

Separation and determination of trace amount of Cu (II) in environmental samples using α -benzoin oxime, dispersive liquid-liquid microextraction and inductively couple plasma atomic emission spectrometry

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Abstract

In present study, a selective and simple method for preconcentration and determination of copper ion was developed by dispersive liquid-liquid microextraction (DLLME) without using disperser solvent followed by inductively coupled plasma atomic emission spectrometry (ICP-AES). One variable at the time method was applied to select the type and volume of extraction and disperser solvent and other parameter that have effect on the microextraction efficiency such as, ligand to metal mole ratio , pH and interfering cations. In the proposed approach, butyl acetate and α -benzoin oxime were used as extracting solvent and chelating agent, respectively. The optimal conditions were: volume of extraction solvent, 400 μ L; the ligand concentration, 0.44 mol L⁻¹ and pH= 8. The linear dynamic range of analysis was 3.0-100.0 μ g L⁻¹ with correlation coefficient of $r^2 > 0.9998$. The method detection limit was 0.96 μ g L⁻¹. The precision (RSD %) of the method was 4.2% for 5 replicates and recoveries of 50.0 μ g L⁻¹ Cu (II) was in the range of 92-110%. The proposed method was successfully applied for determination of trace amount of copper in the tap, mineral and lake water samples satisfactory.

Keywords: Copper, Dispersive liquid-liquid microextraction, Inductively Coupled Plasma atomic emission spectrometry

Introduction

Copper is a widely used heavy metal in different industries such as plating, mining and smelting, brass manufacture, electroplating industries, petroleum refining and etc. [1, 2]. It is vital and toxic for many biological systems [2 -6]. In recent years, pollution of the environment by toxic elements has been dramatically increased; therefore determination of toxic metals in environmental samples is a very important task. The direct determination of metal ions at trace levels such as spectroscopic techniques is limited not only due to insufficient sensitivity, but also by matrix interference. Despite the selectivity and sensitivity of analytical techniques, there is a need for the preconcentration and/or separation of trace elements

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before their determination. Different techniques such as Liquid- Liquid Extraction (LLE), Solid Phase Extraction (SPE), precipitation, extraction and chromatographic separation, solvent extraction, cloud point extraction and different types of extraction can be used to preconcentrate and separate Cu (II) from aqueous solutions. Recently, a new liquid-liquid extraction technique namely Dispersive Liquid Liquid Microextraction (DLLME) has been applied for the determination of trace organic pollutants and metal ions in the environmental samples. This technique uses microliter volume of extraction solvent along with a few microliter of disperser solvents. In this method, an appropriate mixture of a high-density or low density solvent (extraction solvent) compared to water, a water-miscible polar solvent (dispersive solvent) and chelating agent are rapidly injected into aqueous sample by a syringe, and a cloudy state, consisting of fine droplets of the extractant into aqueous phase, is formed. After extraction, phase separation is performed by centrifugation. The advantages of the DLLME method are simplicity of operation, rapidity, low cost, relatively high recovery, high enrichment factors and small volume of organic solvents.

There are different kinds of DLLME method developed to preconcentrate ion metals such as DLLME without the addition of the chelating agent (liganless), ultra sound assisted emulsification for simultaneous microextraction and Air-Assisted Liquid-Liquid Microextraction (AALLME) which are new versions of Dispersive Liquid-Liquid Microextraction (DLLME) methods.

In this survey, DLLME coupled with ICP-AES was applied for preconcentration and determination of trace amounts of copper. The present work offers extraction of Cu (II) with α -benzoin oxime (Figure 1) and n-butyl acetate without using a disperser solvent. The effect of various parameters affecting the extraction efficiency such as type and volume of extraction and disperser solvents, pH, concentration of the chelating agent and effect of foreign ions were studied and optimized.

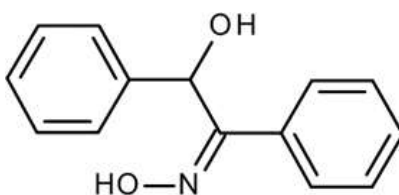


Figure 1. Structure of α -benzoin oxime.

