



## Cloud Point Extraction and FAAS Determination of Copper(II) at Trace Level in Environmental Samples using N-benzamido-N'-benzoyl thiocarbamide and CTAB



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### Abstract

The present work describes a simple method to detect copper(II) using flame atomic absorption spectrometry (FAAS) after pre-concentration and separation by cloud point extraction (CPE) using N-benzamido-N'-benzoylthiocarbamide (HBBTC) complexing agent and cetyltrimethylammonium bromide (CTAB) as a cationic surfactant. The different experimental parameters such as pH, the concentration of the reagent, centrifuging time, and concentration of CTAB and potassium iodide were examined to increase the extraction efficiency of the proposed procedure. Under optimized extraction conditions the limits of detection and limits of quantification were found to be 0.9 and 2.70 ng mL<sup>-1</sup>, respectively. The present work was successfully employed for the determination of copper(II) in synthetic mixtures and in water samples with a recovery% greater than 97% and RSD(%) = 0.18 %.

**Keywords:** N-benzamido-N'-benzoylthiocarbamide (HBBTC); Cloud point extraction (CPE); CTAB; FAAS

### 1. Introduction

In recent years, more focus has been given to the toxicity and impact of trace elements on human health and the ecosystem in contamination and diet studies. Heavy metals are vitally essential to life. Any of these are important to humans such as Cu, Zn, Co, Fe [1]. Others such as Cd, Hg, and Pb are toxic following professional and environmental exposure [2]. Copper is one of the most extensive heavy metal contaminants in the environment. It is one of the essential elements for most life forms as a micronutrient but is also poisonous at high concentrations [1-3]. Although ICP-AES and FAAS [4-6], are commonly employed methods for evaluating trace metals, they are typically ineffective due to matrix interferences and very small metal ion concentrations. For these causes and effective methods of separation, methods are always needed prior to the measuring process. The most commonly used methods of pre-concentration are adsorption on activated carbon, [4, 5], co-precipitation, [6, 7], ion-selective electrode

[8,9], column extraction [10], liquid-liquid extraction (LLE) [11], flotation [12-14], liquid-phase microextraction [15], ion-exchange [16], resins chelation [17], SPE [18, 19], fiber chelation [20], electrochemical deposition [21] and cloud point extraction (CPE) [22]. On account of its points of interest of high enrichment factor, quick recovery, fast phase separation, low cost, low utilization of organic solvents, and the capacity to combine with specific detection, CPE method has become progressively normal contrasted to the classical liquid-liquid extraction process.

Compared to other forms of separation techniques, CPE has much more naturally sustainable characteristics and is healthier as it requires tiny concentrations of non-hazardous surfactants rather than dangerous organic solvents. CPE is an appealing methodology which decreases solvent use as well as exposure and thus decreases the expense of disposal and extraction period required for pre-concentration of metal ions following the creation of sparsely water-soluble complexes. [23-26]

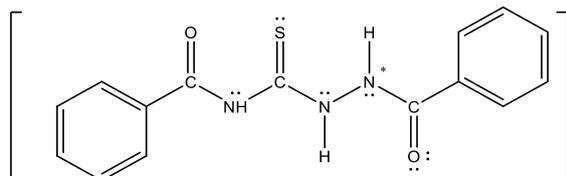
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In the present work, the reagent N-benzamido-N'-benzoylthiocarbamide (HBBTC), (structure 1) is used for pre-concentration, separation by CPE and FAAS determination of copper (II) using CTAB as cationic surfactant. The parameters having effects on the CPE efficiency, for example, solution pH, the amount of metal ions, organic ligand and surfactant, extraction time, and centrifugation period, will be investigated.



