

# Determination of Trace Copper(II) in Food Samples by Flame Atomic Absorption Spectrometry After Cloud Point Extraction

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**ABSTRACT:** A new method for the determination of trace copper(II) in food samples by Cloud Point Extraction(CPE) combined with Flame Atomic Absorption Spectrometry(FAAS) is presented and evaluated. The method is based on the fact that hydrophobic complex of copper(II) with sodium diethyldithiocarbamate (DDTC) was formed at pH 6.0 and subsequently the hydrophobic complex was extracted into surfactant-rich phase. Copper(II) in surfactant-rich phase was analyzed by FAAS after dilution the surfactant-rich phase to 0.5 mL by nitric acid in methanol(0.1 mol L<sup>-1</sup>). The main factors affecting CPE, such as pH, concentration of DDTC and Triton X-114, equilibrium temperature and incubation time, sample volume were investigated in detail. The effect of coexisting ions on the recovery of copper(II) was also investigated. Under the optimum conditions, the detection limit(3 $\sigma$ ) of this method was 1.1 ng mL<sup>-1</sup> for copper(II), and the relative standard deviation was 3.4 % (c=100 ng mL<sup>-1</sup>, n=7). The analytical results for the certified reference tea sample(GBW07605) were in a good agreement with the certified value. The proposed method was successfully applied to determination of trace copper(II) in milk powder and mineral water with satisfactory results.

**KEY WORDS:** Cloud point extraction, Copper, Food samples, Flame atomic absorption spectrometry.

## INTRODUCTION

Copper is an essential element not only for life in mammals but also for plants, and it plays an important role in carbohydrate and lipid metabolism. It has many biological effects as an essential element as well as a toxic one[1]. In general, a daily copper intake of 1.5-2 mg is essential for adults and copper at nearly 40 ng mL<sup>-1</sup> is required for normal metabolism of many living organisms [1, 2]. But, copper(II) at higher levels is toxic and severe oral intoxication will affect mainly the blood and kidneys. Because of these,

the trace copper(II) content in foods must be controlled on a daily basis and the European Commission has fixed the limit of 2  $\mu\text{g mL}^{-1}$  for copper(II) in drinking water and the allowed limit of copper(II) is set to 1.3  $\mu\text{g mL}^{-1}$  in the USA similar to that in Canada (1.0  $\mu\text{g mL}^{-1}$ )[3, 4]. Therefore, there is an increasing need to monitor copper(II) levels in food samples at ever decreasing concentrations. For this purpose, very sensitive, simple, rapid and inexpensive methods are necessary.

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Several atomic spectrometric techniques such as Flame and Electrothermal Atomic Absorption Spectrometry (FAAS and ETAAS)[5-7], spectrophotometry [8], Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)[9], Inductively Coupled Plasma Mass Spectrometry (ICP-MS)[10] have been proposed for the determination of trace copper(II) in different food samples. Since the quantity of copper(II) in food samples is very small and the food sample matrix is very complicated, various separation and preconcentration procedures have been used in combination with the above mentioned techniques for accurate, reliable and sensitive results. These procedures include coprecipitation[11,12], solid phase extraction[13], liquid phase microextraction [14], and cloud point extraction[15, 16].

Nowadays, Cloud Point Extraction (CPE) using non-ionic surfactants has attracted considerable attention as an alternative to the conventional extraction techniques for separation and preconcentration[17-19]. Briefly, above the cloud point temperature, the surfactant solution easily separates into two distinct phases: surfactant-rich phase with small volume and diluted aqueous phase, in which the surfactant concentration is close to the critical micelle concentration. When metal ion formed hydrophobic complex with an appropriate chelating reagent under the adequate conditions, the hydrophobic complex can be trapped in the hydrophobic micelle core, and then extracted into the surfactant-rich phase. As a new separation technique, CPE offers many advantages over traditional liquid-liquid extraction, such as simple, cheap, rapid, no use of organic solvents, high capacity to concentrate a wide variety of analytes with high recoveries and high concentration factors[20].

