

## Sensitive Determination Of Copper By Cloud Point Extraction- Flame Atomic Absorption Spectrometry Method

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**Abstract :** Cloud point extraction has been used for sensitive pre-concentration of copper after complex with dithizone (DZ) followed determination of it's by flame atomic absorption spectrometry method. The analyte is quantitatively extracted to the phase rich in the nonionic Surfactant Triton X-114. The parameters which affecting the separation phase and detection process, were optimized such as pH, DZ, Triton X-114. Calibration graph showed linear trend in rang of 0.2-2 mg l<sup>-1</sup> with detection limit 8 µg l<sup>-1</sup> of copper (II). Copper in waste water samples, which gathered from petrochemical factory, has been measured and gave satisfactory results.

**Key words:** Cloud point extraction, Flame atomic absorption spectrometry, Copper.

### Introduction

Everyone is exposed to trace amounts of copper through air, soil, household dust, food, drinking water and various consumers. Inorganic copper arising from a number of industrial and mining sources occurs in water in the +2 oxidation state<sup>1</sup>.

Copper may be absorbed into the body by ingestion, inhalation and through the skin. Absorption is governed by chemical structure. Short-term exposure to high levels of copper can cause vomiting, diarrhea, convulsions, Coma or even death. However, ongoing exposure to even small amounts of copper can be harmful, especially to infants and young children. Therefore it is very important to monitor the trace levels of it in environments<sup>2</sup>.

In this aspect, reliable and sensitive analytical methods have an important role to evaluate the environmental impact of trace metal<sup>3</sup>. Currently, the most common analytical methods for the trace determination of metals are the flame atomic absorption spectrometry (FAAS)<sup>4,5</sup>, the electrothermal atomic absorption spectrometry (ETAAS)<sup>6-8</sup> and the inductively coupled plasma emission spectrometry (ICP)<sup>9</sup>. Flame atomic absorption spectrometry is by far the most widely employed technique for analyte determination<sup>10,11</sup> but is not sufficiently sensitive for the direct determination of copper and it needs previous separation and preconcentration.

Cloud point methodology has been used for the extraction and preconcentration of metal ions after the formation of sparingly water soluble complexes. Cloud point extraction and atomic spectrometry have been successfully employed for several elements in different matrices and it is an interesting alternative when a complex matrix has to be analyzed<sup>12-14</sup>.

Several ligands such as 1-(2-pyridylazo)-2-naphthol (PAN), 2-(2-thiazoylazo)-4-methylphenol (TAC), 1-(2-thiazoylazo)-2-naphthol (TAN), dialkyldithiophosphates (DDTP), have been used in cloud point extraction of metal ions<sup>15</sup>.

Among various ligands used in separation procedures, including cloud point extraction, Dithizone reagent has been widely employed due several advantages obtained, such as, capacity to form complexes with each metal in suitable condition and low solubility in water. Some studies indicated that the hydrophobicity of ligands and complexes are the fundamental factors which regulate the extraction efficiency<sup>16,17</sup>. In this work, the complexation between copper and DZ has been extracted by CPE method and determined of it's by FAAS.

## Material And Method

### Reagents and solutions

All solutions were prepared with ultra pure water (obtained from HAMILTON, England) Laboratory glass was kept overnight in a 10% (V/V) HNO<sub>3</sub> solution and then rinsed with deionized water. All reagents were made from Merck.

The stock copper solution (1000 mg l<sup>-1</sup>) was prepared by Merck standard solution.

The nonionic surfactant Triton X-114, 0.5% (W/V) prepared by dissolving 0.50 gr surfactant Triton X-114 made up to 100 ml with distilled water. A solution of  $1 \times 10^{-1}$  mol L<sup>-1</sup> DZ was prepared by dissolving 0.0249 gr of this reagent in 50 ml Ethanol. A buffer solution of pH 3 was prepared by using acetic acid and NaOH 0.1 M solution.

### Apparatus

A Varian 240 FS double beam atomic absorption spectrophotometer (AAS) with hollow cathode lamp operating at 5 mA was used for the determination of Copper in the surfactant-rich phase, which was made at 352 nm. An adjustable-capillary nebulizer and supplies of acetylene and air were used for the generation of aerosols and atomization. Deuterium lamp background correction was employed to correct for the non-specific absorbance. Operation in a double beam-background correction mode was imperative due to the complexity of the aspirated sample, which apart from the target metal and excessive chelating agent, causing a suppression of the signal. Measurements were performed in the integration mode.

A centrifuge (Hettich) was used to accelerate the phase separation process. A Methrohm model 780 pH-meter was used for pH measurements. An electronic analytical balance (AE 200 Mettler) was used for weighting the solid materials. A thermostated water bath (Memert) was employed to maintain the experimental temperature.

