



Cu ions determination technique based on fluorescence quenching of CdS quantum dots

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Abstract

The synthesized quantum dots have high solubility and stability in water and have great tendency to copper ion. This detector is based on the fluorescence quenching of cadmium sulfide functionalized quantum dots. Factors affecting on the extraction efficiency and ions fluorescence quenching were evaluated which included the amount of ionic liquid, the amount of methanol, the time of extraction, the time of centrifuge, the amount of quantum dots and pH of buffer. A simple and sensitive method has been presented for micro extraction of negligible amounts of Copper cations in environmental samples. This method is based on using dispersive liquid-liquid micro extraction method on the basis of ionic liquids before spectrofluorimetry. Under optimal conditions, the calibration curve in the range of (0.01-3 $\mu\text{g.L}^{-1}$) was linear. The limit of detection was obtained 0.0033 $\mu\text{g.L}^{-1}$ for copper cation. Relative standard deviation of the method was obtained 5.4% for copper with 5 times of measurement. The proposed method possesses high sensitivity and low limit of detection in comparison with many spectrophotometric and electrochemical methods and even atomic absorption and makes the measurement of copper possible in $\mu\text{g L}^{-1}$ values. This method for Pre-concentration of the Cu ions by dispersive liquid-liquid microextraction is novel and could be employed for various applications in the synthesis of a wide variety of determination of fluorescence quenching of CdS quantum dots.

Keywords:

Nanotechnology, Dispersive liquid-liquid micro extraction, copper, cadmium sulfide quantum dot

Paper type Research paper

1-Introduction

Copper is one of the essential elements required for preserving and maintaining the structure and working and proliferating of cells of mammals, plants and some of organisms. However, excessive amounts of copper can cause abnormal metabolism[1].Copper possesses a large variety of biological applications. In addition, in high concentrations it can be considered a toxic element. Many of the industries' waste streams such as mines, copper industries, and semiconductor industries, use heavy metals in their production process that can be harmful to the environment [2].

In this regard, copper has attracted a lot of attention, since this cation is abundantly used in metallurgy and chemical industries . In addition, it has an important role in building about 30 types of enzymes and glycoproteins in human body and is also used for the hemoglobin synthesis. In human body, it helps in iron absorption from the stomach. It also participates in the transport of iron from tissues into plasma and is important for making brain and bone cells[3].The amount of copper intake for human is 0.9 mg.day^{-1} and can reach up to 3 mg.day^{-1} under certain circumstances.According to the subjects mentioned in terms of pollution, environmental chemistry, geochemistry and control of food and medicine materials, it is required to develop a simple, rapid, sensitive, accurate and selective method to measure the amount of Cu^{2+} . However, direct determination of heavy metals level effects on environmental samples is difficult[4].Because their concentration is lower than the limit of detection of tools. These limitations can be overcome and transcended by applying one step of pre-concentration or filtration before the determining process. Several analytical methods are used for the analysis of the Cu (II) cation including fluorimetry, flame atomic absorption, spectrophotometry, furnace atomic absorption, voltammetry and so on. Core-shell quantum dots of CdSe/CdS covered with *L*-cysteine was presented as a selective fluorescence detector to measure the copper (II) ions by Zhang et al, in 2008 . These prepared quantum dots ($\lambda_{\text{em}}=585$) have high solubility in water. The full width at half maximum intensity of photoluminescence spectrum related to these nano crystals is very narrow and approximately 30 nm and the quantum portion of 15% compared to rhodamine G6 in ethanol[5]. With the addition of excess *L*-cysteine to the solution, the fluorescence intensity of CdSe/CdSquantum dots stabilized with *L*-cysteine, shows a steady improvement[6].The linear range of method from 10^{-8} to 2×10^{-8} the limit of detection (LOD) was 3×10^{-9} . This method was used for the first time to measure the Cu^{2+} in vegetables samples with the recovery percent of (105.8 and 99.6%)[7].In another method, the zinc sulfide quantum dots coated with *L*-cysteine were