Experimental

Instrumentation

An inductively coupled plasma atomic emission spectrometry (ICP-AES, Varian 735ES, radial view, Australia) equipped with V-groove nebulizer and charge coupled device (CCD) detector was used for determination of ions in this study. The instrumental parameters including radio frequency generator power (1.6 KW), viewing height (10 mm), nebulizer gas flow (0.55 Lmin⁻¹) and pump rate (15.0 rpm) were chosen in a way to ignite and maintain plasma. The copper emission spectrum of 224 nm was used in time scan mode to get better sensitivity. The values of pH were measured by a pH-meter (Jenway, model: 3510, England). A centrifuge (Vision, model: VS-5500N, Korea) was applied to accelerate the phase separation.

Reagents such as methanol, ethanol, ammonium acetate, sodium hydroxide, ammonia, acetone, acetonitrile, sodium chloride, trichloromethane, tetrachloromethane, 1-octanol, dodecanol, α -benzoin oxime and acetic acid were purchased from Merck (Darmstadt, Germany). Nitric acid and hydrochloric acid were purchased from Scharlau (Spain). Butyl acetate was purchased

from Fluka (USA). The stock standard solution of Cu (1000 mg L⁻¹) and multi elements standard as interference study (100 mg L⁻¹) of Pb, Zn, Ni, Co, Cr, Cd, Mn, Ba, Sc, Ag, Al, Fe, K, Na, Mg, Ca, Cu were purchased from VHGLABS (USA). The water used was purified on distilled de-ionized water (Millipore, USA).

For DLLME, 6 mL solution sample containing 200 µg L⁻¹ copper as analyte was placed in a screw cap glass test tube. The pH was adjusted to 6 by (ammonium acetate: 1 mol L⁻¹, and ammonia 1 mol L⁻¹, pH=8), then 400 µL of butyl acetate (as extraction solvent) containing % 0.33(w/v) α-benzoin oxime (as chelating agent) were rapidly injected into the sample solution by using a micro syringe. A cloudy solution was formed in the test tube. In this step metal ion complexes in water sample were extracted into the fine droplets of butyl acetate. The mixture was centrifuged for 5 min at 2900 rpm. The dispersed fine droplets were collected at the top of test tube. This phase was quantitatively transferred to a vial. Finally, the organic phase was injected to ICP-AES to determine the analyte concentration.

Results

In the present work, DLLME combined with ICP-AES was developed for the determination of copper in water samples. In order to obtain high extract efficiency, the effect of extraction solvent, disperser solvent, ligand concentration and pH were optimized using one variable at a time optimization method. Some primary experiments showed that the best phase separation can be achieved at least 200 µL butyl acetate should be added for appropriate phase separation. The proposed dispersive liquid-liquid solvent extraction (DLLME) is an equilibrium based extraction technique and, therefore, the amount of analyte transferred into the extraction solvent reaches its maximum when this equilibrium is established. This process can be, thus, explained according to the thermodynamic behavior of liquid-liquid extraction processes at a constant temperature, using the following equations:

$$K = \frac{C_{eq}^o}{C_{eq}^{aq}} \quad (1)$$

$$p = \frac{n_o}{n_t} = \frac{KV_o}{V_{aq} + KV_o} \quad (2)$$

$$E_f = \frac{C_{eq}^o}{C_{ini}^{aq}} = p \times \frac{V_{aq}}{V_o} \quad (3)$$

where C_{eq}^o is the final concentration of analyte in the organic phase, C_{eq}^{aq} and C_{ini}^{aq} are the final and initial analyte concentrations in the aqueous phase, respectively, V_o and V_{aq} are the volumes of organic and aqueous phases, respectively, K is the distribution coefficient, p is fraction of total analyte transferred to organic phase, n_o is number of analyte molecules transferred to the organic phase and n_t is total number of analyte molecules and E_f is the enrichment factor.

