

A novel silicone phthalocyanine for the preconcentration and spectrophotometric determination of copper by ionic liquid-based dispersive liquid-liquid microextraction

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Abstract

Dispersive liquid-liquid microextraction (DLLME) is of interest as an environmentally friendly sample preparation technique due to its simplicity, operating speed and low solvent and reagent consumption. Accordingly, this work reports the development of a new simple ionic liquid-based dispersive liquid-liquid microextraction (IL-DLLME) method for spectrophotometric copper determination. First, the copper was complexed with a novel silicone phthalocyanine and then the complex was extracted into 1-heptyl-3-methylimidazolium hexafluorophosphate dissolving in acetone in the presence of sodium dodecyl sulfate (SDS) as the anti-sticking agent. After centrifuging for 2 min at 3000 rpm, the extracting phase was diluted to 250 μ L with acetone for spectrophotometric detection at 340 nm. Some experimental conditions that influence the procedure were optimized. The pH and complexing reagent concentration are 4.0 and 4.6×10^{-6} mol/L, respectively. The method is linear in the range from 0.03 to 100 μ g/mL with a correlation coefficient (R^2) of 0.9973. The limit of detection (LOD) of the method is 17 μ g/L. The relative standard deviation is 1.7% at 45 μ g/mL Cu^{2+} ($n=6$). The enrichment factor for the method was calculated as 210.

Keywords: Dispersive liquid-liquid microextraction, silicone phthalocyanine, Cu preconcentration, ionic liquids, spectrophotometry

1. Introduction

Most of the scientists who have been researching analytical chemistry for the last ten years have adopted green chemistry and have turned to extraction methods in which fewer solvents were used. This technique is dispersive liquid-liquid microextraction (DLLME) tendering high diversification factors from low volumes of different samples. Its simplicity, low cost, and ease of method development make this technique feasible to virtually all analytical laboratories. [1]. This technique was first applied by Rezaee in 2006 for organic analytes. It has become an increasingly popular technique, not only in chemistry and biochemistry but also in genetic and molecular biology, chemical engineering, environmental science, medicine, engineering, agriculture and

biological sciences, pharmacology, toxicology and pharmacy, social sciences and others [2-3].

Phthalocyanine compounds to which different groups can be easily bound have significant absorbances in the 600-800 nm range. Thanks to the $18-\pi$ electron system of the phthalocyanine ring, it is a good electron donor (e-donor) molecule and has excellent photo-sensitizing properties. Silicone phthalocyanines (SiPc) have received more attention from researchers in the last decade, due to their thermal, chemical stability and bright blue-green colors [4-6]. They were used for PDT application [7-9], dye-sensitized solar cells [10-11], fluorescence sensors [12-13], fluorophores [14-15], and optical, electronic and photo-electronic devices [16-17].

Copper is a trace element that shows a significant role in many biochemical reactions such as hemoglobin synthesis, the usual task of the central nervous system and oxidative phosphorylation [18-19]. For many living organisms, a daily intake of Cu is 0.5 mg/L [20]. If this limit is exceeded, the neurological ailments such as schizophrenia, depression, epilepsy [21] and irritation of nose and throat, nausea, vomiting, and diarrhea will disappear [22]. Some methods to determination of Cu(II) from various samples are liquid-liquid extraction [23], solid phase extraction (SPE) [24] and cloud point extraction (CPE) [25]. Today, microextraction methods placed for minifying organic solvent consumption, facilitating sample preparation steps, providing high enrichment rates and appropriate to automation [26].

In this work, IL-DLLME is used for the determination of Cu(II) with silicone phthalocyanine as an interaction agent. This developed method includes the extraction of Cu(II) in the ionic liquid droplets after interact with silicone phthalocyanine compound (Figure 1).

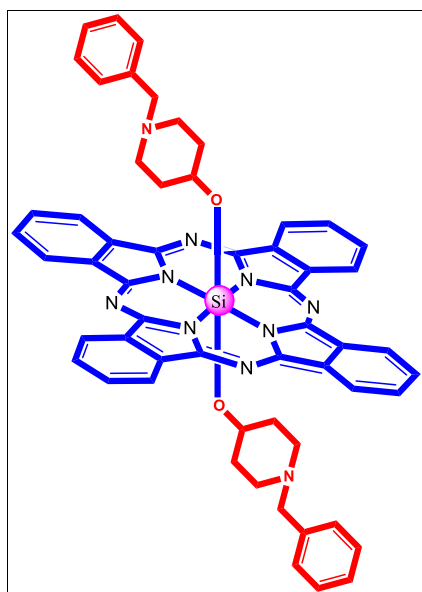


Figure 1. The structure of silicone phthalocyanine.