synthesized in an aqueous environment. These functionalized nanoparticles were used as fluorescent sensor for Cu^{2+} . In this work, a certain amount of zinc sulfide quantum dots were mixed with buffer solution with pH=5 and with a certain concentration of Cu^{2+} and fluorescence intensity of the solution was read at 290 nm [8]. In study of interferences, the fluorescence intensity of the mentioned quantum dots was influenced by Fe^{3+} and Ag^+ ions[9]. The effective Parameters, the effect of solution pH, temperature effect, stability and concentration of nanoparticles were studied. Under optimal conditions, the LOD was 7×10^{-6} M. During cloud point extraction (CPE), an injection method was developed by Javadi and dalali to online measurement of trace amounts of copper (II) using flame atomic absorption spectrometry (FAAS). Copper (II) was extracted using Triton x-114 (as surfactant) and *N*-phenyl benzohydroxamic acid as ligand and sodium sulfate as a desalter. The enriched surfactant phase is collected in a column filled with cotton then the complex was sent into the FAAS's nebulizer using ethanol containing 1 volume percent of nitric acid[10].

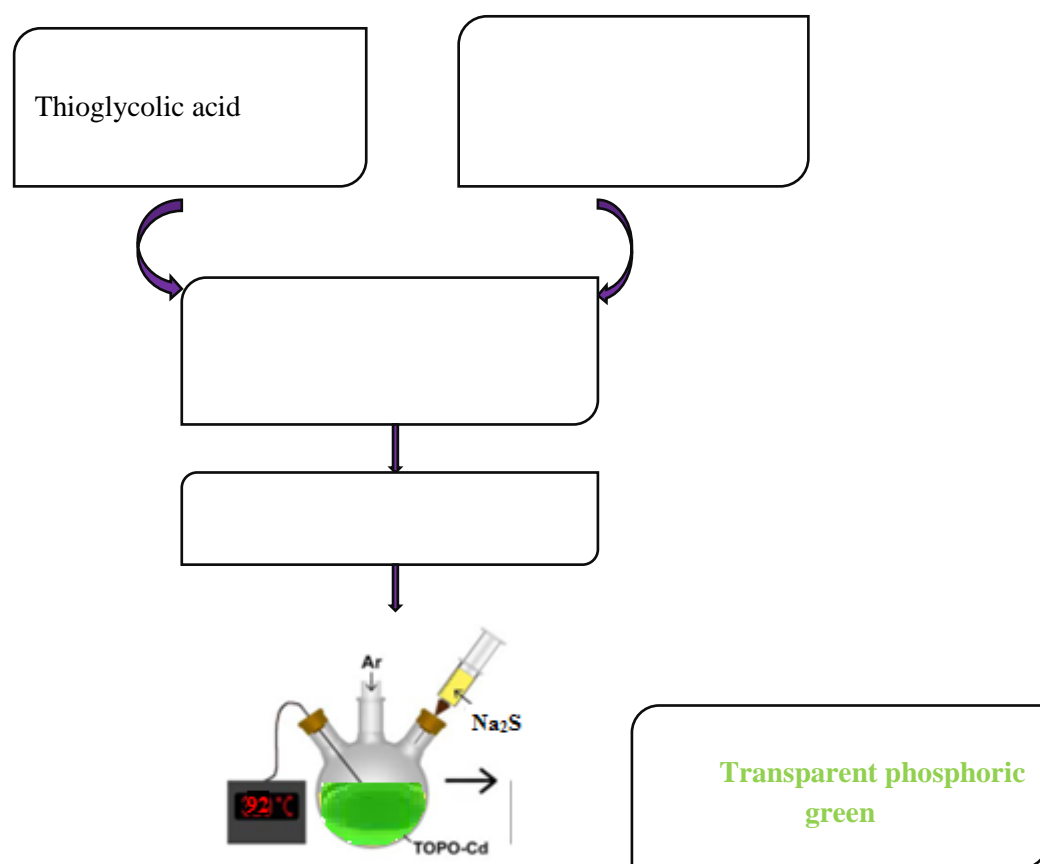
2- Experimental

Materials

Synthesis of cadmium sulfide quantum dots stabilized with thioglycolic acid

The method type was chemical synthesis and in a 250 ml beaker, CdCl_2 (100 mL, 2% M) was mixed with thioglycolic acid solution (100 mL, 5% M). The solution color became opaque white and this solution was highly acidic due to the existence of thioglycolic acid (pH about 0.55). We neutralized this solution through titration with NaOH (1 M). Gradually the solution became transparent and when the pH approached to 8.5, the solution color completely became transparent. In this stage, all the solution was poured into a three-neck flask. One of the flask's openings was connected to the decanter funnel containing Na_2S solution (2% M, 50 mL), and the second opening to a coiled condenser and the third opening to a thermometer and an argon gas cylinder. A magnetic heater-stirrer was placed under the three-neck flask and gradually the temperature was raised until the solution temperature reached to 90 °C. At this time, we slowly opened the entering water stream to the condenser and Argon gas cylinder. Synthesis of quantum dots is possible in an environment of inert gas without oxygen. That's why we used argon gas and controlled the outgoing gas flow and prevent air from entering. The outgoing water slowly went to the waste from the condenser. When the solution temperature reached about 92 °C, the decanter funnel valve was opened to enter Na_2S solution into the mixture and react with CdCl_2 . At this time, the solution became clear phosphoric green. After opening the funnel, the flask containing the solution of quantum dots

