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Dispersive liquid-liquid microextraction for the spectrophotometric determination of Fe^{3+} with a water soluble Cu(II) phthalocyanine compound

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Abstract

DLLME, which is a method that minimizes organic solvent consumption and waste generation, is frequently used for trace analyte determination. In the present work, a simple, selective and sensitive spectrophotometric method based on the dispersive liquid-liquid microextraction was reported. The procedure is based on the formation of a 1:1 complex between Fe^{3+} and a water-soluble Cu(II) phthalocyanine and then extraction of this complex into dichloromethane by dispersive effect of acetone. The experimental parameters that effecting the DLLME such as amount of extractive and disperser solvents, pH, salt concentration, Cu(II) phthalocyanine concentration and centrifuging time and rate were optimized. The linear range of the method is 0.4–70.0 ng/mL with a good correlation coefficient (R^2) of 0.9912. The limits of detection (LOD) and quantification (LOQ) are 0.47 and 1.86 ng/mL, respectively. The relative standart deviation (RSD, %) of the method for 40 ng/mL Fe^{3+} in sample solution (n=11) was 1.4% and the enrichment factor was calculated 240.

Keywords: DLLME, spectrophotometry, iron, Cu(II) phthalocyanine

1. Introduction

Iron is an essential element for biological processes. [1,2]. An healty adult human body contains about 4 grams of iron, mostly in hemoglobin and myoglobin and is lost every day for a variety of reasons. The daily loss must be compensated to maintain the body's iron balance [3,4]. One of the important tasks of iron, which is an element prone to oxidation due to its structure, in the human body is to carry oxygen. Heme iron binds to hemoglobin in the blood and to myoglobin in the muscles, performing the task of transporting oxygen. The human body also needs iron to make some hormones responsible for growth and development. Iron is found in the active site of many important redox enzymes in plants and animals. It increases the efficiency of copper and calcium by helping enzymes in protein metabolism [5–8].

Chemically, the most common oxidation states of iron are Fe^{2+} and Fe^{3+}. Dietary iron exists in two forms, heme iron (Fe^{2+}) and non-heme iron (Fe^{3+}). Heme iron is found in animal sources such as red meat, eggs, fish and chicken. Non-heme iron is obtained from plant sources. Heme iron is better absorbed by the body than non-heme iron. Low pH and the presence of ascorbic acid increase non-heme iron absorption. However, polyphenols such as tannins and chlorogenic acids found in tea, coffee, and some other foods inhibit iron absorption. Although conventional views agree that polyphenols only affect non-heme iron absorption, recent experiments have provided evidence that polyphenolic compounds can inhibit the absorption of heme and non-heme iron. It also showed that polyphenols have a dose-dependent inhibitory effect [9–14].

When the hemoglobin protein in the blood falls below the normal level, it is called anemia. The most common cause of anemia is iron deficiency. Iron deficiency reduces oxygen delivery to cells, leading to fatigue and weakening of the immune system. Iron deficiency, which is commonly observed in children and infants, delays mental development. Iron deficiency is a serious health problem in both developing and developed countries. Chronic blood loss and insufficient absorption in the small intestines are important factors in iron deficiency. However, it is mostly caused by insufficient iron intake in the daily diet [15–18].

Iron is a micronutrient. But high doses of iron are toxic to humans and can cause serious health problems

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such as depression, difficulty breathing, convulsions and heart attacks. Excessive intake of Fe^{2+} creates free radicals in the body. Long-term exposure to high doses of iron can cause diabetes, liver poisoning, and graying of the skin [19–22].

Quantitative determination of iron is especially important for the biological and environmental fields. That is why, various methods have been suggested to determine iron concentration including inductively coupled plasma mass spectrometry (ICP-MS) [23], flame atomic absorption spectrometry (FAAS) [24], polarography [25], high performance liquid chromatography (HPLC) [26], ion chromatography [27] and spectrophotometry [28,29].

Despite the development of high precision analytical instruments for the analysis of trace analytes, problems are often encountered in direct analysis from the sample matrix. Therefore, pretreatment is usually required for the separation and concentration of the analytes from the matrix medium. Microextraction methods, which minimize the use of organic solvents and provide a high enrichment factor, are intensely preferred for sample pretreatment todays [30–32].