When CPE technique was used for the extraction of metal chelates, FAAS was often used as detector[21,22]. Though FAAS has poor sensitivity, it is a very simple, rapid and low cost analytical tool. CPE is also very simple, rapid, environmental friendly separation and preconcentration procedure with high enrichment factor. Combination of CPE and FAAS leads to a very simple, rapid and low cost analytical method with adequate sensitivity.

The aim of this present paper is to evaluate the feasibility of combining CPE preconcentration with FAAS for determination of trace copper(II) in food samples. In this procedure, sodium diethyldithiocarbamate (DDTC) was used as chelating reagent and Triton X-114 as the extracting one.

The main factors affecting CPE were investigated in detail. The developed method was applied to determine trace copper(II) in different food samples with satisfactory results.

## EXPERIMENTAL SECTION

### *Apparatus*

A TAS-986 atomic absorption spectrometer(Beijing purkinje general Instrument Limited Company, Beijing, China) was used for the determination of copper(II) in the surfactant-rich phase. A copper hollow cathode lamp (Beijing Shuguangming Electronic Lighting Source Instrument Limited Company, Beijing, China) was used as the radiation source. The operation conditions of copper hollow cathode lamp were those recommended by the manufacture. The instrumental parameters used were recommended by the manufacture. A thermostatic bath (Jintan Instrument Limited Company, Jiangsu, China) was used for CPE experiments and phase separation was assisted by a centrifuge(80-1 model, Jintan Instrument Limited Company, Jiangsu, China) in 15 mL calibrated centrifuge tubes. All pH measurements were carried out using a PHS-25B digital pH meter equipped with a combined glass-calomel electrode (Shanghai Dapu Instrument Limited Company, Shanghai, China).

### *Reagents and standards*

A stock standard copper(II) solution( $1000 \mu\text{g mL}^{-1}$ ) were prepared by dissolving appropriate amounts of copper nitrate( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) (Tianjin Reagent Company, Tianjin, China) in double distilled water. All stock standard solutions were stored in polyethylene bottles in a refrigerator at  $6^\circ\text{C}$ . Working standard solutions were obtained by appropriate dilution of the stock standard solution just before use. Solution(1.0%, v/v) of Triton X-114 (Sigma, USA) was prepared in double distilled water and was used without further purification. Solution(1.0%, w/v) of DDTC(Shanghai Reagent Company, Shanghai, China) was prepared fresh daily in double distilled water. The buffer solution of pH 4.0 acetic-acetate, HCl and NaOH were used to control pH of the solutions. All chemicals and reagents used in this study were of analytical-reagent grade or higher purity.

### *Procedure for CPE*

Aliquots of 8.00 mL of sample or standard solution, 1.0 mL 1.0 %(w/v)DDTC solution and 1.0 mL 1.0 % (v/v)

Triton X-114 solution was added into a 15 mL calibrated centrifuge tube, and the mixture was buffered to pH 5.0 with acetic-acetate, and then diluted to 15 mL with double distilled water. The resultant solution was kept in a thermostatic water bath at 50 °C for 15 min, separation of the aqueous and surfactant-rich phase was accomplished by centrifugation for 5 min at 3500 rpm. After cooling in an ice bath, the surfactant-rich phase becomes viscous and the supernatant aqueous phase was then separated completely by a syringe centered in the tube. To decrease the viscosity of the surfactant-rich phase, the surfactant-rich phase was diluted to 0.5 mL by nitric acid in methanol(0.1 mol L<sup>-1</sup>) solution, and then the resultant solution was directly introduced into FAAS for determination of copper.

#### Sample preparation

Certified reference tea sample(GBW07605): 0.2000 g of certified reference tea sample was weighed into a 100 mL porcelain crucible, and then the powder was incinerated by a electric furnace. When there is no white smoking emission from the incinerated powder, the porcelain crucible with the powder was heated in a muffle furnace with temperature of 500±25°C for 5h. After cooling, the residue was dissolved in 100 mL 1%(v/v) HNO<sub>3</sub>.

