

Dispersive liquid-liquid microextraction (DLLME) combined with graphite furnace atomic absorption spectrometry (GFAAS) for determination of trace Cu and Zn in water Samples

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Abstract: Dispersive liquid-liquid microextraction (DLLME) combined with graphite furnace atomic absorption spectrometry (GFAAS) was proposed for the determination of trace amounts of Copper and Zinc ions using 8-hydroxyquinoline (8-HQ) as chelating agent. Several factors influencing the microextraction efficiency of Cu and Zn and their subsequent determinations, such as pH, extraction and disperser solvent type and their volume, concentration of the chelating agent and extraction time were studied, and the optimized experimental conditions were established. After extraction, the enrichment factors were 25 and 26 for Cu and Zn, respectively. The detection limits of the method were 0.025 and 0.0033 µg/L for Cu and Zn, and the relative standard deviations (R.S.D) for five determinations of 1 ng/ml Cu and Zn were 8.51% and 7.41%, respectively.

Keywords: Dispersive liquid- liquid micro extraction (DLLME), Graphite furnace atomic absorption spectrometry, copper, Zinc, water samples.

Introduction

In recent years, pollution of the environment by heavy metals has received considerable attention (Carasek et al., 2002). Exposure to these toxic elements imposes risks not only to human health, but also to plants, animals and microorganisms (Estela et al., 2004). Therefore, the determination of various toxic metals such as copper and zinc in environmental samples is very important task (Anthemidis et al., 2004).

Traditional solvent extraction has been used as a basic and powerful method of concentrating for a long time. However, it requires extensive amounts of organic solvents. A special attention is nowadays focused on techniques, which are characterized by a considerable reduction or complete elimination of organic solvents. The solvent-free techniques such as gas phase extraction, membrane extraction and solid phase extraction are limited to volatile and relatively volatile organic compounds, volatile nonpolar compounds and relatively low volatile compounds (Zygmunt et al., 2001). Despite good developments in the modern analytical instruments, which allow great enhancement in aspects of analysis, in many cases the available

analytical instrumentation does not have enough sensitivity for the analysis of natural samples. Sample preparation is still a bottleneck for overall throughput because the involved steps often employ large volumes of hazardous organic solvents (Bidari et al., 2007). Although, the determination of trace metal ions in natural waters is difficult due to various factors, particularly their low concentrations and matrices effects. Pre-concentration and separation can solve these problems and can lead to a higher confidence level and easy determination of the trace elements. Several methods have been reported for the separation and preconcentration of metal ions, such as coprecipitation (Wang et al., 2006), liquid-liquid extraction (LLE) (Pan et al., 2007), solid-phase extraction (SPE) (Taher et al., 2005) and cloud point extraction (CPE) (Ghaedi et al., 2008).

DLLME is a modified solvent extraction method and its acceptor-to-donor phase ratio is greatly reduced compared with other methods. In DLLME, the appropriate mixture of the extraction and disperser solvents is rapidly injected by syringe into aqueous samples containing analytes. Thereby, a cloudy solution forms. In fact, the cloudy state results from the formation of fine droplets of the extraction solvent

which disperse in the sample solution. Then, this cloudy solution is centrifuged and the fine droplets become sediment at the bottom of the conical test tube. The determination of analytes in the sedimented phase can be performed by instrumental analysis. In this extraction method any component in the solution, directly or indirectly after previous (or simultaneous) derivatization reaction, interacts with the fine droplets of the extraction solvent and consequently gets extracted from the initial solution and concentrates in the small volume of the sedimented phase. Simplicity of the operation, rapidity, low sample volume, low cost, high recovery and high enrichment factor are some advantages of DLLME.

DLLME is a miniaturized sample pre-treatment technique. On the other hand, graphite furnace atomic absorption spectrometry (GF AAS) is a microamount sample analysis technique. Therefore, it makes it perfect when a combination of both DLLME and GF AAS is used. The applicability of the approach has been demonstrated for the determination of copper and zinc in water samples.