Dispersive liquid-liquid microextraction (DLLME) is a relatively novel miniaturized sample pretreatment protocol. It was suggested by Rezae at al. in 2006 [33]. It based on a ternary component solvent system inclusive extractive solvent, dispersive solvent and aqueous sample phase. The mixture of appropriate amounts of extractive and dispersive solvents are quickly applied to the aqueous sample phase by a syringe. Extraction is completed in a short time after formation of cloudy solution because of huge surface area between the extractive and aqueous phases. Following centrifugation, the small droplets of extraction solvent containing analyte is gathered at the base of test tube. Finally, appropriate instrumental technique is applied to the residue for quantitative calculations about analyte [34–39].

In this study, a novel spectrophotometric iron determination method based on DLLME has been reported. The short content of this method is the extraction of Fe^{3+} from the sample medium by the DLLME method, following the formation of a complex with a water soluble Cu(II) phthalocyanine (Cu(II)-Pc) ligand that was prepared as stated in relevant literature [40].

Phthalocyanines are synthetic macrocyclic compounds with a highly conjugated planar 18-π electron system. Phthalocyanines, which are formed by the condensation of four iminoisoindoline units, have a very tense structure. During the production of metal phthalocyanines, the template effect of the metal ion in the environment increases the product yield. The chemical properties of a phthalocyanine compound depend on the central atom and the substituents. They have high thermal stability and blue-green color. Phthalocyanines can be coordinated with almost all metals. The most important limitation in the application of phthalocyanines is their low solubility in water and most organic solvents. [41–43].

2. Experimental

2.1. Materials

All the reagents and solvents were analytical grade from Merck (Darmstadt, Germany) and Sigma Aldrich (Taufkirchen, Germany). Ultrapure water was used for the entire study from Sartorius (Arium-Pro). Fe^{3+} working standard solutions were prepared by daily stepwise dilution of standard stock solution ($Fe(NO_3)_3.6H_2O$, $1x10^{-3}$ mol/L). The sensor ($1x10^{-5}$ mol/L) solution was prepared weekly by dissolving an appropriate amount of Cu(II)-Pc in 25 mL of water and kept at 4 °C.

2.2. Equipment

A Thermo Scientific Evaluation Array Spectrophotometer and a 250 µL volume quartz cuvette were used for the absorbance measurements. The pH values were measured by a Hanna HI 2211 model pH meter. Benchtop Centrifuge, K2015R model centrifuge was used to achieve phase separation.

2.3. Preconcentration procedure

For DLLME, initially 10 mL of water solution containing the Fe^{3+} analyte was poured into a 15 ml conical glass tube. Then 400 µL of Cu(II)-Pc ($1x10^{-5}$ mol/L) was added as sensor. The pH of the tube was adjusted to 4.0 with 0.1 mol/L di-sodium hydrogen phosphate/potassium dihydrogen phosphate buffer solution after 150 µL of NaCl (1.0 M) was joined. Complexation was waited for 1 min. Followed by the mixed solution of 120 µL dichloromethane and 1.0 mL acetone was rapidly sheded onto the mixture by a 2.0 mL syringe. It was observed that the solution became cloudy because of dispersing of very fine dichloromethane droplets. So, the formed complex between Fe^{3+} ion and Cu(II)-Pc was extracted into these fine droplets. After that, the solution was centrifuged at 4000 rpm for 3 min. The dispersed slim droplets of dichloromethane were collapsed at the ground of the glass tube. The supernatant aqueous phase was ejected with a glass Pasteur pipette. After all, the organic phase was diluted to 400 µL with ethanol and absorbance was measured by using a quartz micro-cell at 355 nm.

3. Results and Discussion

3.1. Absorption spectra

Phthalocyanine compounds have strong $\pi \rightarrow \pi^*$ transitions, known as the Q band, in the 600–700 nm range. Metallic phthalocyanines form a single band in this region. The n-π^* transitions observed in the range of 320–400 nm resulting from the characteristic colors of the phthalocyanine compounds are called the B (Soret) band. In accordance with the literature, the absorption spectra of the water soluble Cu(II)-Pc ligand has a sharp Q band at 680 nm and a B band at 335 nm.

