

Determination of Trace Amounts of Copper in Samples of Sarcheshmeh Copper Mine Using Dispersive Liquid-Liquid Microextraction Based on the Solidification of Floating Organic Droplets Prior to FAAS

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Abstract: In this article dispersive liquid-liquid microextraction [1, 2] based on the solidification of floating organic drop (DLLME-SFO) [3] was successfully used as a sample preparation method prior to flame atomic absorption determination of trace amount of copper in standard and wastewater samples [4]. Several factors that may be affected on the extraction process, such as extraction and disperser solvent, the volume of extraction and disperser solvent, effect of salt, pH of the aqueous solution and extraction, time and Ions effect were optimized [5]. Under the best experimental conditions, the calibration curve was linear in the range of 0.8 ng mL^{-1} - $0.5 \text{ } \mu\text{g mL}^{-1}$ of copper and detection limit was 0.2 ng mL^{-1} in the original solution (3Sb/m). The relative standard deviation seven replicate determination of $0.1 \text{ } \mu\text{g mL}^{-1}$ copper was $\pm 1.9\%$. The high efficiency of DLLME-SFO to carry out the determination of copper in complex matrices was demonstrated. Finally, the proposed method has been applied for determination of trace amount of copper in standard and wastewater samples of Sarcheshmeh Copper mine and other factory with satisfactory results.

Keywords: DLLME, Solidification, Wastewater

1. Introduction

Copper is found as a pure metal in nature, and this was the first source of the metal to be used by humans, ca. 8000 BC [6, 7]. It was the first metal to be smelted from its ore, ca. 5000 BC, the first metal to be cast into a shape in a mold, ca. 4000 BC and the first metal to be purposefully alloyed with another metal. Copper is essential to all living organisms as a trace dietary mineral because it is a key constituent of the respiratory enzyme complex [8]. In molluscs and crustacea copper is a constituent of the blood pigment hemocyanin, replaced by the iron-complexed hemoglobin in fish and other vertebrates [9]. In humans, copper is found mainly in the liver, muscle, and bone [10, 11]. The adult body contains between 1.4 and 2.1 mg of copper per kilogram of body

weight. Hence a healthy human weighing 60 kilogram contains approximately 0.1 g of copper. However, this small amount is essential to the overall human well-being [12]. Copper compounds are also used as bacteriostatic agents, fungicides, and wood preservatives. A freshly exposed surface of pure copper has a reddish-orange color. [13] It is used as a conductor of heat and electricity, [14, 15] as a building material and as a constituent of various metal alloys, such as sterling silver used in jewelry, cupronickel used to make marine hardware and coins and constantan used in strain gauges and thermocouples for temperature measurement.

Numerous copper alloys have been formulated, many with important uses. Brass is an alloy of copper [16] and zinc. Bronze usually refers to copper-tin alloys, [17] but can refer

to any alloy of copper such as aluminium bronze. Copper is one of the most important constituents of silver and carat gold and carat solders used in the jewelry industry, modifying the color, hardness and melting point of the resulting alloys. Some lead-free solders consist of tin alloyed with a small proportion of copper and other metals. [18]

2. Instrumentation

Varian model AA 220 flame atomic absorption spectrometer (Australia), a selenium hollow cathode lamp as radiation source (Hamamatsu Photonics, Japan) at 196.0 nm with a slit width of 0.7 nm, 23 mA current and deuterium background corrector, was used for measurement.

The pH values were measured with a Metrohm pH-meter (model: 827, Swiss) supplied with a glass combined electrode. The Centurion Scientific centrifuge (model SIGMA3-16, Germany) was used for centrifuging.

2.1. Reagents and Solutions

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Deionised water was used for all dilutions. Stock solutions of diverse elements were prepared from high purity compounds. The calibration standards were not submitted to the preconcentration procedure. All reagents were evaluated for their contribution to Cu contamination in the blanks. HNO₃ (65%), HCl (37%), H₃PO₄ and NaH₂PO₄·2H₂O (analytical grade) and NaOH solutions was used for adjust pH. Phosphate buffer solutions (H₂PO₄⁻/H₃PO₄) were prepared by mixing of appropriate volumes of 1 mol L⁻¹ sodium dihydrogene phosphate and phosphoric acid solutions for pH 4.