Materials and Methods

The experiments were performed using a PerkinElmer atomic absorption spectrophotometer AAnalyst800 with a graphite furnace atomizer. A copper hollow cathode lamp, operated at a current of 10 mA and a wavelength of 324.8 nm was used. A zinc hollow cathode lamp, operated at a current of 10 mA and a wavelength of 213.9 nm was used. Pyrolytically coated graphite tubes were used. The sample injection volume was 20 μL in all experiment. The temperature program for the graphite atomizer are listed in Table 1. The pH values were measured with a Metrohm pH-meter (Model: 827, Herisau, Switzerland) supplied with a glass-combined electrode. The Centurion Scientific centrifuge (Model ALC 4232-D) was used for centrifuging.

All solutions were prepared using ultra pure water. The stock solution of copper and zinc (1000 mg L^{-1} for atomic spectroscopy standard) was purchased from Merck (Darmstadt, Germany). Working standard

solutions were prepared by serial dilutions of the stock solution with ultra pure water prior to analysis.

In DLLME method, 5 mL of aqueous sample containing Cu and Zn was placed in a 10 mL screw cap glass test tube. Then, 1.5 ml of methanol (as disperser solvent) containing 250 μL of chloroform (as extraction solvent) and 0.05 $\text{mmol}\cdot\text{L}^{-1}$ 8-hydroxyquinoline (as chelating agent) was rapidly injected into a sample solution by using 2.00 ml syringe. A cloudy solution was formed and separation of the phases was achieved by centrifugation at 3000 rpm for 3 min. After this process, a small droplet of chloroform was sedimented in the bottom of conical test tube. 190 μL sedimented phase was withdrawn into the microsyringe and then injected into the GFAAS for analysis.

Results and discussion

In order to obtain a high enrichment factor, the effect of different parameters affecting the complex formation and extraction conditions, such as kind of extraction and disperser solvent and their volume, pH, concentration of the chelating agent and extraction time were optimized.

Effect of disperser solvent type and volume

The disperser solvent must be miscible in extraction solvent (organic phase) and also sample solution (aqueous phase). Therefore, acetone, methanol, ethanol and acetonitrile were tested. The effect of these solvents on the extraction efficiency of DLLME was investigated using 1.5 ml of each solvent containing 250 μL of CHCl_3 as the extraction solvent. The maximum extraction efficiency of DLLME was obtained by using methanol as a disperser solvent. That is due to the high compatibility of methanol with aqueous solution than other solvents. Therefore, methanol was selected for further experiments.

After finding the disperser solvent type, it was necessary to find the optimum volume of it. Various experiment were performed with different volume of methanol in the range of (0.5 – 3 ml). However, by increasing the volume of methanol, the solubility of complex in water increased also, thereby, analytical signal decreased. So, 1.5 ml methanol was chosen in the following work.

Table 1 The graphite furnace temperature program for copper and zinc determination

Step	Temperature ($^{\circ}\text{C}$)	Ramp (s)	Hold (s)	Argon flow rate (mLmin^{-1})
1: Dry	130	15	30	250
2: Pyrolysis	1200	10	20	250
3: Atomization	2000	0	5	0
4: Cleaning	2450	1	3	250

Effect of extraction solvent type and volume

Choosing the most suitable extraction solvent is of primary importance to achieve good selectivity of the target compounds. This solvent must be immiscible with water and the solubility of analytes in this solvent in organic phase should be higher than the donor phase to promote the extraction of the analytes and in the case of DLLME, the density of the extraction organic solvent must be higher than water. Dichloromethane (CH₂Cl₂), chloroform (CHCl₃), Bromobenzene (C₆H₅Br), Carbon disulfide (CS₂) and carbon tetrachloride (CCl₄) were studied as extraction solvent. A series of sample solution were studied by using 1.5 ml of methanol and 250 μL of different kind of extraction solvents. Three replicate tests were performed for each of these solvents under the same conditions. The results showed (Fig 1) that, extraction efficiency of CHCl₃ is higher than CH₂Cl₂, C₆H₅Br, CS₂ and CCl₄. Therefore, CHCl₃ was selected as extraction solvent for subsequent experiments.

To study the effect of volume the extraction solvent, a series of solutions containing increasing volumes of CHCl₃ (100–500 μL) dissolved in a fixed volume of methanol were subjected to DLLME. The results was observed that the extraction efficiency was increased for increasing volume of CHCl₃ (100–250 μL) and then extraction efficiency was decreased for increasing volume of CHCl₃ (300–500 μL). The decreased ratio lowers the number of droplets formation available for extraction thereby lowering the extraction efficiency. Based on these observations, 250 μL CHCl₃ was used for further experiments.