The spectral changes were recorded in the 320–500 nm range after the DLLME procedure. It was observed that increasing Fe^{3+} concentration in the range of 0.4–70.0 ng/mL at 355 nm regularly increased the absorbance of the ligand (Fig. 2).

3.2. Optimization of DLLME

3.2.1. *Effect of extractive solvent kind and volume*

The choice of organic solvent which is one of the basic parameters of DLLME significantly affects the enrichment factor. To allow phase separation, it must be immiscible with water while miscible with disperser solvent. Besides, the extractive solvent must be denser than water [44–46]. For the proposed DLLME procedure, various organic solvents such as chloroform, carbon tetrachloride and dichloromethane were tested. When the experimental data were examined (Fig. 1), it was seen that the extraction efficiency of dichloromethane was higher than all of them due to the highest absorbance value. Therefore, dichloromethane was chosen as the extractive solvent.

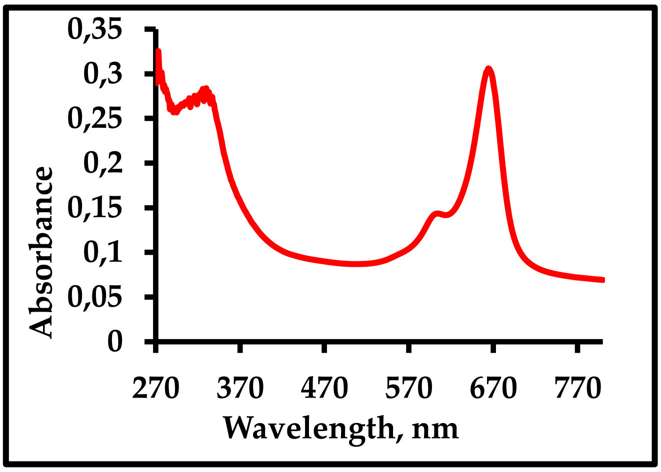

Figure 1. The Uv-Vis spectra of Cu(II)-Pc in water ($1x10^{-5}$ mol/L)

To state the effect of selected extractive solvent volume on the proposed DLLME procedure, varied volumes (40, 80, 120, 160, 200, 240 and 280 μL) of dichloromethane were applied to experimental procedure. Since after 120 μL of dichloromethane the extraction efficiency decreases as the solvent volume increases, as seen in Fig. 2, 120 μL of dichloromethane was chosen as the optimum extractive solvent volume.