was separated from the condenser and placed on the iced-water (for 2 minutes) till the solution temperature reached the ambient temperature (32 °C). The quantum dots of cadmium sulfide are stable and if they are preserved in cool and dark environment, they will have the lifetime of about 4 months. In order to purify the synthesized quantum dots, we use ethanol and distilled water. **Scheme 1**



Scheme 1 Preparation stages of Cadmium- sulfide quantum dots

3-Results and discussion

3.1.Emission spectrum of CdS quantum dots in the presence of various concentrations of copper

In the present research work, at first the CdS quantum dots stabilized with thioglycolic acid were chemically synthesized in an aqueous stage. These synthesized quantum dots with high solubility in water, long lifetime, fast reaction rate, high sensitivity and high selectivity were used for the measuring lead ions in aqueous samples. For this purpose, copper cations were pre-concentrated using dispersive liquid-liquid micro extraction method based on ionic liquids and reverse extraction was performed with dilute nitric acid (1 M)[11]. Then considering the quenching effect of fluorescence intensity related to CdS quantum dots and using the Stern-Vollmer equation, analytes were quantitatively studied. Various factors, which could be effective on this work, were investigated and experimental parameters such as the quantum dots volume, pH influence, the amount of used ligand, and the amount of solvents used for extraction and dispersion were optimized in order to achieve the maximum sensitivity and the widest linear range[12]. In these investigations, the single-parameter optimization method (one variable at a time) was used. The quenching phenomenon in this system by copper (II) metals has been attributed to the effective electron transfer from thioglycolic acid to analyte ions. The formation of ultrafine CuS particles show that the analyte ions effectively quench the quantum dots fluorescence by facilitating the non-radiative pairing (recombination) of excited electrons in conductive band and in vacant cavities (^+h) of the valence band. Figure 1 shows the calibration curve related to emission

spectrum of cadmium sulfide quantum dots in the presence of various concentrations of copper [13].

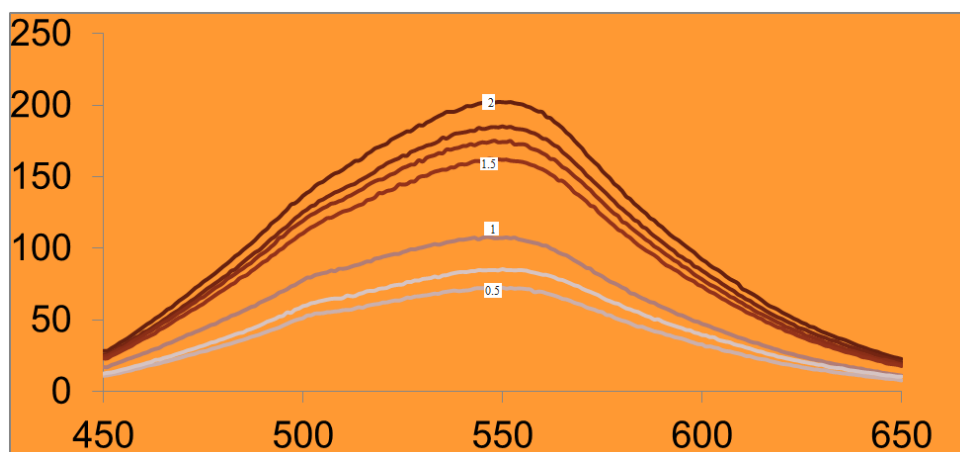


Figure 1. Emission spectrum of CdS quantum dots in the presence of various concentrations of copper (0.01, 0.1, 0.5, 1, 1.5, and 2 $\mu\text{g/L}$). The volume of CdS quantum dots in all concentrations was constant (200 μL).

