. Bezerra, *J. Hazard. Mater.,* 2008, **159,** 245–251.

50 V.N. Bulut, A. Gundogdu, C. Duran, H.B. Senturk, M. Soylak, L. Elci, M. Tufekci, *J. Hazard. Mater.,* 2007, **146,** 155-163.

51 M. Ghaedi, F. Ahmadi, Z. Tavakoli, M. Montazerozohori, A. Khanmohammadi, M. Soylak, *J. Hazard. Mater.* 2008, **152,** 1248-1255.

Table 1 Effect of some foreign ions on the microextraction of Cu(II) (N=3).

Foreign Ions	Added as	Amount of foreign Ions (mg L^{-1})	Recovery, %
Na^+	$NaNO_3$	3000	101 ± 4
K^+	KCl	3000	100 ± 2
Mg^{2+}	$Mg(NO_3)_2.6H_2O$	2000	98 ± 4
Ca^{2+}	$Ca(NO_3)_2.4H_2O$	2000	106 ± 6
Cl^-	KCl	3000	98 ± 3
SO_4^{2-}	Na_2SO_4	1000	95 ± 3
Mn^{2+}	$Mn(NO_3)_2.4H_2O$	10	97 ± 2
Cr^{3+}	$Cr(NO_3)_3.9H_2O$	10	101 ± 3
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	10	101 ± 4
Zn^{2+}	$Zn(NO_3)_2.6H_2O$	10	101 ± 3
Co^{2+}	$Co(NO_3)_2\cdot6H_2O$	10	102 ± 2
Pb^{2+}	$Pb(NO_3)_2$	5	96 ± 1
Fe^{3+}	$Fe(NO_3)_3\cdot9H_2O$	2.5	98 ± 4
Ni^{2+}	$Ni(NO_3)_3\cdot6H_2O$	2.5	96 ± 4

Table 2 Addition recovery/test procedure for environmental water samples (N=5).

Tap water from Canakkale			Well water from Sivas			Marmara Sea water from Istanbul		
Added (µg)	Found (µg) [a]	% Recovery	Added (µg)	Found (µg) [a]	% Recovery	Added (µg)	Found[a] (µg)	% Recovery
0.00	0.023±0.005	-	0.00	0.028±0.004	-	0.00	0.039±0.009	-
0.25	0.268±0.030	98	0.25	0.281±0.007	101	0.25	0,282±0.007	97
0.50	0.532±0.030	102	0.50	0.516±0.007	98	0.50	0,539±0.009	100

[a] Mean ± standard deviation

Table 3 Addition recovery/test procedure for human hair (N=5).

Added (μg)	Found (μg)[a]	Recovery,%
0.00	0.140 ± 0.020	-
0.50	0.479 ± 0.021	96
1.0	0.948 ± 0.039	95

[a] Mean ± standard deviation

Table 4 The analysis results for certified reference materials (N: 5).

TMDA-51.3 Water - Trace Elements ($\mu g\ L^{-1}$)			TMDA-64.2 Water - Trace Elements ($\mu g\ L^{-1}$)			NCS ZC 8100 2b Human Hair ($\mu g\ g^{-1}$)		
Certified value	Found	Recovery (%)	Certified value	Found	Recovery (%)	Certified value	Found	Recovery (%)
89.2	88.8 ± 8 [a]	100	274	263 ± 10	96	33.6 ± 2.3	31.9 ± 1.2	95

[a] Mean ± standard deviation

Table 5 The application of the developed method in hair and water samples (N= 5).

Sample	Concentration of copper μg g^{-1}
Hair sample 1	4.8 ± 0.7 [a]
Hair sample 2	21.1 ± 0.7
	Concentration of copper, μg L^{-1}
Well water from Kayseri	126 ± 5
Sea water from Marmara sea from Çanakkale	158 ± 5
Underground water from Kayseri	353 ± 2

[a] Mean ± standard deviation

Table 6 Characteristic data obtained by using microextraction (SM-DLLME) for determination of copper by FAAS and comparison with other similar extraction techniques

Method	Sample	EF[a]	LOD [b] (μg L^{-1})	RSD [c] (%)	Ref
DLLME	Water	42	3.00	5.1	43
UA-IL-DLLME	Food	100	0.17	3.0	44
DLLME	Cereals, Vegetables	55	0.16	1.5	45
UA-IL-DLLME	Water	50	1.90	3.8	46
SFODME	Water	333	0.40	0.9	47
MWNTs	Water	60	1.46	-	48
CPE	Food	29	1.50	6.4	49
SM-DLLME	Water, human hair	60	0.11	2.2	This work

a: Enrichment factor, b: Limit of detection, c: Relative standard deviation; DLLME: Dispersive liquid–liquid microextraction, UA-IL-DLLME: ultrasonic assisted-ionic liquid based-liquid–liquid microextraction, SFODME: Floating organic organic drop microextraction, MWNTs: Solid phase extraction on multi-walled carbon nanotubes, CPE: Cloud-point extraction, SM-DLLME: Supramolecular solvent liquid–liquid microextraction.