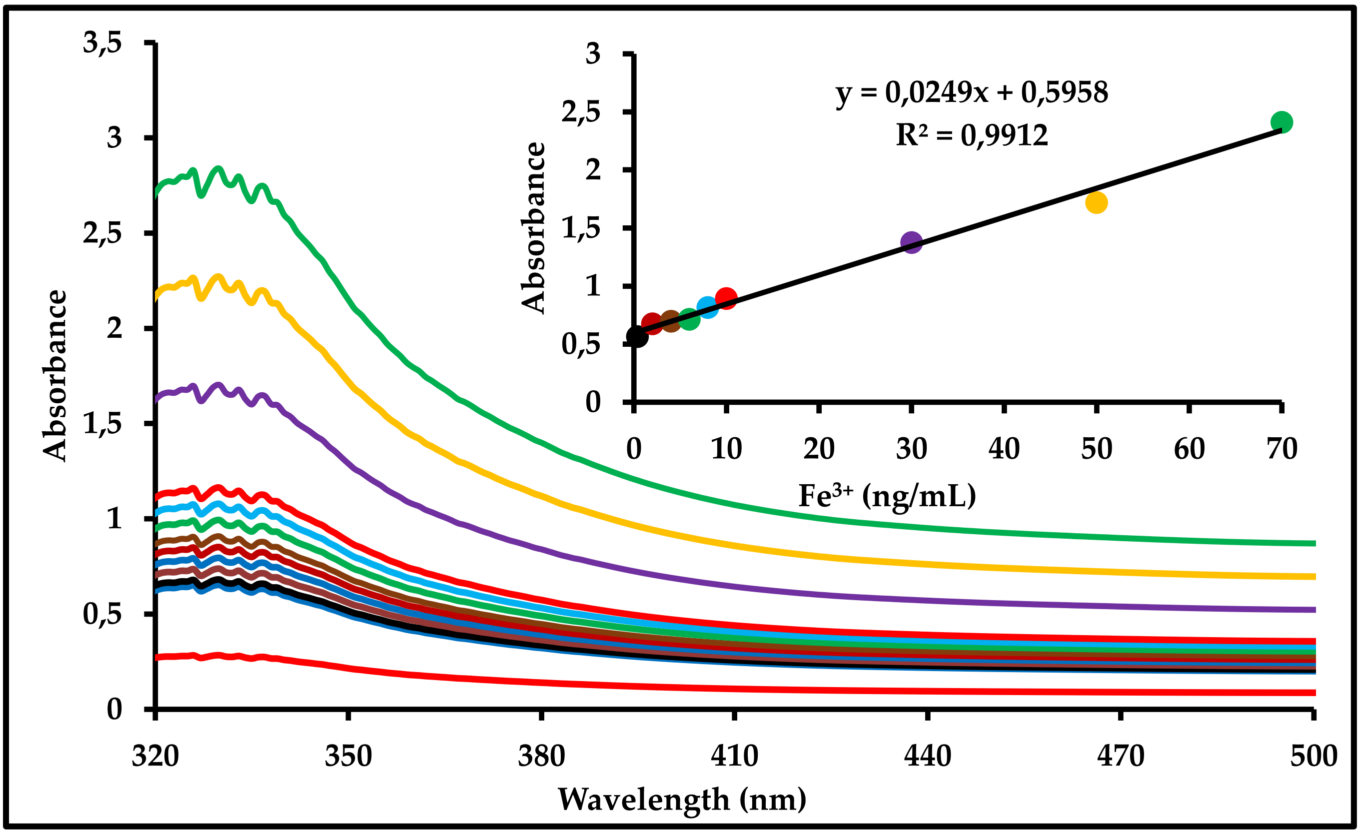

Figure 2. Changes in absorption spectra of Fe^{3+}:Cu(II)-Pc after DLLME procedure Extraction conditions: 10.0 mL sample volume; 120 μL dichloromethane; 1.0 mL acetone; $1x10^{-5}$ mol/L Cu(II)-Pc; 1.0 M NaCl; pH 4.0 Inset: Changes in absorbance in 355 nm. Iron(III) concentration is between 0.4–70.0 ng/mL

3.2.2. *Effect of nature and volume of disperser solvent*

The choice of a dispersing solvent depends on its miscibility in both the extraction solvent and the aqueous sample solution [47–49]. Ethanol, methanol, acetone and acetonitrile that are the most commonly used dispersion solvents in DLLME procedures were tried for this proposed method. It was observed that the precipitated phase was the highest when acetone was used as the dispersing solvent. Looking at Fig. 3, it is clear that the absorbance value agree with the observation. Therefore, acetone was chosen as the disperser solvent.

For the best disperser solvent volume the enrichment factors of the samples containing different volumes of acetone 0.25, 0.50, 0.75, 1.0, 1.5 and 2.0 mL containing 120 μL of dichloromethane were compared. In the presence of 0.25 mL of acetone, the enrichment factor is somewhat lower because dichloromethane is not sufficiently dispersed as seen in Fig. 4. The enrichment factor decreased after the acetone volume exceeded 1.0 ml because excess acetone volume increased the solubility of the complex. As a result of detailed examination of Fig. 4, 1.0 mL was chosen as the optimum dispersive solvent volume.

3.2.3. *Effect of sample pH*

Sample pH has a major role in the metal-ligand interaction and the following microextraction procedure especially in ternary complex formation [50]. The effect of pH on the extraction of Fe^{3+} was studied in the pH range of 2.0 to 12.0. Experimental results (Fig. 5) showed that absorption had reached its maximum at pH 4.0. Considering the results, a pH value of 4.0 was selected as optimum for microextraction procedure.