3.2. Optimization of experimental parameters for pre-concentrating of copper and its measuring

Optimization of the buffer type in copper measuring

The effect of different buffers and their ionic strength on the relative fluorescence intensity of quantum dots in the measurement of copper was investigated and the results are shown in Figure 2. Results in Figure 2 show that the relative fluorescence intensity of acetate (CH_3COOH) is more than that of the phosphate buffer (NaH_2PO_4); this is in agreement with the scheme of transcendent sections related to chemicals varieties. Therefore the acetate buffer was selected as the optimal buffer[14].

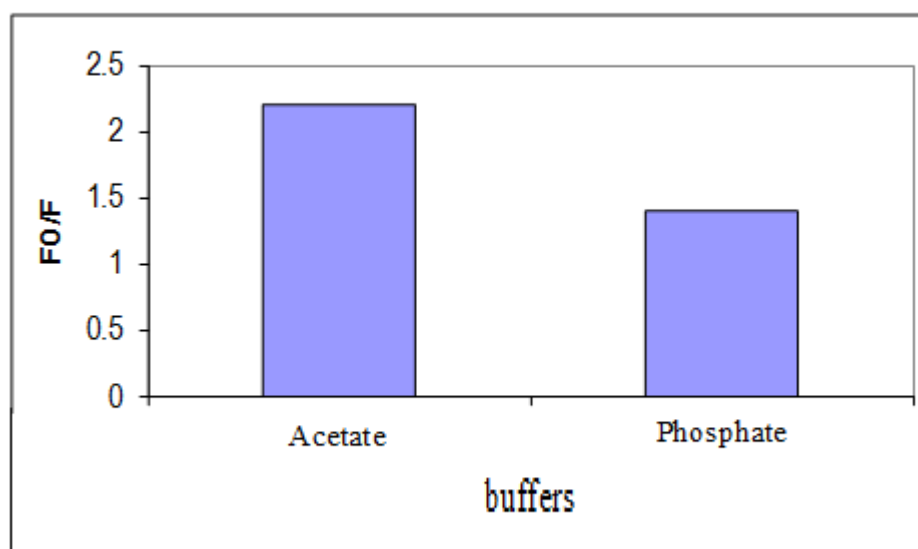


Figure 2. The effect of buffer type on copper measuring (lead=1 μ g/LQD=200 μ l and buffer =100 μ l)

3.3.Optimization of the quantum dots volume in the measurement of copper (II)

The effect of nanoparticles amount (quantum dots) on the fluorescence quenching has been studied for copper ions and the results are presented in Figure 3. When the amount of quantum dots reached 150 micro liters, the amount of F_0/F reaches its maximum. After this volume, the relative fluorescence intensity decreased. So the 150 μ L of nanoparticles was selected as the optimum amount for continuation of the investigation. The shift of the volume plasmon energy with particle size in cadmium sulphide nanoparticles was examined by energy filtered transmission electron microscopy. This technique allowed the plasmon energy of individual, well-separated particles to be measured. The measured plasmon energy was found to increase with decreasing particle size, in general agreement with the theoretical approximation for plasmon shifting due to the quantum size effect. The nanoparticle diameters ranged between 1.5 and 3.8 nm and they were prepared by mechanochemical processing techniques and then electrophoretically deposited on the transmission electron microscope specimen grids [15].