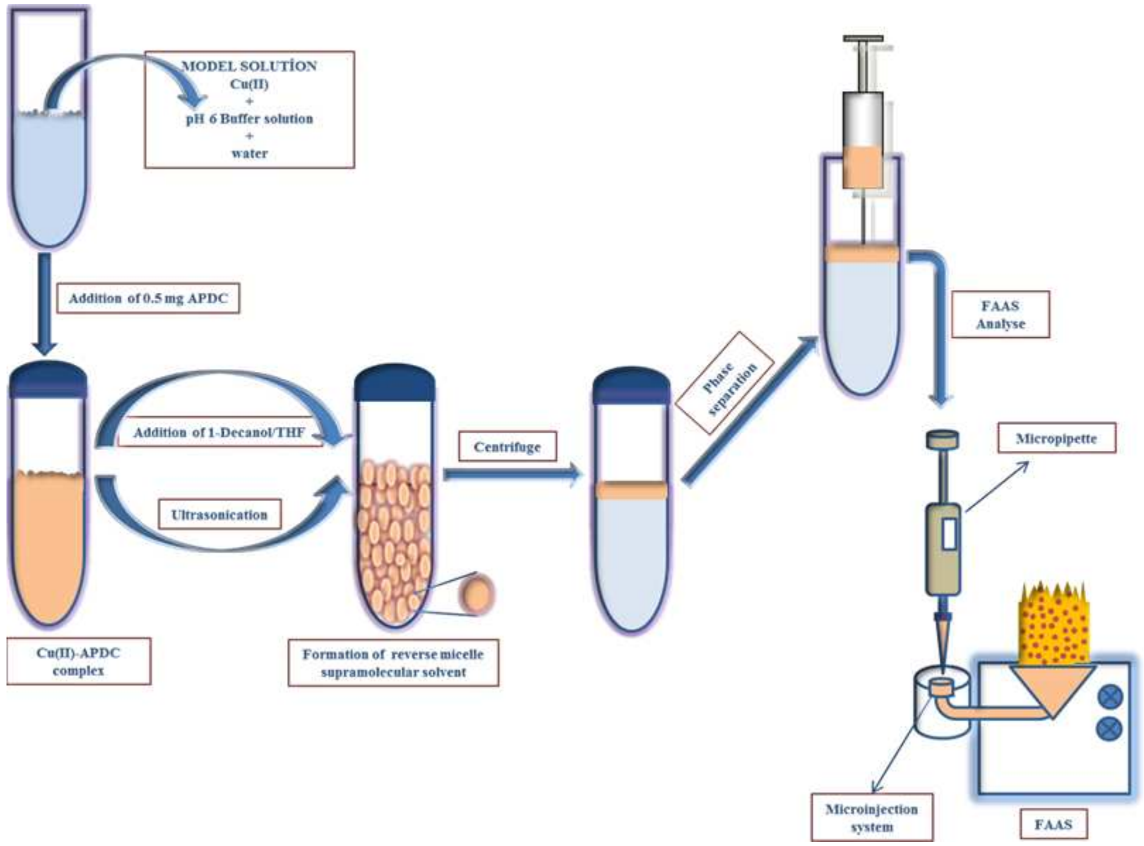

Fig. 1 Schematic presentation of the presented procedure (SM-DLLME)

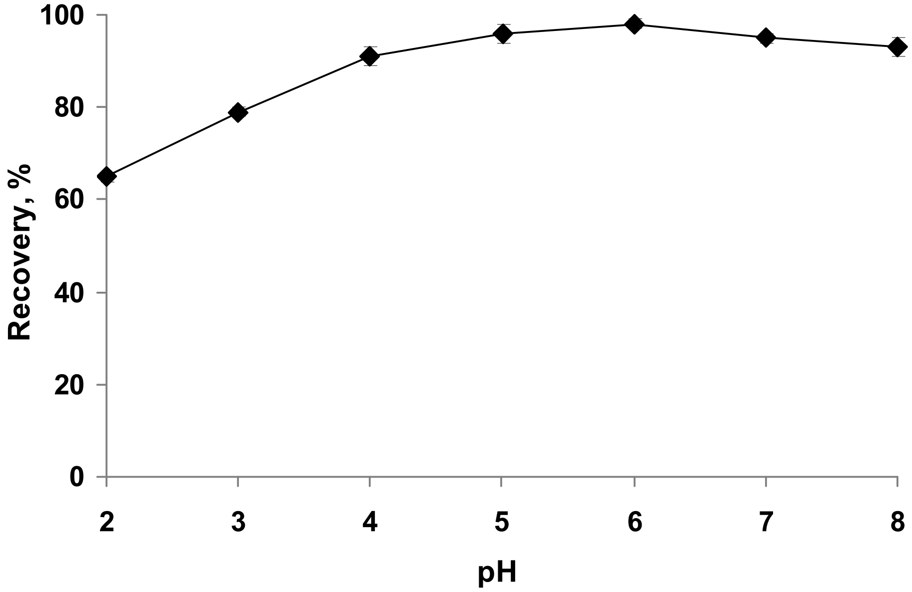

Fig. 2 Effect of the pH on the recovery of Cu(II) by SM-DLLME (N=3).