3.2.4. *Effect of salt*

The varied NaCl concentrations (0.0–2.0 M) were studied to investigate the ionic strength effect on DLLME procedure. The result showed that (Fig. 6), the addition of salt increased the extraction efficiency in 1.0 M NaCl. The addition of more salt caused a decrease in absorbance as it prevented the transition of Fe^{3+}:Cu(II)-Pc complex to the extractive solvent [51].

3.2.5. *Study of centrifuging time and rate*

To understand of effect of centrifuging parameters such as the centrifuging time and rate on the proposed DLLME procedure, they were studied in the range of 1.0 to 8.0 min and 1000–6000 rpm, respectively. According to the results of the experiment, 3 min and 4000 rpm were chosen as the optimum centrifugation parameters.

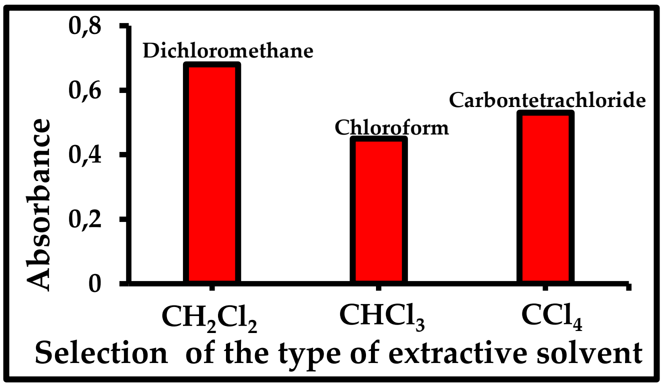

Figure 3. The selection of the extractive solvent kind. Extraction conditions: 10.0 mL sample volume; 1.0 mL acetone; $1x10^{-5}$ mol/L Cu(II)-Pc; 1.0 M NaCl; pH 4.0

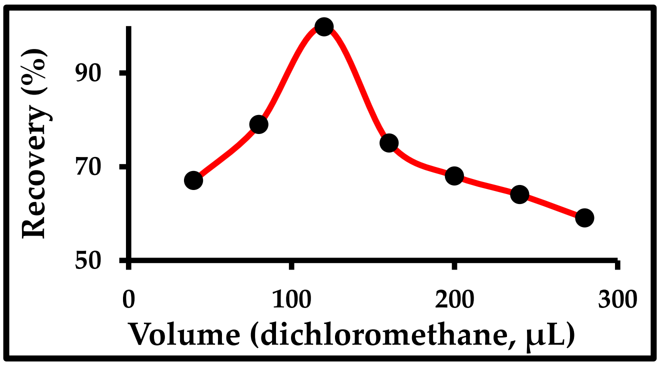

Figure 4. The effect of the dichloromethane volume on extraction recovery. Extraction conditions: 10.0 mL sample volume; 1.0 mL acetone; $1x10^{-5}$ mol/L Cu(II)-Pc; 1.0 M NaCl; pH 4.0

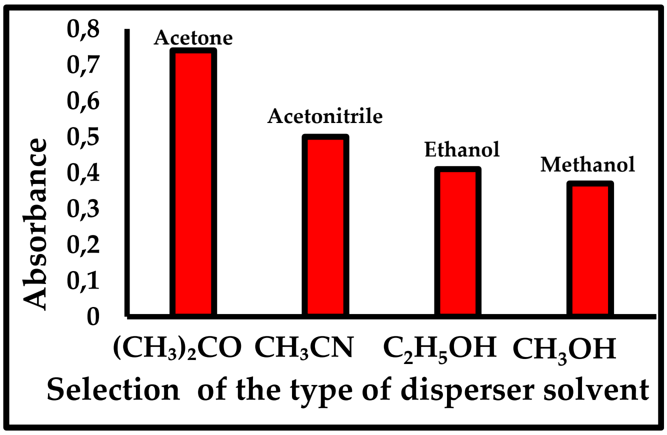

Figure 5. The selection of the disperser solvent kind. Extraction conditions: 10.0 mL sample volume; 120 μL dichloromethane; $1x10^{-5}$ mol/L Cu(II)-Pc; 1.0 M NaCl; pH 4.0