### Procedure

For the cloud point extraction, an aliquots of 10 ml of a solution containing Copper, and 1 ml of buffer solution pH=3, 2 ml Triton X-114 0.5% (W/V), 0.5 ml of DZ  $1 \times 10^{-1}$  mol l<sup>-1</sup>, then diluted to 10 ml by doubly distilled water and placed in a centrifuge tube and heated in a thermostat water bath at 47°C for 15 min. After heated, the resultant solution was subjected to centrifugation at 4000 rpm for 10 min for phase separation, and then cooled in an ice-water for 10 min in order to increase the viscosity of the surfactant-rich phase. The supernatant aqueous phase was easily decanted by simply inverting the tube. To decrease the viscosity of the surfactant phase and rich facilitate sample handling, 1 ml of methanol was added. The resultant solution was introduced into the flame by conventional aspiration.

## Preparation Of Real Samples

### Waste water samples

Waste waters were collected from some Mahshar petrochemical industry (These locked in Mahshar city and is the important river in Khozestane province). They were filtered through Watman No. 42 and stored in glass bottles at 4°C. Then the samples were ready for purposed procedure.

## Results And Discussion

### Effect of pH

The pH plays a unique role on metal-chelate formation and subsequent extraction, and is proved to be a main parameter for CPE<sup>18,19</sup>. The influences of pH of the aqueous solutions on the extraction yield of Cu (II) as DZ chelate was investigated in the pH range 1-9. For obtain better sensitivity pH values, several buffer agents such as phosphate, carbonate, boric acid / sodium hydroxide, and universal buffer were tested for pH adjustment, the best result was found for acetic acid/ sodium hydroxide buffer solution. Fig. 1 shows that the best recovery is in pH 3 on extraction of copper complex.

### Effect of DZ Concentration

The amount of chelating agent is another important indicator as to whether the chelating action processed completely. The effect of DZ concentrations on the recovery were determined in the range of 0.05-0.25 ml of 0.1 M. As is shown in Fig. 2 on adding over 0.15 ml solution, the extraction efficiency was the most and close to 100%, hence, 0.15 ml of 0.1 mol l<sup>-1</sup> DZ solution in ethanol was chosen.

### Effect of Triton X-114 concentration

Triton X-114 was chosen for the formation of the surfactant rich phase due to its low cloud point temperature and commercial availability in a high purified homogeneous form, low toxicological properties, cost and high density of the surfactant rich phase, which facilitates phase separation by centrifugation.

Fig. 3 has shown the effect of TritonX-114 concentration on the CPE pre-concentration of copper. The signals of copper increased as the Triton X-114 concentration increased from 0.25- 1.0% (W/V) and approximately constant when, Triton X-114 concentration was increased larger than 1.0% (W/V). Hence a concentration of Triton X-114, 1.0% (W/V), was employed for the rest of this work.

### Selection of the dilution agent for the surfactant – rich phase:

An organic solvent should have characteristics such as low viscosity, low surface tension and combustible for use in atomic absorption<sup>18</sup>. Different solvents for the surfactant–rich phase were tested so as to select the one producing the optimal results regarding sensitivity. Acetone, methanol, ethanol and DMF were tested for this purpose. Methanol dissolved completely the surfactants which in its extracted complex of copper and DZ and the best recovery were obtained and an optimum volume is 1 ml.

### Practical parameter

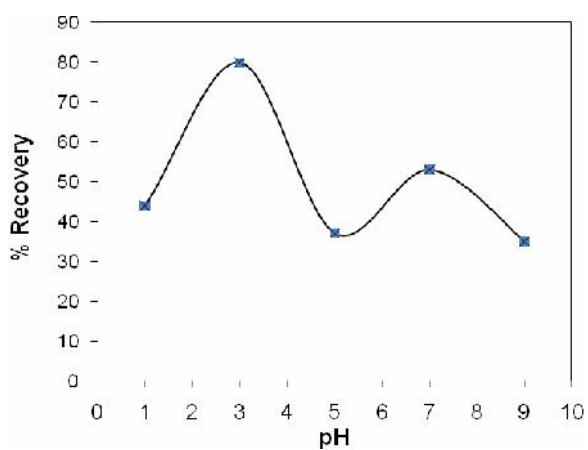
The dependence of extraction efficiency on equilibration temperature and time were studied within a range of 30 –60 °C and 5–25 min, respectively. The results showed that an equilibration temperature of 47 °C and an equilibration time of 20 min are enough to get quantitative extraction of the ions. The effect of the centrifugation time on the extraction efficiency was also studied within a range of 5–25 min. A centrifugation time of 15 min at 4000 rpm was selected for the entire procedure, since analyte extraction in this time is almost quantitative.