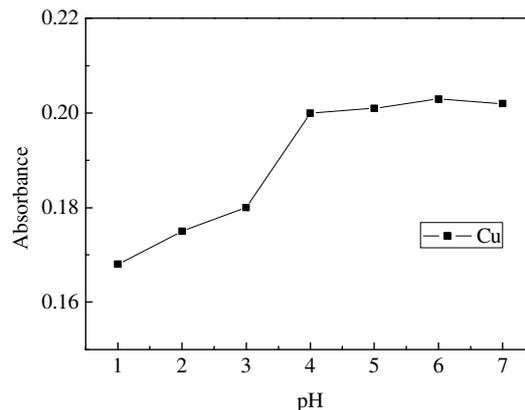
Milk Powder: Milk powder was purchased in the supermarket, produced by Dumex China). The sample preparation procedure for milk powder was similar with that for certified reference tea sample.

Mineral water: The purified water was purchased in the supermarket, and no special sample pretreatment was required for this clean water samples.

## RESULTS AND DISCUSSION

### Effect of pH

The pH plays an important role on metal-chelate formation and subsequent extraction. In this part of study, the effect of pH on the signal intensity of copper(II) in the surfactant-rich phase was evaluated at pH values varying from 1.0 to 7.0. As can be seen from Fig.1, the quantitative extraction of copper(II) was achieved at pH range of 6-7. At lower pH values, the hydrophobic complex of Cu(II)-DDTC does not form completely, so the extraction efficiency of copper(II) is low. Hence, pH 6.0 was selected as the working value.



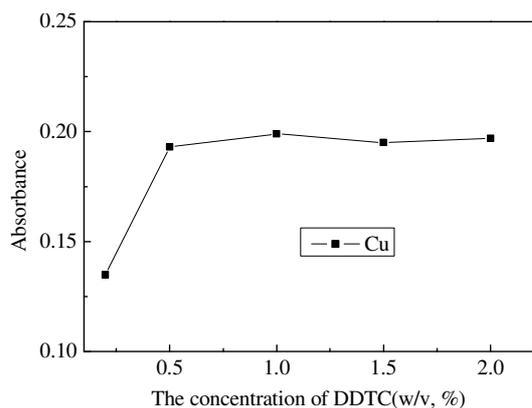
Fi. 1: Effect of pH on the signal intensity in surfactant-rich phase. Condition: Copper(II) standard solutions(125 ng mL<sup>-1</sup>, 6.00 mL), 1.0 mL 1.0%(w/v) DDTC, Triton X-114 concentration 0.066%(v/v), pH 1.0-7.0, equilibrium temperature 50 °C and incubation time 15 min.

### Effect of DDTC concentration

The CPE efficiency depends on the hydrophobicity of the ligand and the complex formation, the apparent equilibrium constants in the micelle medium, the kinetics of the complex formation, and the mass transference between the phases. The variation of the analytical signal as a function of the DDTC concentration in the range of 0.2-2.0% (w/v) was studied, and the experimental result was demonstrated in Fig.2. It could be seen that the analytical signal of copper(II) nearly kept constant when DDTC concentration within 0.5-2.0% range. For further studies, DDTC concentration of 1.0 %(w/v) was chosen.

### Effect of Triton X-114 concentration

Compared with Triton X-100, Triton X-114 has lower cloud point temperature(18 °C) and higher density of the surfactant-rich phase. It makes more convenient for inducing the phase separation and collecting the surfactant-rich phase by centrifugation. The effect of Triton X-114 concentration upon sensitivity and extraction was studied within Triton X-114 concentration varied from 0.013-0.166%(v/v). Fig.3 showed the effect of Triton X-114 concentration on signal intensity of copper(II) in surfactant-rich phase. It is obvious that a quantitative extraction was observed with the Triton X-114 concentration in the range of 0.066-0.099%(v/v). Therefore, 0.066%(v/v) Triton X-114 concentration was employed for further studies.



**Fig. 2:** Effect of DDTC concentration on the signal intensity of copper(II). Condition: Copper(II) standard solutions ( $125 \text{ ng mL}^{-1}$ ,  $6.00 \text{ mL}$ ),  $1.0 \text{ mL}$   $0.2\text{-}2.0 \%$  (w/v) DDTC, Triton X-114 concentration  $0.066\%$  (v/v), pH 6.0, equilibrium temperature  $50^\circ\text{C}$  and incubation time 15 min.