N-benzamido-N'-benzoylthiocarbamide (HBBTC)

## 2. Experimental

### 2.1. Chemicals and reagents

Otherwise, it has been found that all the reagents used are classified as analytical reagents. A solution of  $1 \times 10^{-3}$  mol L<sup>-1</sup> HBBTC is prepared by dissolving 0.030 g of HBBTC in 100 ml acetone. A stock solution of Cu (II) (0.01 mol/L) was prepared by dissolving 1.705 g CuCl<sub>2</sub>·6H<sub>2</sub>O in 100mL DDW. The surfactant, cetyltrimethyl ammonium bromide (CTAB) (Acros Chemicals, Ottawa, ON, Canada) is used without additional purification. One gram of CTAB is dissolved in 1L DDW to yield a (0.1% w/v) of CTAB solution. The pH was measured with a digital pH meter. The nitrate salts of interfering ions were dissolved in DDW to get proper concentrations in double-distilled water.

### 2.2. Preparation of HBBTC

To NH<sub>4</sub>SCN (0.1 mole) in hot Et OH (25cm<sup>3</sup>), PhCOCl (0.1mole) was included drop by drop. After the initial reaction had subsided, the mixture was heated for 5min, and afterward a hot solution of PhCONHNH<sub>2</sub>(0.1mole) in Me CN(75ml) was added, gradually with steady stirring. Upon pouring the mixture into five times its vol. of H<sub>2</sub>O, pale yellow crystals were precipitated. The product was removed by filtration, washed with water, recrystallized from absolute EtOH and dried in a vacuum desiccator over anhydrous CaCl<sub>2</sub> to yield a pale yellow compound.[27]

### 2.3. Apparatus

Traces of Cu (II) were detected by FAAS using Perkin- Elmer 2380 atomic absorption spectrometer. A digital pH meter (Hanna Instruments, model 8519). (Hanna instruments, Germany). A CH90-2 centrifuge

(Hinotek Technology Co. Ltd., China) was utilized to improve the stage partition of the nontransparent sample into the CTAB-rich layer and watery layer

### 2.3. Recommended method

For extraction and determination of copper, part of the sample solution containing 2 mg/l Cu<sup>+2</sup> was transferred to a 10 ml centrifuge tube. Then, 2 ml of an acetate buffer solution with pH 7, one ml of  $1 \times 10^{-3}$  mol L<sup>-1</sup>HBBTC and 2 ml of  $\approx$  (0.1W/V) CTAB, were added. The solution was diluted to about eight milliliter using DDW. At that point 2 ml of 1 mol L<sup>-1</sup> of KI was included. The last volume of the solution is made to 10 ml utilizing DDW, subsequent to including all the reagents, permitted to represent 3 min at room temperature. After this equilibration time, the arrangement was centrifuged for 10 minutes at 3500 rpm

The centrifuge tube is kept for 5 minutes in an ice bath. The CTAB rich phase will be settled at the bottom of the centrifuge tube and the aqueous layer above it is then easily removed by aspiration [28]. 2.0 ml of (5: 1) acidified methanolic -HNO<sub>3</sub> solution was added to the CTAB rich layer. The diluted sample was, then, introduced to FAAS to measure the concentration of Cu(II) at 324.7 nm.

The Separation efficiency of CPE was (E %) was calculated in the CTAB-rich phase from the relation:

$$E \% = (C_f/C_i) \times 100$$

Where C<sub>i</sub> was the initial concentration of the analyte in the mother liquor before CPE and C<sub>f</sub> was the concentration of analyte after CPE in the CTAB-rich phase.

As an alternative, the CPE efficiency (E, %) of Cu (II) in mother liquor was determined from the relation:

$$E \% = (C_i - C_f) / C_i \times 100 \%$$

Where C<sub>i</sub> was the initial concentration of the analyte in the mother liquor before CPE and C<sub>f</sub> was the concentration of analyte after CPE in the mother liquor.