2.2. General Procedure

A solution contains 5.0 µg L⁻¹ Cu, NaCl 10% and baffle was placed in a screw cap glass test tube with conical bottom. 1.5 mL of ethanol (disperser solvent) contains 25 µL of 1-2 dekanol (extraction solvent) was injected rapidly into a sample solution. A cloudy solution (resulted from dispersion of fine droplets of 1-2 dekanol in aqueous sample) was formed in the test tube. The mixture was then centrifuged for 5 min at 4000 rpm. The sediment phase was removed by using a 50 µL micro syringe and 0.50 mL of ethanol was added to it. The final solution was aspirated directly into the flame of AAS against the blank.

2.3. Result and Discussion

In this study, a combination of DLLME with FAAS was developed for determination Copper. Several factors that may affect the preconcentration and extraction process, including pH, type and volume of disperse and extraction solvent, salt type and volume, centrifuging time and rate and extraction time were optimized.

2.3.1. Effect of pH

Since the pH of the aqueous sample solutions is an

important analytical factor in DLLME. The influence of pH on the preconcentration of the analyte ions was examined in the pH range of 4–11 keeping the other parameters constant. The pH of the metal sample solutions was adjusted by using with NaOH and HNO₃ solutions. The results are shown in Figure 1 and showed that maximum recovery for the analyte ions were obtained in the pH range of 4. Accordingly, the further studies were down at pH 10 by using 0.1 mol L⁻¹ phosphate buffer solutions.

2.3.2. Effect of Volume of Disperser and Extraction Solvent

In order to test the effect of solvent volume on the recovery, different volumes of disperser solvent (0.5-3.0 mL ethanol) and different volumes of extraction solvent (15-75 µL 1-2 dekanol) were studied. It was observed that quantitative recovery was obtained at 1.5 mL of ethanol and 25 µL of 1-2 dekanol. However, for convenience, all the experiments were performed with this result.

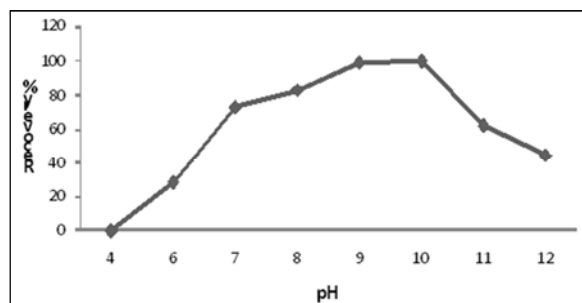


Figure 1. Effect the pH on the extraction of Cu.

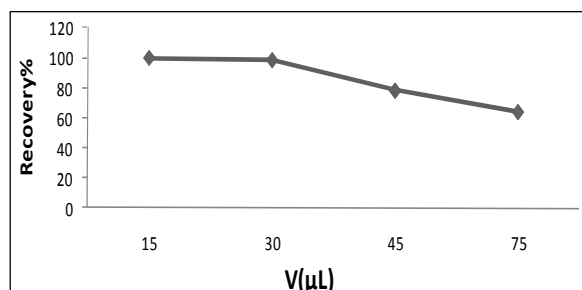


Figure 2. Effect the extraction solvent on the extraction of Cu.

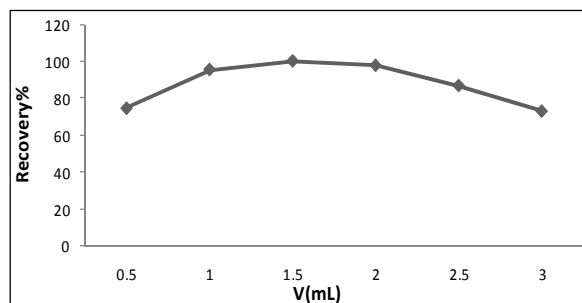


Figure 3. Effect the volume of disperser solvent.

2.3.3. Effect of Salt

The influence of ionic was evaluated at 10% (w/v) NaCl levels while other parameters were kept constant. It was observed that 1ml of NaCl 10% increase recovery and more

than this volume decrease. Therefore 1 mL was used in all experiments.

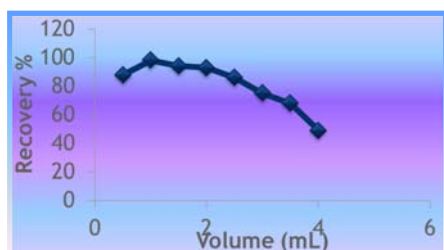


Figure 4. Effect the salt volume on the extraction of Cu.

2.3.4. Effect of the Extraction Time

The extraction of Cu was also studied as a function of extraction time at the optimum conditions. Extraction time was measured by varying the equilibrium extraction time in the range of 1-7 min. The extraction efficiency of Cu showed that after 3 min, maximum recovery was obtained. Therefore, extraction time 3 min was used in all subsequent experiments.