Effect of pH

The pH of the sample solution is an important factor affecting the formation of complexes and the subsequent extraction. The effect of pH on the DLLME extraction of Cu and Zn was studied in the pH range of 4 to 12. The highest recovery intensity of Cu and Zn

was obtained at pH 6.0. Therefore, pH 6.0 was selected for further study.

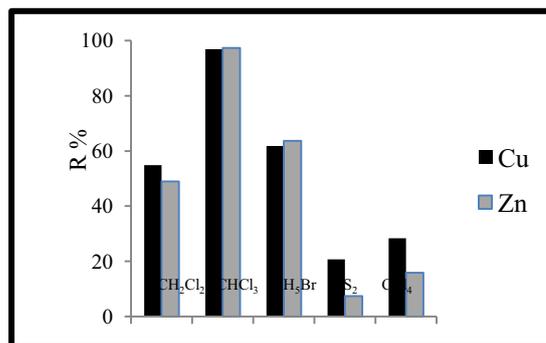


Fig. 1. Effect of different extraction solvent on Cu and Zn determination

Effect of the extraction time

In DLLME, the extraction time is defined as interval time between the injection of the disperser and extraction solvents and the starting of centrifuge. The effect of extraction time was examined in the range of 10 s to 5 min with the constant experimental conditions. The obtained results showed that the extraction time was no significant effect on the signal of copper and zinc. Therefore, the DLLME method was time-independent, which was the most important advantage of this technique.

In this method, the most time-consuming step was the centrifuging of sample solution in the extraction procedure.

Effect of 8-HQ concentration

The influence of the amount of 8-HQ as chelating agent was also evaluated and the results showed that the signals of Cu and Zn were increased with the increase of 8-HQ amount from 0.005 to 0.05 mmol.L⁻¹ and then decreased to 0.75 mmol.L⁻¹. In this study, a 8-HQ amount of 0.05 mmol.L⁻¹ was employed.

Table 2. Study of interfering ions

Interfering ions	Tolerable concentration (analyte: interfering ion)
Si ⁴⁺ , As ³⁺ , Co ²⁺ , Ni ²⁺ , Cr ³⁺ , Al ³⁺ , Fe ³⁺	1:10
Mn ²⁺	1:100
Sr ²⁺ , Ba ²⁺ , Ca ²⁺ , Mg ²⁺	1:2500
So ₄ ²⁻ , H ₂ PO ₄ ⁻ , CH ₃ COO ⁻ , Cl ⁻ , NO ₃ ⁻ , PO ₄ ³⁻	1:5000

Study of interferences

Interferences were studied in the presence of a constant concentration of analyte (1 μg.L⁻¹) and different amounts of foreign ions (analyte: foreign ion ratio 1:10, 1:100, 1:2500 and

1:5000). Tolerable concentration of foreign ions was considered that concentration in which less than 10% deviation in absorbance reading was observed in comparison with the case in which interfering ion was absent. The obtained results are given in Table 2.

Figures of merit

The calibration graph was linear in the range of 10–50 ng.mL⁻¹ and 1-4 ng.mL⁻¹ for Cu and Zn, respectively. The limits of detection based on three times of the blank standard deviations were 0.025 for Cu and 0.0033 µg.L⁻¹ for Zn. The relative standard deviations (R.S.D.) for seven replicate measurements of 1µg.L⁻¹ of Cu and Zn were 8.51%, 7.41%, respectively.

Natural water analysis

The proposed methodology was applied to the speciation of copper and zinc in several water samples. Well water, Mineral water and Tap were collected from the Saveh of Iran and were

analyzed by DLLME combined with GFAAS (Table 3).

Conclusion

The aim of this study was determination of Cu and Zn by Dispersive liquid-liquid microextraction (DLLME) using chloroform as an extraction solvent, methanol as a disperser solvent and 8-HQ as a chelating agent. The determination of extracted ions was done by graphite furnace atomic Absorption spectroscopy. Enrichment factor and recovery for the target analyte were obtained about 25 and 96% for Cu and 26 and 97% for Zn, respectively.

Table 3. Determination of Cu and Zn in tap, well and mineral water samples

Sample	Cu concentration (mg.L ⁻¹)	Zn concentration (mg.L ⁻¹)
Well water	0.318	0.250
Mineral water	0.078	0.104
Tap were	0.183	0.259

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