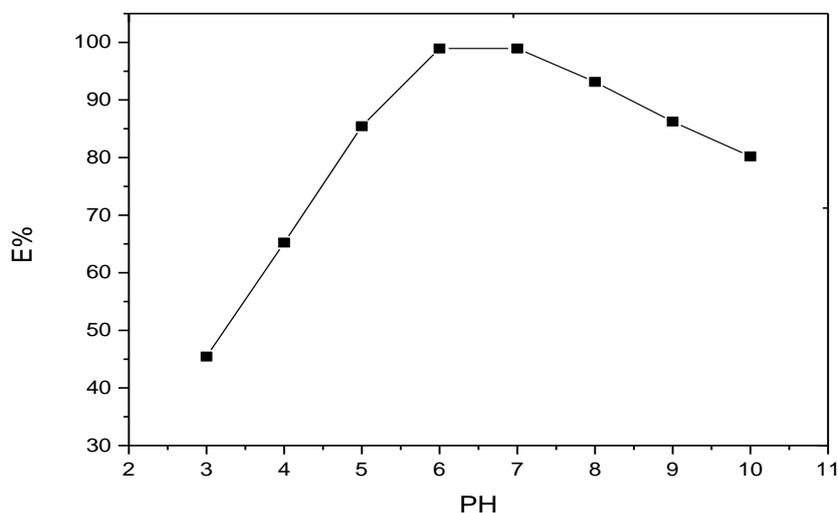
## 3. Results and discussions

### 3.1. Influence of hydrogen ion concentration

The pH of sample solution is one of the most important parameters having effects on the chelation and efficiency of the pre-concentration of the analyte. The influence of pH on Cu(II) ion extraction in the pH range (3 - 9) keeping the other factors stable.,

(Figure1). As it can be noticed, the separation of Cu(II) ions starts to increase at pH 3 and arrives at a most extreme at pH 6-7. Hence, pH 7 was chosen to

isolate the particles inspected in every ensuing investigation.

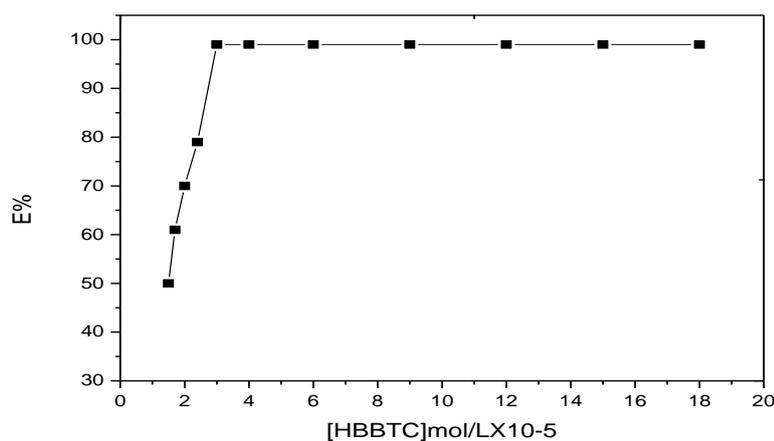


**Figure 1.** Effect of the pH on the extraction efficiency of Cu(II). Conditions:  $3 \times 10^{-5}$  mol L<sup>-1</sup> metal ion;  $3 \times 10^{-5}$  mol L<sup>-1</sup> HBBTC ; 0.18 mol L<sup>-1</sup> KI;  $3.84 \times 10^{-4}$  mol L<sup>-1</sup> CTAB; centrifuge time 10 min.

### 3.2. Influence of HBBTC concentration

The CPE of Cu(II) ions is carried out in the absence and in the presence of HBBTC. In the absence of, The E, % didn't exceed 10%. In the presence of HBBTC, [in the range of  $1.0 \times 10^{-5}$  to  $2 \times 10^{-3}$  mol L<sup>-1</sup>], the E,% of Cu(II) starts to increase steadily

with the increase of HBBTC concentration to reach its maximum(100%) at ratio L:M of 1:1. The E (%), remains constant upon further increase of the ligand concentration, (Fig. 2). An amount of  $3.0 \times 10^{-3}$  mol L<sup>-1</sup> is used in the subsequent experiments.