#### Effects of equilibrium temperature and incubation time

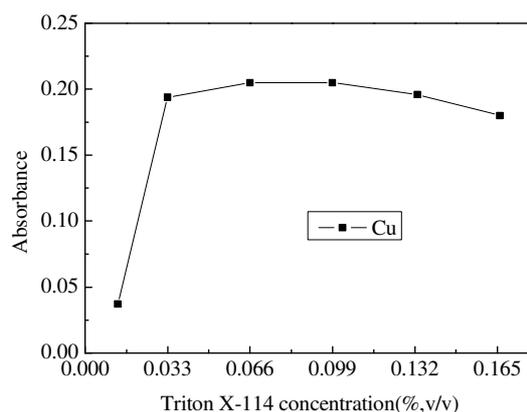
The effect of equilibrium temperature was investigated from room temperature to  $70^\circ\text{C}$ . It was found that the solutions became turbid as soon as the solutions were put into the water bath with temperature higher than  $40^\circ\text{C}$ , and the temperature had no considerable effect upon the extraction efficiency and the analytical signal kept constant at temperature range of  $40^\circ\text{C}$  -  $70^\circ\text{C}$ . Thus,  $50^\circ\text{C}$  was chosen as the equilibrium temperature. Keeping the equilibrium temperature of  $50^\circ\text{C}$ , the influence of incubation time on CPE was studied within the range of 5-30 min. It was observed that, 15 min was sufficient to achieve a quantitative extraction of analyte. Then, 15 min incubation time was employed for CPE procedure.

#### Effect of sample volume

In order to obtain a higher enrichment factor, a large volume of sample solution is required. For this purpose, 5.00, 6.00, 7.00, 8.00, 9.00, 10.00 mL of sample solutions containing 750 ng of copper(II) were extracted according to the procedure of CPE. It was shown that quantitative extraction of the analyte was obtained with the sample volumes less than 8.00 mL. For further studies, 8.00 mL of sample volume was selected.

#### Interferences of coexisting ions

The effect of potential interference of some metal ions on the preconcentration and determination of copper(II)



**Fig. 3:** Effect of Triton X-114 concentration on the signal intensity of copper(II). Condition: copper(II) standard solutions ( $125 \text{ ng mL}^{-1}$ ,  $6.00 \text{ mL}$ ),  $1.0 \text{ mL}$   $1.0 \%$  (w/v) DDTC, Triton X-114 concentration  $0.013\text{-}0.166\%$  (v/v), pH 6.0, equilibrium temperature  $50^\circ\text{C}$  and incubation time 15 min.

was examined. In these experiments, solutions containing copper(II) ( $125 \text{ ng mL}^{-1}$ ) and the added interfering ions were treated according to the recommended procedure under the optimum conditions, and the results were given in Table 1. As could be seen, the developed method is fairly selective.

#### Analytical performance

Under the optimum conditions described above, the detection limit ( $3\sigma$ ) of this method for copper(II) was  $1.1 \text{ ng mL}^{-1}$ , the relative standard deviation (R.S.D) was  $3.4 \%$  ( $c = 100 \text{ ng mL}^{-1}$ ,  $n=7$ ), the linear range was  $5\text{-}300 \text{ ng mL}^{-1}$ , and the enrichment factor was 11. Enrichment factor was calculated by the ratio of the slopes of the calibration graphs obtained with and without preconcentration. The corresponding linear equations with and without preconcentration are as follow:

$$A = 1.3236C + 0.00103 \text{ (with preconcentration),}$$

$$A = 0.1203C + 0.00102 \text{ (without preconcentration).}$$

#### Analysis of real samples

For real sample analysis, the standard calibration curve was employed. In order to establish the validity of the proposed procedure, the method has been applied to the determination of trace copper(II) in the certified reference tea sample (GBW07605). The analytical results showed a good agreement between determined values ( $16.64 \pm 0.35 \mu\text{g g}^{-1}$ ) and the certified values ( $17.30 \pm 0.31 \mu\text{g g}^{-1}$ ).