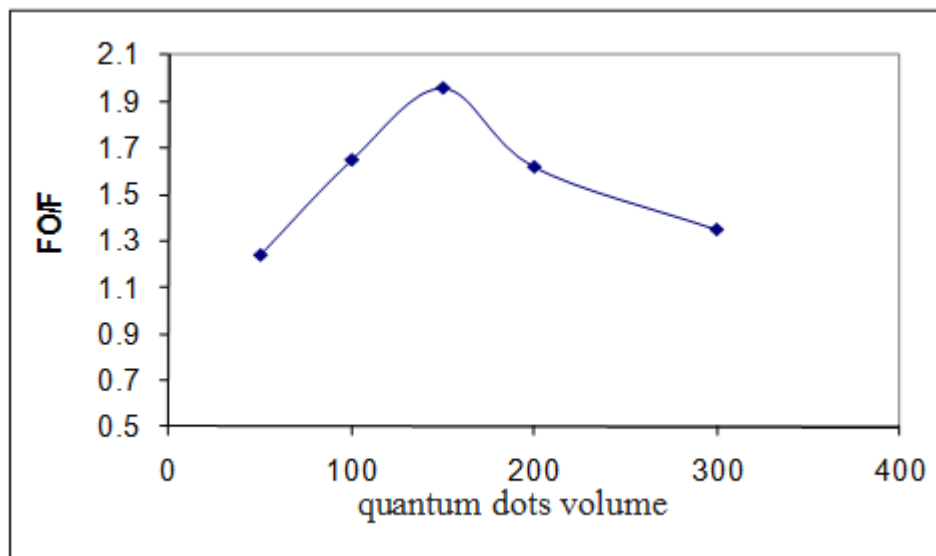


Figure 3. Optimization of the quantum dots volume in copper measuring (copper=1 μ g/L, acetate buffer 300 μ L, quantum dots 200 μ L and pH=5)

3.4. Analysis of the transmission electron microscopy (TEM) image

Figure 4 shows the TEM images of CdS quantum dots. Various magnifications of Figure 4 show that ultrafine CdS nanoparticles are diffused on the surface of thioglycolic acid as substrate. In fact, these images indicate that the surface of thioglycolic acid has been covered by the nanoparticles which are actually quantum dots. The particles are in the size range of 0.63-1.5 nm.



Figure 4. TEM images of the CdS quantum dots

3.5. Study the effect of extraction time on the measurement of copper (II) ion

Results related to investigation of the rest time effect are shown in Figure 5. For this evaluation, times of (0, 5, 10, 15, 20 and 25) minutes were applied. As it is clear from Figure 8, after 10 minutes, the maximum relative fluorescence intensity is observed and along with increasing the rest time, reduction in the signal can be seen. So in order to achieve the best extraction yield and the best relative fluorescence intensity, the time of 10 minutes was selected to continue the research[16].

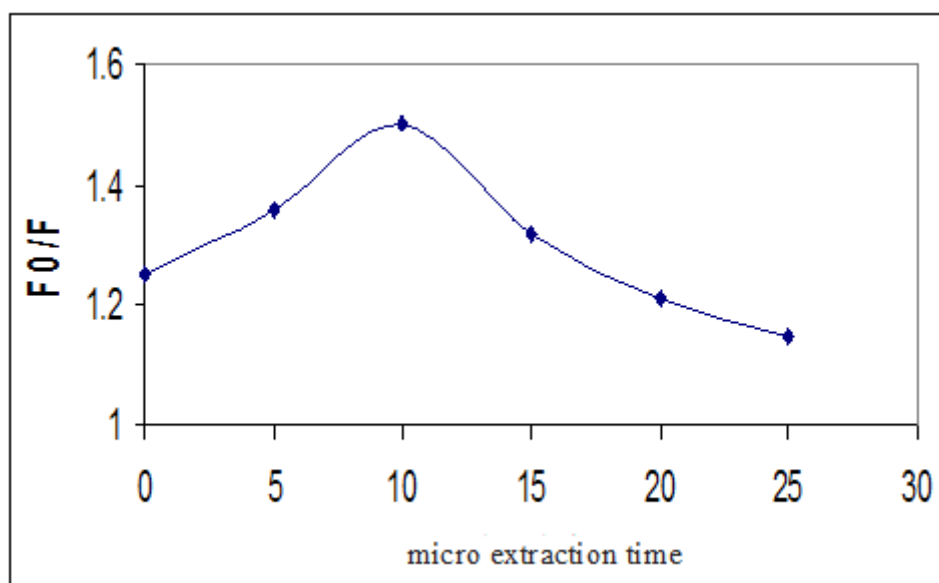


Figure 5. Study of the micro extraction time in copper measuring (copper=1 $\mu\text{g/L}$, acetate buffer 300 μL , quantum dots 150 μL , pH=5 and with 100 μL dithizone and 70 μL ionic liquid

3.6. Calibration graph of Copper (II)

After optimization of the experimental parameters, the calibration curve was plotted based on F_0/F against the concentration of Cu (II). For this purpose, we plotted the graph according to the optimized experimental values and in accordance with the suggested method described[17]. At first, the fluorescence spectrum of the quantum dots was recorded in the absence of copper and then in the presence of various concentrations of copper. F_0/F was calculated at each concentration and the results are shown in Figure 6. Copper quenches the quantum dots fluorescence linearly which is expressed by the Stern–Vollmer equation. In the case of copper, the linear equation between concentration and relative fluorescence intensity is in the form of $y=0.5024x+1.0879$ which matches with the Stern-Vollmer equation [18].