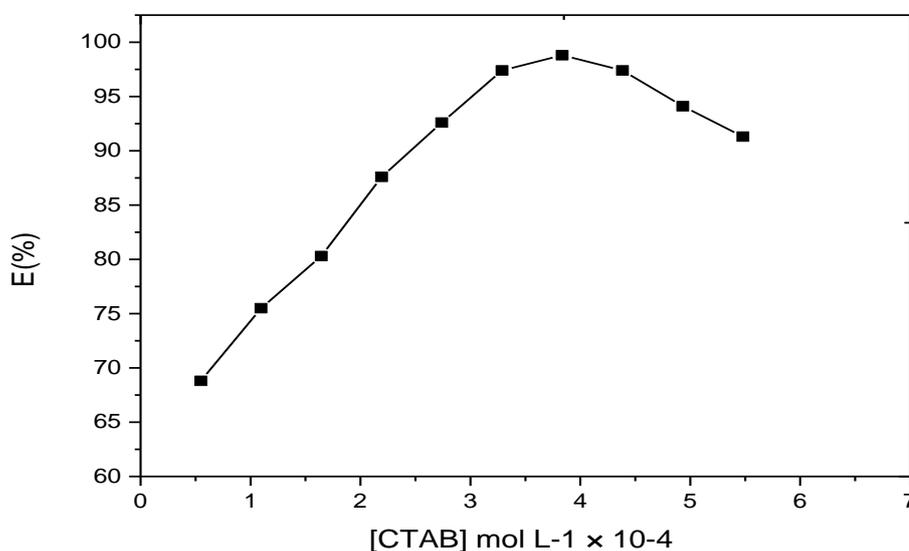
**Figure 2.** Effect of the HBBTC concentration on the extraction efficiency of Cu(II) ions. Conditions:  $3 \times 10^{-5}$  mol L<sup>-1</sup> metal ion; pH 7; 0.18 mol L<sup>-1</sup> KI;  $3.84 \times 10^{-4}$  mol L<sup>-1</sup> CTAB; centrifuge time 10 min.

### 3.3. Influence of CTAB concentration

The influence of the CTAB amount on the separation efficiency was assessed all through a wide scope of concentrations ( $0.55$  to  $5.5$ )  $\times 10^{-4}$  mol L<sup>-1</sup>, keeping other experimental factors fixed. The E(%) of Cu(II) ions reaches its maximum(100%) at  $3.84 \times 10^{-4}$  mol L<sup>-1</sup> CTAB, Fig. 3. Further increase of CTAB concentration would decrease the E, % of Cu(II). This might be ascribed to the improvement of charges in the micelles causing abhorrence between the micelles which makes them increasingly hydrophilic and ensuing diminishing in the E,%. A concentration of  $3.84 \times 10^{-4}$  mol L<sup>-1</sup> of CTAB was selected for further studies.

#### 3.4. Influence of electrolytes

The impact of various salts, for example (KI, KNO<sub>3</sub>, KCL, and Na<sub>2</sub>SO<sub>4</sub>) was explored over the concentration range ( $0.02$ –  $0.2$  mol L<sup>-1</sup>) to get lower cloud point temperatures. It was seen that the development of cloud point happens just within the sight of the considered electrolytes. Further, the use of KI gives the most noteworthy proficiency to Cu(II) extraction at room temperature ( $25^{\circ}\text{C}$ ). It was found likewise that the E,% of Cu(II) expanded with expanding KI concentration arriving at a most extreme at a concentration of  $0.18$  mol L<sup>-1</sup>. All further measurements were carried out at a concentration of  $0.18$  mol L<sup>-1</sup> KI.



**Figure 3** Effect of the CTAB concentration on the extraction efficiency of Cu(II) ions. Conditions:  $3 \times 10^{-5}$  mol L<sup>-1</sup> metal ion; pH 7;  $0.18$  mol L<sup>-1</sup> KI;  $3 \times 10^{-4}$  mol L<sup>-1</sup> HBBTC; centrifuge time 10 min.

