TRACE ANALYSIS OF COPPER BY MICROEXTRACTION COUPLED WITH UV-VIS SPECTROPHOTOMETRY IN NATURAL WATERS

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ABSTRACT

Ultra-trace detection of Copper ions by complexation with Neocuproin as an organic chelating agent using dispersive liquid-liquid microextraction combined with UV/Vis Spectrophotometry was investigated as a quite simple and rapid method in water samples. Some factors influencing on the extraction efficiency of copper were studied and optimized, such as the extraction and dispersive solvent type and volume, pH, chelating concentration, extraction time and salting effect. The proposed method showed a linear calibration curve in the concentration range of 20-200 ppb (R² = 0.9996) with a limit of detection of 0.1 ppb (3Sb/m) following a very nice enrichment factor of >136 for the analyte. The relative standard deviation for seven replicate determination was ≤3.5%. The proposed protocol has been applied for determination of Copper in standard and water samples with satisfactory results.

KEYWORDS: Dispersive liquid–liquid microextraction, Copper determination, Preconcentration.

I. INTRODUCTION

The quantification of heavy metals in the environment has been one of the great interests of scientists, since in this modern age industries are growing along with their waste and their dangerous effects on the ecosystem and human health depend on their dose and toxicity. Copper as one of the heavy metals which is important for human body and nature in one hand but on the other hand, it is highly toxic for organisms like algae, fungi and many bacteria or viruses [1]. Copper is also said to be, cause of infant liver damages. Drinking water can be a potential source of copper intake. Hence, copper trace quantification in natural water samples is a notable analytical task. Trace detection of heavy metals and other elements in water and food samples are quite difficult as their concentration level is fairly low and the interference due to matrix cannot be always eliminated. Therefore, to overcome with these problems of real samples with such a complex matrix, separation and enrichment protocols are necessary prior to do measuring of metal ions. For the preconcentration of metal ions diverse procedures such as, solid phase extraction (SPE), liquid–liquid extraction (LLE), coprecipitation and cloud point extraction (CPE) have been developed [2–4]. While, limitations, such as being time-consuming, undesirable enrichment factors, large amounts of organic solvents as secondary waste makes their applications limited.

Dispersive liquid–liquid microextraction (DLLME) is a highly sensitive, efficient and powerful method for the preconcentration and quantification of trace amounts of organic and inorganic analytes in aqueous media [3]. In DLLME methods, the adequate mixture of the organic (as extraction) and disperser solvents is quickly inserted by micropipette into water samples. As a result of that, a cloudy solution is appeared and the extraction occurred. Considering DLLME is one of the methods including miniaturized sample pre-treatment techniques, the techniques which are reported for the detection of metal ions in micro amounts by DLLME are including, ICP-OES [5], GFAAS[6–8] and FAA[9,10].

In this work, UV–Vis spectrophotometry as a much more cost-efficient and simple method was applied to combine with DLLME measuring of Copper. Compared with the other costly techniques, the conventional
spectrophotometry is notably limited by its low sensitivity, but its economic cost makes it a common detection method which normally uses more often than others. Recently, some researches coupled miniaturized pretreatment techniques with small volume to UV–Vis spectrophotometer[11-13] and fulfilled to the detection of non-metal analyte [13]. By coupling some advanced sample pre-treatment techniques with ordinary spectrophotometer, which could improve the sensitivity of method significantly thus to improves its fields of applications. Considering the widely use of the instrument, the study of this hyphenation is meaningful. To the best of our knowledge, there has been no report on application of DLLME for the detection of copper complexed with Neocuproine coupled with spectrophotometer. The DLLME technique was so simple and rapid which only about 5 min was needed for each sample extraction and determination. To get the optimum condition the main parameters influencing extraction and determination were studied in detail. The characteristics and performance parameters of the proposed method are described below.

II. EXPERIMENTAL

Instrumentation
UV-VIS spectrophotometer 160 made by Shimadzu- Japan, Centrifuge 101 made by Sigma USA, pH meter – mettler Swiss, 200-1000 µl sampler –Acon, 10-100 µl sampler –Acon, 10 µl UV microcells made by Starna England, 10 ml glass tube with caps and conic ends.

Reagents
All chemicals that used in this research had an analytical grade. Copper sulphate, sodiumcitrate, Neocuproine, hydroxyl amine hydrochloride and extraction solvents including carbon tetrachloride, chloroform, dichloromethane, tetrachloroethylene and disperser solvents include acetone, methanol, propanol, acetonitril. All purchased from Germany Merck. Inorganic acids and bases purchased from May and Baker (USA).