2. Experimental

2.1. Reagents and apparatus

All the reagents and apparatus that used were given in the supplementary material file.

3. Results and discussion

3.1. Optimization of IL-DLLME procedure

3.1.1. Selection of IL

In this study, we used ionic liquids as extraction solvent. The selected ionic liquids should be hydrophobic and have high extraction ability of the target molecules. 1-hexyl-3-methylimidazolium hexafluorophosphate ([C6-mim][PF₆]), 1-butyl-3-methylimidazolium hexafluorophosphate ([C4-mim][PF₆]), 1-methyl-3-octylimidazolium hexafluorophosphate ([C8-mim][PF₆]), 1-heptyl-3-methylimidazolium hexafluorophosphate ([C7-mim][PF₆]), and 1-butyl-3-pentylimidazolium hexafluorophosphate ([C4-C5im][PF₆]) were studied as extracting solvents using 1000 mL of acetone as disperser solvent.

According to the results, 1-heptyl-3-methylimidazolium hexafluorophosphate was opted as the extraction solvent for further experiments (Fig. 2).

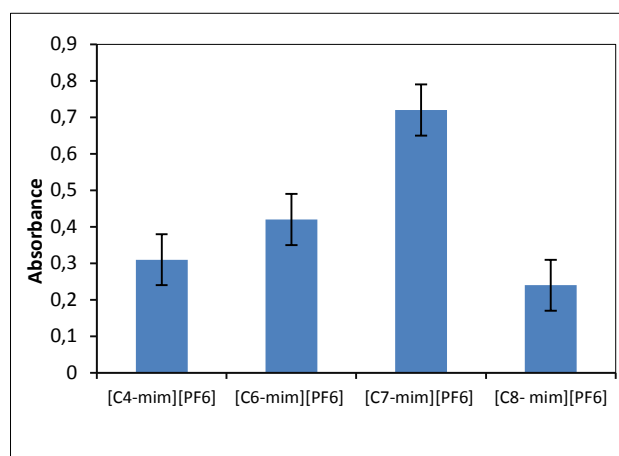


Figure 2. Effect of IL. Conditions: sample volume 15 mL, pH=4.0, disperser solvent (acetone) 1000 mL, silicone phthalocyanine 4.6×10^{-5} mol/L, centrifugation 2 min at 3000 rpm. The error bar is the standard deviation (n=3).

3.1.2. Selection of the disperser solvent

In DLLME that is a three-component solvent system, the disperser solvent has to be miscible with both water and ionic liquid [27, 28]. Acetone, acetonitrile, ethanol, and methanol as the commonly used disperser solvent were examined. When the results were evaluated, it was decided that acetone was the most suitable dispersion solvent (Fig 3).

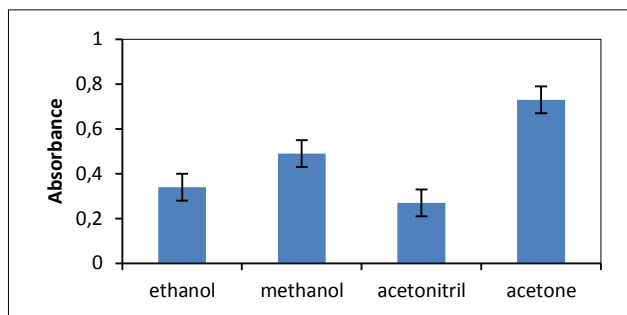


Figure 3. Effect of disperser solvent. Conditions: sample volume 15 mL, pH=4.0, extractive solvent (IL) 300 μ L, silicone phthalocyanine 4.6×10^{-5} mol/L, centrifugation 2 min at 3000 rpm. The error bar is the standard deviation (n=3).