**Table 1: Interferences of coexisting ions on extraction and determination of copper(II).**

| Coexisting ions  | Mass ratio <sup>a</sup> | Recovery(%) | Coexisting ions  | Mass ratio <sup>a</sup> | Recovery(%) |
|------------------|-------------------------|-------------|------------------|-------------------------|-------------|
| K <sup>+</sup>   | 1000                    | 101.6       | Co <sup>2+</sup> | 40                      | 102.0       |
| Na <sup>+</sup>  | 1000                    | 99.8        | Ni <sup>2+</sup> | 40                      | 101.0       |
| Mg <sup>2+</sup> | 1000                    | 101.0       | Mn <sup>2+</sup> | 30                      | 103.0       |
| Ca <sup>2+</sup> | 1000                    | 100.2       | Zn <sup>2+</sup> | 20                      | 95.2        |
| Al <sup>3+</sup> | 50                      | 102.0       | Pb <sup>2+</sup> | 30                      | 95.1        |
| Cr <sup>3+</sup> | 30                      | 96.8        | Fe <sup>3+</sup> | 30                      | 96.6        |

a) coexisting ion/copper(II) (The concentration of copper(II) was 125 ng mL<sup>-1</sup>).

**Table 2: Analytical results for copper(II) in food samples(mean±SD, n=3).**

| Samples                              | added | found     | Recovery(%) |
|--------------------------------------|-------|-----------|-------------|
| Milk powder (µg g <sup>-1</sup> )    | 0     | 7.2±0.20  | -           |
|                                      | 3.0   | 10.1±0.26 | 96.7        |
|                                      | 6.0   | 13.4±0.40 | 103.4       |
| Mineral water (ng mL <sup>-1</sup> ) | 0     | 5.3±0.16  | -           |
|                                      | 30    | 35.7±1.1  | 101.1       |
|                                      | 60    | 73.4±2.3  | 113.5       |

**Table 3: Comparison among several CPE methods for copper(II).**

| Reagent            | Surfactant   | Sample volume(mL) | Detection Limit (ng mL <sup>-1</sup> ) | Enrichment factor | Ref.      |
|--------------------|--------------|-------------------|--|-------------------|-----------|
| Me-BTABr           | Triton X-114 | 10                | 1.08                                   | 17                | 23        |
| TAN                | Triton X-114 | 50                | 0.27                                   | 64.3              | 24        |
| O,O-DDTP           | Triton X-100 | 10                | 0.94                                   | 33.3              | 22        |
| Pyrogallol         | Triton X-114 | 60                | 0.05                                   | 85                | 25        |
| Me-BDBD            | Triton X-114 | 10                | 1.5                                    | 14                | 26        |
| H <sub>2</sub> mdo | Triton X-114 | 20                | 0.31                                   | 65                | 27        |
| ARS                | Triton X-114 | 12                | 1.07                                   | 21                | 21        |
| DDTC               | Triton X-114 | 8                 | 1.1                                    | 11                | this work |

The method was also applied to the determination of trace copper(II) in milk powder and purified water samples. The analytical results and the recoveries for the spiked samples were given in Table 2. It can be seen that the recovery for the spiked samples is between 96.7 % and 113.5 %.

#### Comparison to other methods

For comparative purposes, the performance characteristics of the proposed method and other selected CPE-FAAS systems reported in the literature are given in Table 3.

As seen from the table, the detection limit and enrichment factor for the method are comparable to those given by many methods in the table. It is important to emphasize that sample volume in the present study was 8.0 mL, and the whole preconcentration procedure was done just in a 15 mL centrifuge tube within 30 min.

#### CONCLUSIONS

A new method for the determination of trace copper(II) by CPE combined with FAAS was proposed in this paper. The advantages of the proposed method are

summarized as follows: (1) simplicity, selectivity, safety and low cost; (2) The combination of CPE with FAAS is a kind of combination of simple, high efficiency sample preparation method with simple, quick detection technique, and lower detection limit could be achieved.

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