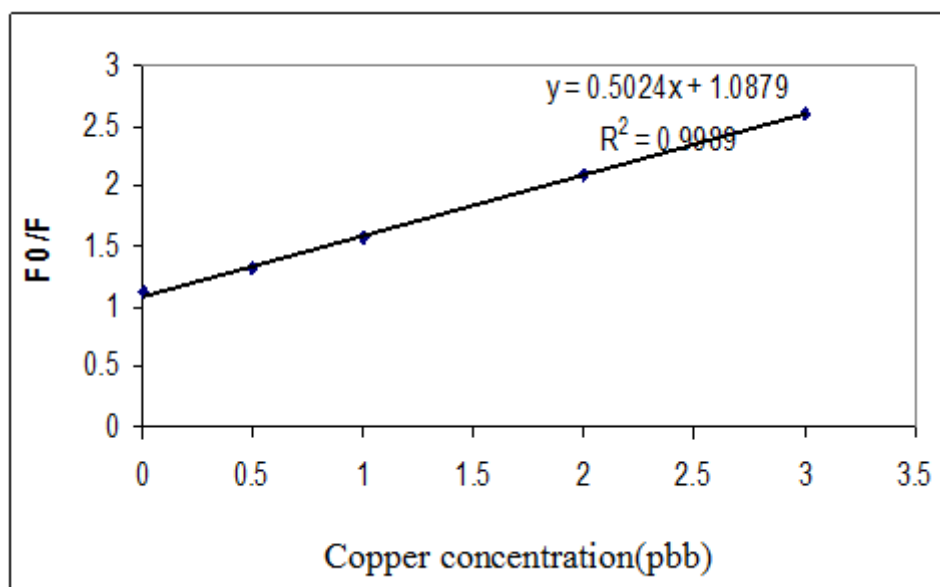


Figure 6. The calibration curve at various concentrations of copper (the Stern-Vollmer curve under the optimal conditions)

3.7. Analysis of real samples

In order to confirm the possibility of using the present method for analyzing real samples, the invented method has been applied to measure copper in aqueous samples. Recovery percentages were calculated by comparing the obtained results before and after addition of copper to real samples. Recovery percentages are in the range from 95.2-103% and the RSD values obtained from them are in the range from 1.15-8.3% which indicates the applicability and validity of the method.

3.8. Study of interferences in the measurement of copper

In order to evaluate the selectivity of the method, the effect of some common cations including Pb^{2+} , K^+ , Zn^{2+} , Hg^{2+} , Li^+ and some important anions such as carbonate, sulfate, nitrate on lead quenching was investigated on the fluorescence intensity of quantum dots and results obtained are shown in the Table 1. In all experiments, the copper solution with the concentration of $1 \mu\text{g.L}^{-1}$ along with other optimal conditions was prepared according to the proposed method for measuring copper and the related fluorescence intensity was measured (without interfering factors).

Foreign ions	limit of interference for copper (II)	Copper relative error (%)
Li^+	250	3
Hg^{2+}	50	4.6
Pb^{2+}	10	4.3
Fe^{3+}	100	3.1
K^+	250	4.5
CO_3^{2-}	2000	3
Zn^{2+}	50	2.7
NO_3^-	500	3

Table 1 Investigation of foreign ions interference in the measurement of copper ions

Table 1 shows that in the case of copper, zinc, mercury, iron, and lead metals affect the fluorescence of quantum dots. But other cations make less interference. The results showed that the present method possesses good selectivity. Interference caused by transition metals can be removed through the addition of ligands which make complex with the interfering factors although they do not react with the desired metal[19.20]

Conclusion

Pre-concentration of Cu^{2+} cation by dispersive liquid-liquid micro extraction based on ionic liquids and their measurement applying the method called fluorescence quenching of cadmium sulfide quantum dots stabilized with thioglycolic acid is possible in aqueous samples. The proposed method possesses high sensitivity and low limit of detection in comparison with many spectrophotometric and electrochemical methods and even atomic

absorption and makes the measurement of copper possible in $\mu\text{g L}^{-1}$ values. The suggested method for measuring copper has a wide range of dynamic concentration ($0.01\text{-}3\ \mu\text{g.L}^{-1}$) which this range is more extensive in comparison with many analytical methods. The presented method has good accuracy, more speed and good repeatability.

Acknowledgements

The authors gratefully acknowledge Mahabad Branch, Islamic Azad University and Iranian Nanotechnology Initiative for providing financial support and encouragement.

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