Selection of extraction solvent

The type of extraction solvent in DLLME is an essential consideration for efficient extraction. Low water solubility and different polarities were considered. High density extraction solvents have high back ground emission in ICP-AES; hence solvents with lower density than water were used. Several solvent such as n-Butyl acetate (density, 0.88 g mL⁻¹), 1-Octanol

(density, 0.82 g mL⁻¹) and Dodecanol (density, 0.83 g mL⁻¹) were applied to choose a suitable extraction solvent. After DLLME procedure the collected organic phase was injected into ICP-AES and copper emission signal was determined. The pH was adjusted to 6 by 1.0 M of ammonium acetate, then 400 μ L of butyl acetate (as extraction solvent) containing 0.33(w/v%) α -benzoin oxime and 300 μ L ethanol as disperser solvent were added. The butyl acetate is the most polar solvent between used solvents in this study. The structure of copper- α -benzoin oxime complex is polar and can be extracted only by polar solvents. The results indicated that maximum peak area was achieved as following order: n-butyl acetate, 1-octanol and finally dodecanol (data was not given) (Figure 2).

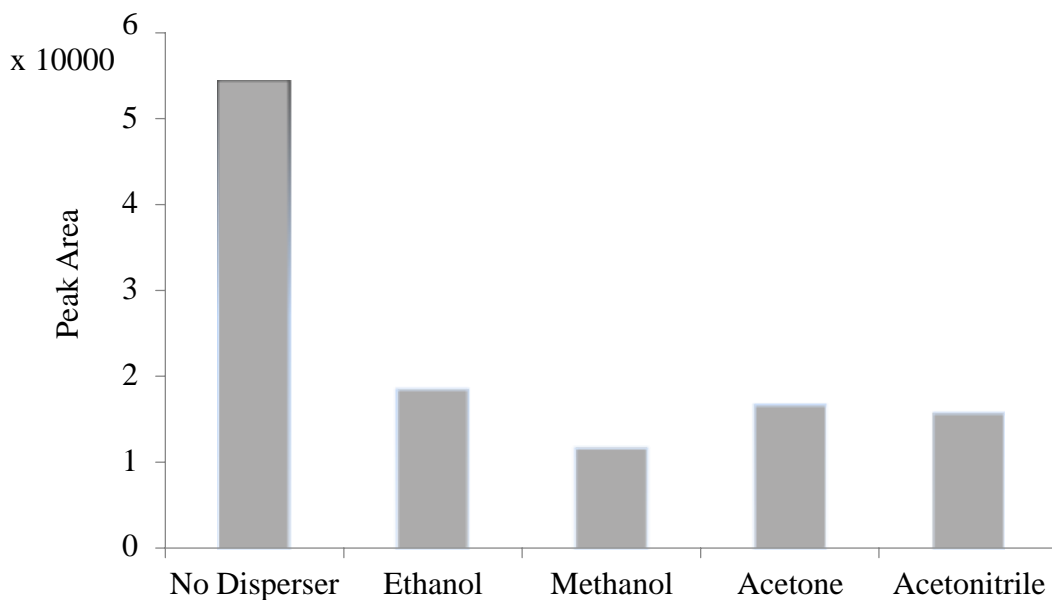


FIG. 2. Effect of type of disperser solvents on the peak area of Cu obtained from DLLME. Extraction conditions: sample solution.

Discussion and Conclusion

In the present study, DLLME has been combined with ICP-AES for determination of trace amount of copper. The main benefits of DLLME were low consumption of organic solvents, simplicity, low cost, reasonable sensitivity and specifically fast analysis time. The short extraction time is related to the infinitely large surface area between extraction solvent and aqueous phase after formation of cloudy solution. Thereby, complex formation / transfer from aqueous phase to extraction solvent are fast. Subsequently, equilibrium state is achieved quickly therefore. Lower cost and less pollution in the proposed procedure are related to not using of disperser solvent. Finally the proposed method was successfully applied in the determination of target analytes in different aqueous sample at μ g L⁻¹ level.

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