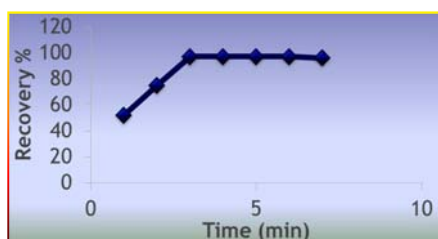


Figure 5. Effect of the extraction time on the extraction of Cu.

3. Analytical Figures of Merit

Under the optimal conditions, the calibration curve for Cu were linear in the range of 0.50- 0.80 $\mu\text{g mL}^{-1}$ in the final solution. Detection limit based on eight times the standard deviation of the blank was 0.20 ng mL^{-1} in the final solution. seven replicate determination of 0.1 $\mu\text{g mL}^{-1}$ of Cu give a relative standard deviation of 1.9% obtained.

4. Application to Real Samples

The high efficiency of proposed method to carry out the determination of Copper in complex matrices was demonstrated. The proposed method has been applied for determination of trace amount of Cu in wastewater copper factory and satisfactory results were obtained. The results are shown in Table 1.

Table 1. Determination of Cu in wastewater.

Sample	Added ($\mu\text{g/mL}$)	Found ^a ($\mu\text{g/mL}$)	Recovery%
No. 1	0.0	10.7 \pm 0.5	----
	50.0	62.0 \pm 2.7	102.6
No. 2	0.0	18.3 \pm 0.8	----
	50.0	69.8 \pm 2.7	103.0
No. 3	0.0	29.7 \pm 1.1	----
	50.0	78.3 \pm 3.1	97.2

Sample	Added ($\mu\text{g/mL}$)	Found ^a ($\mu\text{g/mL}$)	Recovery%
No. 4	0.0	83.1 \pm 2.9	----
	50.0	134.7 \pm 5.5	103.2

^a Average of three determinations \pm standard deviation.

5. Conclusion

This work has been demonstrated combination of DLLME with flame atomic absorption spectrometry provides a novel route for trace determination of Cu in wastewater samples. The main benefits of the DLLME methodology were: minimum use of toxic organic solvent, simplicity, low cost, enhancement of sensitivity, and rapid analysis time.

References

- [1] F. Priego-capote, M. D. Luque de Castro, Trends Anal. Chem. 23 (2004) 644.
- [2] V. Camel, Spectrochim. Acta Part B 58 (2003) 1177.
- [3] M. Ma, F. F. Cantwell, Anal. Chem. 70 (1998) 3912.
- [4] H. Prosen, L. Zupancic-Kralj, Trends Anal. Chem. 18 (1992) 272.
- [5] S. Bjergaard, K. Rasmussen, T. Halvorsen, J. Chromatogr. A 902 (2000) 91.
- [6] G. D. Christian, Anal. Sci. 15 (1999) 1033.
- [7] A. Skoog, M. Donald, Fundamentals of Analytical Chemistry, 4th ed., Holt-Saunders International, 1982.
- [8] M. F. Apendurada, J. Chromatogr. A 889 (2000) 3.
- [9] N. Compillo, R. Penalver, I. Lopez-Garcia, M. Hernandez, J. Chromatography A, 1216 (2009) 6735.
- [10] T. Chen, C. Breuil, S. Carriere, TAPPI J. 77 (1994) 235.
- [11] P. D. Mc Donald, E. S. P. Milford "Solid Phase Extraction", Walters, Milford, MA, 6th ed., 1992, p. 287.
- [12] W. L. Hinze, E. Pramauro, CRC Crit. Rev. Anal. Chem. 24 (1993) 133.
- [13] D. M. Templeton, F. Ariese, R. Cornelis, L. G. Danielsson, H. Muntau, H. P. Van Leeuwen, R. Lobinski, Pure Appl. Chem. 72 (2000) 1453.
- [14] T. Kumazawa, X. P. Lee, K. Sato, O. Suzuki, Anal. Chim. Acta 492 (2003) 49.
- [15] H. Kataoka, H. Lord, J. Pawliszyn, J. Chromatogr. A 880 (2000) 35.
- [16] J. P. Hutchinson, L. Setkova, J. Pawliszyn, J. Chromatogr. A 1149 (2007) 127.
- [17] A. Bidari, E. Zeini Jahromi, Y. Assadi, M. R. Milani Hosseini, Microch. J. 87 (2007) 6.
- [18] P. Vinas, I. Lopez-Garcia, B. Merino-Merono, N. Campillo, M. Hernandez-C'ordoba, Anal Chim Acta 535 (2005) 49.