### Figures of merit

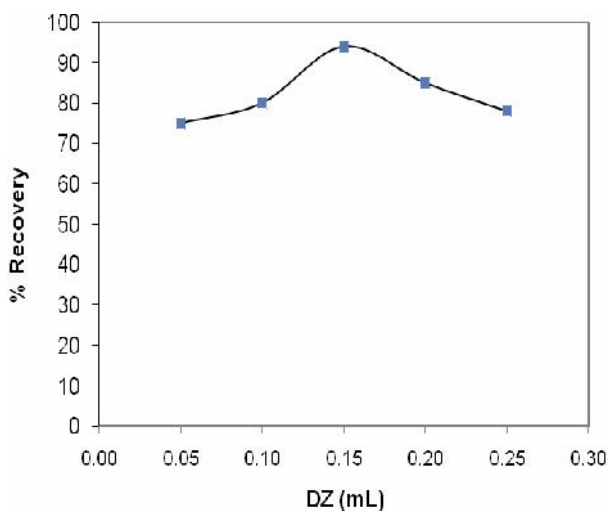
Calibration graph was obtained by pre–concentrating 10 ml of a sample containing known amounts of analysts in presence of 2.0 mL of 0.5% Triton X-114 in a medium buffered at pH 3. Final solution was introduced into flame atomic absorption spectrometry by conventional aspiration following the addition of 1 ml of methanol. Under the specified experimental conditions the calibration curve for Cu was linear from 0.2 to 2.0 mg l<sup>-1</sup> with a correlation coefficient of 0.9986. The relative standard deviation (RSD, n=5) for 1 mg l<sup>-1</sup> concentration of lead was 2.57% and the limit of detection (LOD) under the optimal condition was 8.0 µg l<sup>-1</sup> (Table 1).

### Determination of copper in waste water samples

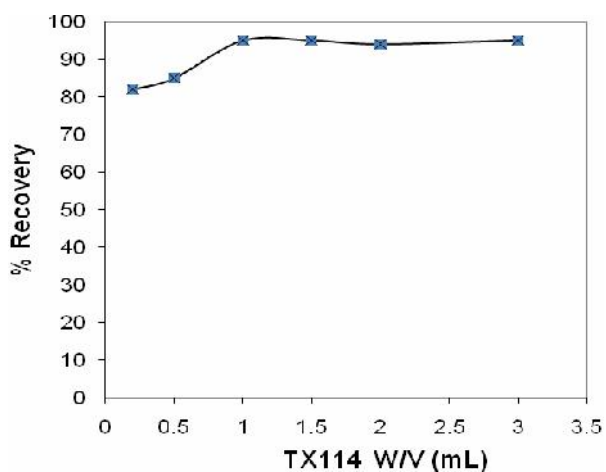
In order to test the reliability of the proposed methodology the assaying were done for determination of copper in waste water samples of Ghadir petrochemical by perposed method. The results are shown in Table 2 which gave satisfactory results.



**Fig. 1.** Effect of pH on the CPE-preconcentration performance.



**Fig. 2.** Effect of the volume of DZ 0.1 M on the recovery of Cu(II) by proposed method.



**Fig. 3.** Effect of the Triton X-114 concentrations on the on the extraction recovery of copper.

**Table 1.** Properties of merit obtained by the proposed method

Parameters	Cu
Linear Range ( $\text{mg L}^{-1}$ )	0.2-2.0
Correlation Coefficient	0.9986
Detection Limit ( $\mu\text{g L}^{-1}$ ) (n =5)	8
RSD % (n =5)	2.57

**Table 2.** Determination of Cu in waste water of Ghadir petrochemical samples.

Sample	$\text{Cu}^{2+}$ ( $\mu\text{g L}^{-1}$ ) <sup>a</sup>		% Recovery
	Added	Found	
Waste water 1	-	ND <sup>b</sup>	-
	20	47.32±0.3	108.6
	50	79.50±0.4	107.8
Waste water 2	-	ND	-
	20	22.23±0.3	111.1
	50	54.51±0.4	109.0

a) After appropriate dilution

b)ND: Not detection

## Conclusion

Cloud point extraction using Triton X-114 shown to be an efficient, simple, easy, safe, rapid, inexpensive and versatile pre-concentration technique to determine Cu by FAAS. In this method DZ is a reagent selectivity and sensitivity for determination of copper in waste water samples. Phase separation can be achieved at relatively low temperatures and extraction efficiency is high, resulting in low detection limits and high enrichment factors and good R.S.D. The proposed method has promising application in environmental analysis for trace copper.

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