#### 3.5. Assessment of separation and centrifugation times

The separation time is considered as the duration between the arrangement of a shady solution with the expansion of electrolytes and the point where centrifugation of the liquid-liquid microextraction in the dispenser has traditionally started. The extraction time was estimated between (1 - 10) minutes. The results obtained showed that maximum E,% could be achieved in 3 minutes and that a more prolonged extraction time did not significantly improve extraction efficiency.. The effect of centrifugation on extraction efficacy was tested at an interval of (5 to 25) minutes at 3500 rpm. After 10 minutes, the

surfactant-enriched phase was completely separated. Therefore, this optimum spin time was selected as 10 min.

#### 3.6. Impact of interfering ions

The effect of interfering ions on the CPE of Cu(II) ion under the optimum conditions was examined. The results shown in Table1 showed that most of the tested foreign cations did not interfere in the recovery of Cu(II). The effects of some other foreign ions that have little interfering effects were completely removed by increasing the concentration of HBBTC

**Table 1.** Tolerance limits of potentially interfering ions in the determination of 2 mg L<sup>-1</sup> Cu(II) ions, (n= 3).

	Foreign ions	Concentration(mg/L)	E%
1	Co <sup>+2</sup>	10	96.21
2	Ni <sup>+2</sup>	10	97.28
3	Zn <sup>+2</sup>	10	96.78
4	Al <sup>+3</sup>	10	99.0
5	Hg <sup>+2</sup>	10	98.41
6	Mn <sup>+2</sup>	10	99.87
7	Pb <sup>+2</sup>	10	99.85
8	Ba <sup>+2</sup>	10	99.86
9	Fe <sup>+3</sup>	10	98.71
10	Cd <sup>+2</sup>	10	99.61
11	Ti <sup>+2</sup>	10	97.1
12	C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	440	98.8
13	CH <sub>3</sub> COO <sup>-</sup>	295	99.64
14	CL <sup>-</sup>	177.5	99.1
15	NO <sub>3</sub> <sup>-</sup>	310	97.6
15	SO <sub>4</sub> <sup>-</sup>	480	99.99
16	NO <sub>2</sub> <sup>-</sup>	230	97.14
17	Na <sup>+</sup>	230	99.91

### 3.7. The analytical characteristics

Upon using optimum conditions mentioned in the proposed methodology, the calibration curve showed good linearity over the range 0.1 - 9.0 mgL<sup>-1</sup> Cu(II). The analytical detection limit of a standard aqueous solution is 0.9 ng/L for Cu(II) with a relative standard deviation (n = 3) of 0.18% for Cu (II). The analytical characteristics of the present method are shown in Table2.

### 3.8. Analytical applications

#### 3.8.1. In Natural water sample

The proposed combined HBBTC-CPE-FAAS system was successfully applied to determination of Cu (II) in several natural water samples. The recoveries % of spiked known additions of Cu(II) to different water samples are greater than 97%, and the RSD (n=3) is 0.18%, as shown in Table 3.

**Table 2** Analytical characteristics of the method

Parameter	Analytical feature
Linear range (mg/L)	0.1- 9.0 mg/L
RSD % (n=3)	0.18%
LOD (ng/mL)	0.9 (3Sb, ng mL <sup>-1</sup> )
LOQ(ng/mL)	2.7(10 Sb, ng mL <sup>-1</sup> )
Enrichment factor	80
Correlation coefficient(r <sup>2</sup> )	0.9991
Regression equation	Y=1.5955x+0.0095
Sample volume (ml)	10

**Table 3.** Determination of Cu(II) in spiked water samples by the proposed procedure

Sample	Added/mg L <sup>-1</sup>	Recovery (%)
Seawater	2	99.31
	4	98.63
	6	99.22
Nile water	2	98.32
	4	98.17
	6	98.23
Tap water	2	99.46
	4	99.27
	6	99.41

### 3.8.2. In synthetic mixtures

An aliquot of 10 ml of an aqueous sample solution, is prepared, containing different compositions of other metal ions (Cd (II), Zn (II), Mn (II) and Co (II), Fe (III), Al (III)) and different amounts of the analyte, 3.0 x10<sup>-3</sup> mol/L of HBBTC. The CPE procedures were performed under the previously mentioned optimum conditions and the recovery of the analyte was determined. (Table 4) showed that there were high recoveries of the analyte from samples containing different synthetic mixtures. It was observed that the presence of nickel, cobalt, and zinc reduced the efficiency of the separation, and was overcome by adding an excess amount of ligand HBBTC.