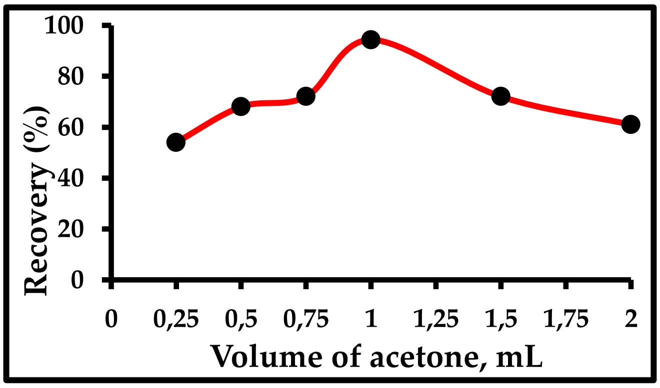

Figure 6. The effect of the acetone volume on extraction recovery. Extraction conditions: 10.0 mL sample volume; 120 μL of dichloromethane; $1x10^{-5}$ mol/L Cu(II)-Pc; 1.0 M NaCl; pH 4.0

3.2.6. *Effect of concentration of Cu(II)-Pc*

The effect of different concentration of the Cu(II)-Pc in the range of 1x10^{-4} to 1x10^{-6} mol/L were studied while the other parameters were kept constant. The highest absorbance was seen for 1x10^{-5} mol/L Cu(II)-Pc. Last of all, 1x10^{-5} mol/L Cu(II)-Pc was optimum for Fe^{3+} detection.

3.2.7. *Assessment of probable interferences*

In order to show the selectivity of Fe^{3+} determination with the proposed DLLME method, the effects of several probable interfering metal cations were carefully studied. Different concentrations of these ions were added to samples containing 40 ng/mL Fe^{3+}. The highest concentrations of probable interfering ions no causing more than 5% change in sample absorption were calculated as the tolerance limit. As can be seen in Table 1, since the tolerance limits of the studied ions are quite high, the matrix effect can be neglected in Fe^{3+} analysis in real samples with the proposed DLLME method.

3.3. Complex stoichiometry

The Job method was applied to determine the stoichiometries of Fe^{3+}:Cu(II)-Pc complex formed. The resulting Job graph showed us that the M:L ratio was 1:1.

3.4. Method validation

Validation of the proposed method under optimum conditions was evaluated based on limits of detection (LOD), limits of quantification (LOQ), linear range, enrichment factor and relative standard deviation (RSD, %). The LOD was 0.47 ng/mL defined as 3 times the ratio of the standard deviation of the blank to the calibration graph. The LOQ was 1.86 ng/mL defined as 10 times the ratio of the standard deviation of the blank to the calibration graph. The calibration curve is linear in the range of 0.4–70.0 ng/mL with a good correlation coefficient (R^2) of 0.9912. The relative standard deviation (RSD, %) of the proposed method for 40 ng/mL Fe^{3+} in sample solution (n = 11) was 1.4%. The enrichment factor was calculated 240.

Table 1. Tolerance limits of coexisting ions for the spectrophotometric determination of Fe^{3+} at 355 nm

Foreign ion added	DLLME
Ag^+	165
Cu^{2+}	118
Co^{2+}	93
Cr^{3+}	152
Pb^{2+}	141
Ni^{2+}	68
Cd^{2+}	199
Zn^{2+}	227
Mn^{2+}	106
Na^+	356
NO_3^-	235
SO_4^{2-}	94
PO_4^{3-}	178