3.1.3. Effect of the IL volume

Different volumes (50, 100, 150, 200, 250, 300, 350 and 400 μ L) of 1-heptyl-3-methylimidazolium hexafluorophosphate was tested to ensure maximum extraction efficiency in the proposed DLLME procedure. The results showed that the extraction efficiency increased with the increasing volume of 1-heptyl-3-methylimidazolium hexafluorophosphate from 50 to 300 μ L, and then decreased. 300 μ L was selected as an optimum volume of extracting solvent.

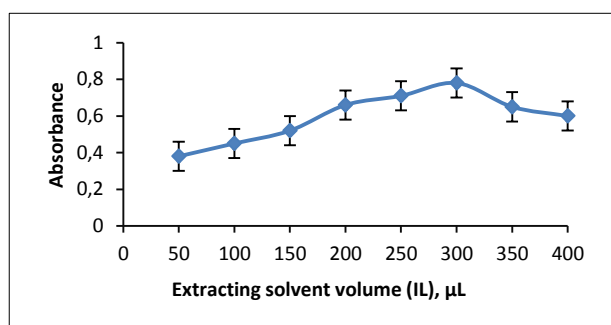


Figure 4. Effect of IL volume. Conditions: sample volume 15 mL, pH=4.0, disperser solvent (acetone) 1000 mL, silicone phthalocyanine 4.6×10^{-5} mol/L, centrifugation 2 min at 3000 rpm. The error bar is the standard deviation (n=3).

3.1.4. Effect of the disperser solvent volume

The disperser solvent volume has quite influence in DLLME procedure because affects the dispersion of the extraction solvent in aqueous analyte phase. In the range of 400 to 1200 mL of acetone containing 300 μ L of 1-heptyl-3-methylimidazolium hexafluorophosphate was researched to specify ideal disperser solvent volume. Considering the results 1000 mL of acetone was chosen as an ideal disperser solvent volume in the microextraction procedure (Fig. 5).

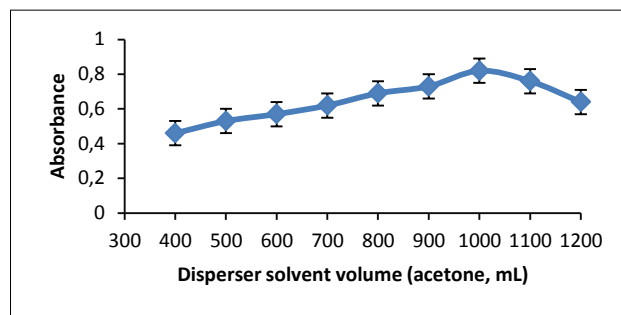


Figure 5. Effect of disperser solvent volume. Conditions: sample volume 15 mL, pH=4.0, extracting solvent (IL) 300 μ L, silicone phthalocyanine 4.6×10^{-5} mol/L, centrifugation 2 min at 3000 rpm. The error bar is the standard deviation (n=3).

3.1.5. Effect of pH

Determination of the optimum pH in the DLLME procedure is an important step because pH influences the chelation of Cu(II)-silicone phthalocyanine and subsequent extraction into the IL phase. Various sample solutions ranging from pH 1-10 were prepared and extraction efficiencies were examined. The experimental results are spotted in Fig. 6. The highest extraction yield of Cu(II)-silicone phthalocyanine into the ionic liquid was obtained at pH 4.0. The absorbance increased when the pH of the sample solution increased from 2.0 to 4.0. After pH 4.0, absorbance began to decrease. In the pH range of 8-10, absorbance leveled off.

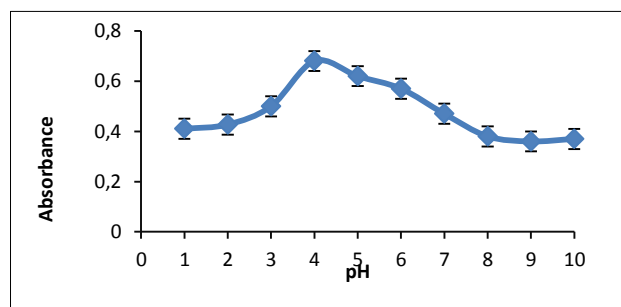


Figure 6. Effect of pH. Conditions: sample volume 15 mL, extracting solvent volume (IL) 300 μ L, disperser solvent (acetone) 1000 mL, silicone phthalocyanine 4.6×10^{-5} mol/L, centrifugation 2 min at 3000 rpm. The error bar is the standard deviation (n=3).