### 3.9. Comparison of the proposed CPE procedure with other cited methods

Determination of Cu(II) ion in water samples by the proposed combined CPE- FAAS using HBBTC chelating agent and CTAB surfactant, was compared with other methods recently reported (Table 5). As can be seen, the proposed CPE-FAAS method is greatly comparable to the previously reported methods.

## 4. Conclusion

The CPE-HBBTC is proved to be efficient for the separation of the HBBTC-Cu complex under the optimum conditions reported. The existence of KI decreases the cloud point temperature of selected surfactants so that the extraction can be carried out at room temperature. The extensive study of interference leads to the possibility of separation of the copper metal ions from different concomitants. At the latest, it can be concluded that the proposed CPE procedure is well suited for pre-concentration and separation of Cu(II) in a wide array of samples with high accuracy and reproducibility.

**Table 4.** Recovery of 2mg L<sup>-1</sup> Cu(II) in different synthesized mixtures.

	Foreign ion(s)	Concentration mg/L	Recovery%
1	Fe (III)+Zn(II)	20 mg/l	96.7
2	Mn (II)+Ni(II)	20 mg/l	96.22
3	Pb (II)+Hg(II)	20 mg/l	99.86
4	Al(III) +Ba(II)	20 mg/l	99.2
5	Co (II)+ Cd(II)	20 mg/l	96.12
6	Fe (III) +Zn(II) +Mn(II)	30 mg /L	96.15
7	Pb(II) +Hg(II)+Ba(II)	30 mg /L	98.5
8	Mn (II)+ Ni(II)+Co(II)	30 mg /L	95.4
9	Al(III)+Ba(II) +Cd(II)	30 mg /L	99.64
10	Fe(III) +Zn(II) + Mn (II) + Ni(II)	40 mg /L	95.5

**Table 5.** Comparison between the present methodology and some recent studies on pre-concentration-separation of Cu (II) ion.

Method	System	DL	EF enrichment factor	R.S.D, %	Ref.
SFODME	FI-AAS	1.1 ng mL <sup>-1</sup>	324	0.9%	[29]
DLLME	FAAS	0.69 µg L <sup>-1</sup>	-	-	[30]
DSPME	FAAS	1.8 µg·L <sup>-1</sup>	35	1.5%	[31]
SPE	GF AAS	2 ng g <sup>-1</sup>		below 2%.	[32]
SPE	FAAS	50 µg L <sup>-1</sup>	25	<10%	[33]
DLLME	FAAS	0.04 µg L <sup>-1</sup>	560	2.1%	[34]
CPE	FAAS	1.07 ng mL <sup>-1</sup>	21	-	[35]
adsorption	FAAS	0.012 µg ml <sup>-1</sup>	-	-	[36]
SPE	FAAS	0.06 ng mL <sup>-1</sup>	280	-	[37]
SPE	ASS	1.46 µg L <sup>-1</sup>	60		[38]
Flotation	spectrophotometric	-	-	<1.5%	[39]
SPE	FAAS	0.33 µg L <sup>-1</sup>	-	-	[40]
Flotation	FAAS	0.7 ng mL <sup>-1</sup>	93	-	[41]
adsorption	AAS	2.9 µg mL <sup>-1</sup>		1.2	[42]
adsorption	FAAS	0.36 µg g <sup>-1</sup>		below 10%	[43]
CPE	FAAS	0.9 ng/mL	80	0.18%	This work

SFODME: Solidified floating organic drop micro-extraction; DLLME: Dispersive liquid-liquid micro-extraction; DSPME: dispersive solid-phase microextraction; SPE: Solid-phase extraction

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