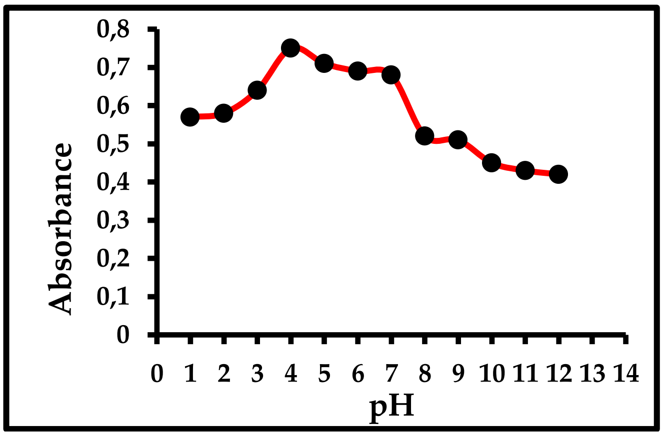

Figure 7. The effect of pH on extraction procedure. Extraction conditions: 10.0 mL sample volume; 120 µL of dichloromethane; 1.0 mL acetone; 1x10^{-5} mol/L Cu(II)-Pc; 1.0 M NaCl

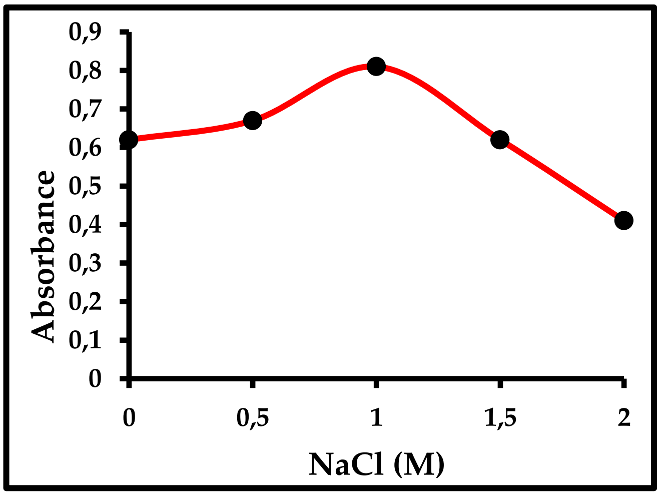

Figure 8. The effect of concentration of salt on extraction procedure. Extraction conditions: 10.0 mL sample volume; 120 µL of dichloromethane; 1.0 mL acetone; 1x10^{-5} mol/L Cu(II)-Pc; pH 4.0

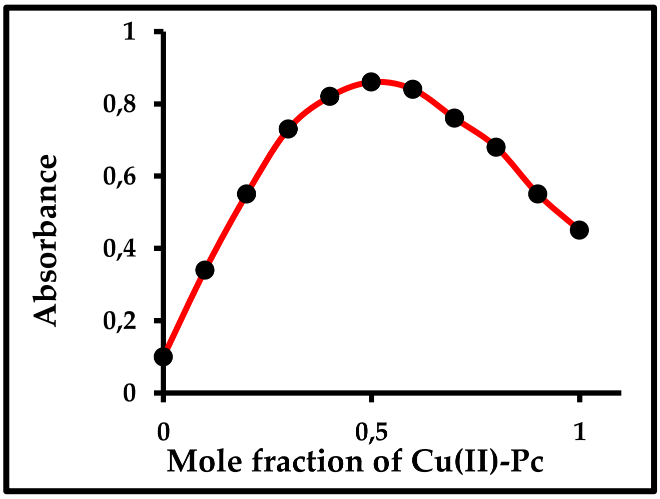

Figure 9. The Job plot to determine the Fe3$^+$:Cu(II)-Pc stoichiometry

Table 2. The analytical features of the optimized method

Parameter	
Correlation coefficient (R^2)	0.9912
Linear range (ng/mL)	0.4–70.0
LOD (ng/mL)	0.47
LOQ (ng/mL)	1.86
RSD,% (n=11)	1.4
Enrichment factor	240

4. Conclusion

In the DLLME procedure, the selection of the chelating reagent is a very important parameter that affects the extraction efficiency. Phthalocyanines are very suitable materials for developing chelating cation sensors. As the synthesis of water-soluble phthalocyanines increases, their utility in spectroscopic metal determination also increases. In this proposed DLLME method, a water-soluble Cu(II) phthalocyanine containing 3- (pyridin-4-yl) propane-1-oxy groups in non-peripheral positions is used as the chelating reagent. The method is simple, selective, and low cost.

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