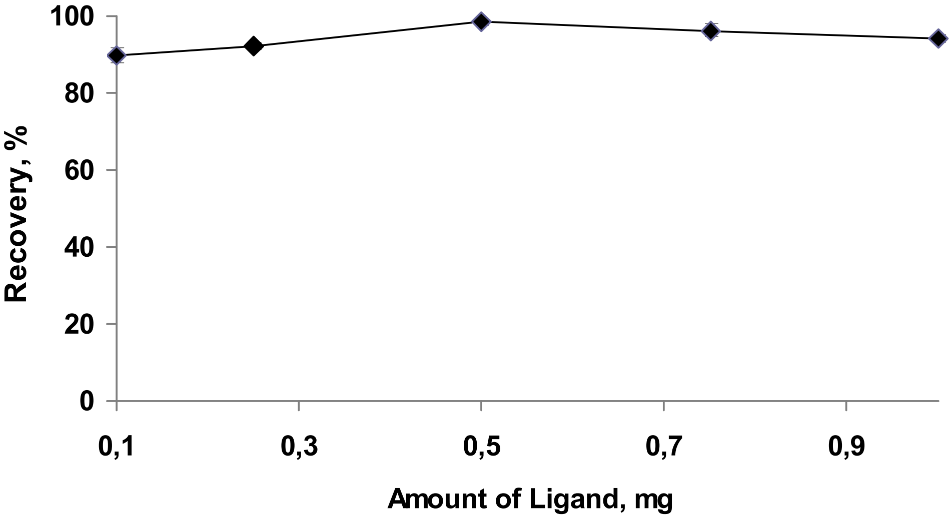

Fig. 3 Effect of amount of APDC on the recovery of Cu(II) obtained from SM-DLLME (N=3).

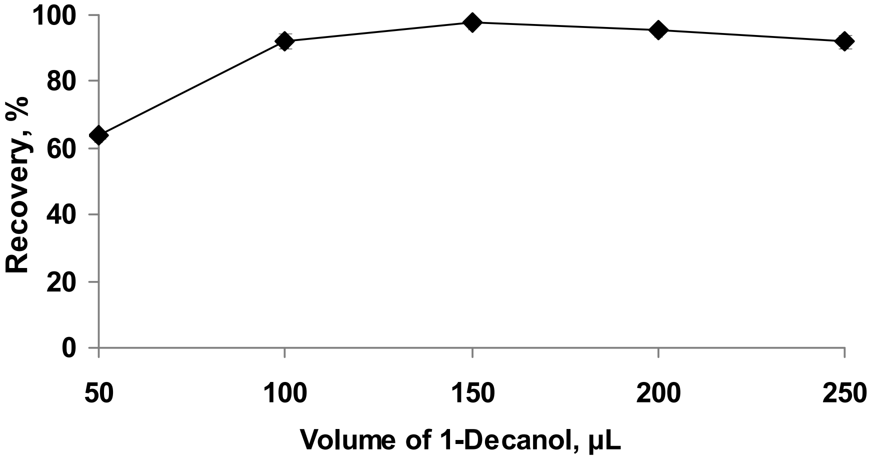

Fig. 4 Effect of volume of 1-decanol on the recovery of Cu(II) by SM-DLLME (N=3).

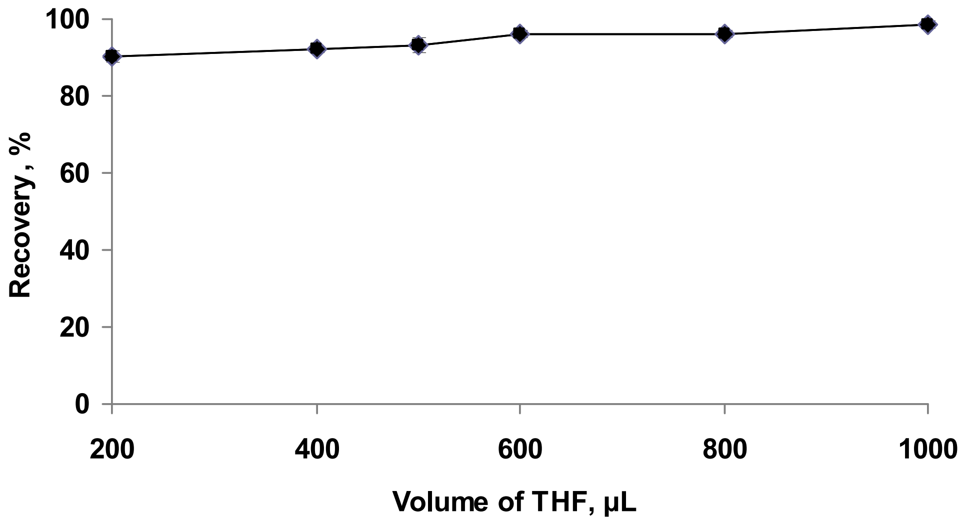

Fig. 5 Effect of volume of THF on the recovery of Cu(II) obtained from SM-DLLME (N=3).