Extraction of copper-DLLME procedure
5 milliliters of copper water solution with a definite concentration that contained 1% hydroxyl amine hydrochloride and it’s pH was adjusted with a sodium acetate/acetic acid buffer, on pH = 5, transferred to a 10 milliliters glass tube. In a glass vial 105µl of chloroform added to 1250 micro liter of Neocuproine solution in methanol with a 2×10^{-3} M concentration (here methanol use as a disperser solvent). Then the vial contains injected via a 1000 µl sampler while it was under pressing to the glass tube contains. A cloudy solution (water, methanol and chloroform) produced. Then the tube cap was closed and shacked well. In this stage copper reacted with the Neocuproine and a complex formed and was extracted to the chloroform particles that was dispersed by the methanol. After this stage, centrifugation (2 min at 4000 rpm) was used to sediment these droplets to the bottom of the conical tube. After removing bulk aqueous phase by a sampler, 15µl of sedimented phase transferred to spectrophotometer. The adsorption determinations of copper-neocuproine complex were read in 457 nm. For reference microcell, prepared a blank solution by using double distillated water while the extraction steps were same. The steps of extraction was shown below.
III. RESULTS AND DISCUSSION

Effect of type and volume of extraction solvent

To investigate the best extraction solvent a range of organic solvent including carbon tetrachloride, chloroform, dichloromethane and tetrachloroethylene was selected. Thus, chloroform has the highest efficiency of Cu-Neocuproin extraction comparing other solvents (Fig. 1). According Fig. 2, the optimum volume of 105 µl has been used to have best efficiency of extraction.

![Fig. 1. Effect of extraction solvent](image)
Effect of type and volume of dispersive solvent
To study the effect of dispersive solvent, according their miscibility in organic phase (extraction solvent) and liquid phase (sample solution), Ethanol, Acetonitril, Aceton, Methanol and Propanol were chosen. Consequently, methanol was picked up among other dispersive solvent as it has highest effect of dispersing in this method and best volume of it has been selected as 1250 µl. (Fig. 3 and 4).
Effect of pH
Effect of pH solution is another factor which should not be ignored in the extraction. Thus, sample solutions with a range of 2 to 8 were made and the highest extraction was performed when the pH was 5 (Fig. 5).

![Fig. 5 pH Effect](image)

Effect of salt
Ionic strength as the one of probable effective factors in this work was investigated. While, according Fig. 6 there is no significant effect in extraction procedure with various concentration of NaCl. Therefore the experiments were done without adding electrolyte.

![Fig. 6 Salt Effect](image)

Ligand Concentration
It is also necessary to figure out the level of organic ligand in the solution. Thus, different concentrations of Neocuproin between $6 \times 10^{-4}$ to $1 \times 10^{-2}$ M were made and the optimum concentration was chosen in $2 \times 10^{-3}$ M for further experiments (Fig. 7).
Analytical figures of merit
The proposed method showed a linear calibration curve in the concentration range of 20–200 ppb ($R^2 = 0.9996$) with a limit of detection of 0.1 ppb (3Sb/m) following a good enrichment factor of >136 for the analyte. The relative standard deviation for seven replicate determination was ≤3.5%. In Table 1 the summarized analytical figures of merit has been reported.

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<th>Table 1. Analytical figures of merit</th>
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<tr>
<td>RSD</td>
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<td>Enrichment factor</td>
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<td>Linear range ($\mu$g.L$^{-1}$)</td>
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<td>LOD($\mu$g.L$^{-1}$)</td>
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<td>$R^2$</td>
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<td>Recovery</td>
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Sample analysis
To investigate the accuracy of the proposed method, different water samples with various matrixes such as tap and mineral waters (which the mine is located in Kerman-Iran near the copper industry of Kerman) was studied. Water samples kept at 4 °C and pH 2 prior to use. In order to validate the proposed method, recovery values were calculated by spiking samples with a certain amount of copper ions (Table 3).

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<th>Determination of Cu in real and certified reference samples Table 3</th>
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<td>Evaluation method of Qalezari mine ($\mu$g.L$^{-1}$) Tap water ($\mu$g.L$^{-1}$)</td>
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<td>External calibration</td>
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<td>Spiked</td>
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<td>Standard</td>
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IV. CONCLUSION
In this study, an effective method for preconcentration and quantification of Cu (II) are reported. UV/Vis spectrophotometry as an effective and commonly used method was coupled with dispersive liquid–liquid microextraction, which minimizing organic solvent (as being toxic) consumption and meantime increase the sensitivity of copper detection. Simplicity of protocol, rapidity, low sample volume, more economic and high...
enrichment factor is some benefits of DLLME. Spectrophotometric instrumentations have merits of simplicity, cost-effective, portability and so on. Through this hyphenation investigated in the present work, the conventional spectrophotometer can accomplish trace metal detection thus to expand its applications.

V. REFERENCES


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