3.1.6. The concentration of silicone phthalocyanine

The silicone phthalocyanine concentration directly affects the complexation of Cu(II). Sample solutions containing various concentrations (1×10^{-4} - 1×10^{-6} mol/L) of silicon phthalocyanine were prepared and the proposed microextraction procedure was applied to these solutions. It was found that the absorbance signal of the Cu(II) complex increased by increasing the silicon phthalocyanine concentration up to 4.6×10^{-5} mol/L and then it remained fixed. So,

4.6×10^{-5} mol/L was assigned as working concentration.

3.1.7. Selection of the anti-sticking agent

The loss of some extraction phase in the centrifugation step when ionic liquid is used in the DLLME procedure is an important problem that must be overcome. The addition of a surfactant to the sample solution is often used to solve this problem. Drops of ionic liquid are surrounded by surfactant molecules and their interaction with the test tube is reduced [29]. We also investigated the effect of some surfactants such as SDS, Triton X-100 and Triton X-114 on increasing extraction efficiency. The results showed that these 3 surfactants were effective in preventing sticking but the best yield was obtained with SDS.

3.2. Interferences

The potential interference effects of various cations (Co^{2+} , Ni^{2+} , Zn^{2+} , Ag^+ , Cr^{3+} , Mn^{2+} , Fe^{3+}) and anions (NO_3^- , SO_4^{2-} , PO_4^{3-}) on the proposed method were investigated. For this purpose, the absorbance values of the solutions with and without foreign ions at 340 nm were compared. The concentration of foreign ions that did not cause a difference of more than 5% was determined as the tolerance limit. In this step, a 10 ml sample solution of 0.1 $\mu\text{g/mL}$ Cu(II) was used. The results are given in Table 1. The results show that the proposed ionic liquid-based DLLME method for spectrophotometric Cu(II) determination is highly selective.

Table 1. Tolerance limits of coexisting ions.

Ion	Tolerance limits $\mu\text{g/mL}$
Co^{2+}	438
Ni^{2+}	491
Zn^{2+}	523
Ag^+	675
Cr^{3+}	389
Mn^{2+}	210
Fe^{3+}	660
NO_3^-	790
SO_4^{2-}	809
PO_4^{3-}	205

3.3. Analytical characteristic

The proposed DLLME method was validated using 10 ml of standard Cu(II) solution under optimum conditions. Some basic parameters such as linear

range, correlation coefficient (R^2), limit of detection (LOD), limit of quantification (LOQ), relative standard deviation (RSD) and enrichment factor (EF) were examined for validation. The data obtained are remarked in Table 2. A linear increase between the absorbances and the concentrations of Cu(II) in the range of 0.03-100 $\mu\text{g/mL}$ was observed. The correlation coefficient was 0.9973. The LOD was 17 $\mu\text{g/L}$ based on three times Sd/m ratio and The LOQ was 42 $\mu\text{g/L}$ based on nine times Sd/m ratio, where the Sd was the standard deviation of eleven blank and m was the slope of the calibration graph. The EF was calculated as 210 using the ratio of analyte concentrations in the ionic phase and initial aqueous phase. The RSD for 45 $\mu\text{g/mL}$ of Cu(II) was 1.7% ($n=6$).

Table 2. Analytical features of proposed method under optimum conditions.

Correlation coefficient (R^2)	0.9973
Linear range ($\mu\text{g/mL}$)	0.03-100
LOD ($\mu\text{g/L}$)	17
LOQ ($\mu\text{g/L}$)	42
RSD, %($n=6$)	1.7
Enrichment factor	210

4. Conclusion

The selective determination of metal ions in environmental samples has been a subject of considerable interest. Despite significant advances in technology, few techniques allow direct determination from sample matrix [30]. Thus, a pre-concentration step is often required. DLLME is an effective pre-concentration method that is widely used nowadays.

In this study, a novel DLLME method was developed for the spectrophotometric determination of Cu (II). The method is simple, fast, selective and inexpensive. Furthermore, since we use an ionic liquid as an extraction solvent, it is very environmentally friendly. Ionic liquids are good alternatives to conventional organic solvents because of their low vapor pressure, high thermal stability, wide liquid range, relatively high viscosity, and especially low toxicity. They are widely recognized as so-called green solvents. When the method performance is evaluated, the proposed method seems to be very suitable for the determination of Cu in environmental samples.

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