

## Determination of copper(II) in various samples by flame atomic absorption spectrophotometry after column separation by adsorption of its N-benzoylphenylhydroxylamine complex on benzophenone

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**Abstract:** A sensitive technique for the determination of trace Cu(II) in various samples after the column preconcentration by adsorbing its N-benzoylphenylhydroxylamine (BPHA) onto benzophenone was developed. Several experimental conditions such as the pH of the sample solution, the amount of chelating agent, the amount of benzophenone, and the flowrate of sample solution and so forth were optimized. The interfering effects of diverse concomitant ions were investigated. Fe(III) and  $\text{CN}^-$  interfered with more seriously than any other ions. However, the interference by these ions could be overcome sufficiently by adjusting the added volume of 0.01M BPHA to 10 mL. The dynamic range, the correlation coefficient ( $R^2$ ) and the detection limit obtained by this proposed technique were 5.0~120 ng/mL, 0.9974, and 2.1 ng/mL, respectively. For validating this proposed technique, the aqueous samples (stream water, reservoir water, and wastewater), the plastic sample and the diluted brass sample were used. Recovery yields of 93~102% were obtained. These measured data were not different from ICP-MS data at 95% confidence level. This method was also validated by the rice flour CRM (normal, fortified) samples. Based on the results from the experiment, it was found that this proposed technique could be applied to the determination of Cu(II) in various real samples.

**Key words:** preconcentration, N-benzoylphenylhydroxylamine, benzophenone, Copper(II)

### 1. Introduction

Cu(II) is a gastrointestinal tract irritant but is generally not harmful to humans at low  $\mu\text{g/mL}$  concentration. In surface water, however, Cu(II) can be toxic to aquatic plants and some fishes at concentration less than 1.0  $\mu\text{g/mL}$ .<sup>1</sup> Thus, Cu(II) tends to be much more of an environmental hazard than a human hazard. Most environmental, biological and alloy samples generally have trace amount of

Cu(II) at level of ng/mL. Therefore, the accurate and precise determination of trace Cu(II) is becoming increasingly important.

In the determination of Cu(II), various methods including UV-Vis spectrophotometry,<sup>2</sup> FAAS,<sup>3</sup> ET-AAS,<sup>4</sup> ICP-AES,<sup>5</sup> ICP-MS,<sup>6</sup> anodic voltammetry,<sup>7</sup> ion chromatography<sup>8</sup> and spectrofluorimetry<sup>9</sup> have been used.

ET-AAS, ICP-MS, and anodic stripping voltammetry among these methods can measure directly at

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ng/mL level. However, some of these methods are time-consuming, require complicated and expensive instruments, have complex operational conditions, are not free from various types of interference and have high maintenance cost.

If instruments with high sensitivity were not used when the concentration of Cu(II) to be determined was at level of ng/mL, UV-Vis spectrophotometer and FAAS which had commonly in general laboratory could be utilized. However, their main problem is the low sensitivity for trace metal ions at ng/mL level. This limitation can be overcome by the use of some preconcentration techniques.

In techniques that trace Cu(II) in aqueous solution can be preconcentrated, there are a liquid-liquid extraction<sup>10</sup> and a solid phase extraction. Particularly, a solid phase extraction has severe conditions in which metal ions or metal chelates can be adsorbed or desorbed on solid adsorbents, but it has many advantages, including the attainability of large preconcentration factors, the facility for separation and enrichment using systems with continuous flow, and the needlessness of toxic organic solvents.<sup>11</sup> In common solid adsorbents, there are activated carbon,<sup>12</sup> chitosan,<sup>13</sup> silica gel,<sup>14</sup> naphthalene,<sup>15</sup> benzophenone<sup>16</sup> and Amberlite XAD resin.<sup>17</sup>

Particularly, benzophenone has been widely used as a good adsorbent for metal chelates containing  $\pi$  electrons. And N-benzoylphenylhydroxylamine (BPHA) as a complexing agent used in this work has  $\pi$  electrons abundantly, is stable on heat and light, and a good chelating agent for Cu(II).<sup>18</sup> So, it was expected that Cu(II)-BPHA complex would be adsorbed on microcrystalline benzophenone well and rapidly.

The preconcentration technique using benzophenone has some advantages that the adsorption time on benzophenone is shorter than that on any other solid adsorbent, the desorption time is very short as benzophenone adsorbed metal complex can be easily dissolved in ethanol or acetone, and the errors arise from desorption process also can be eliminated.

The aim of this work is to develop and to validate a method for preconcentration and separation of ng/

mL levels of Cu(II) from matrix constitutes in real samples such as aqueous samples, brass, plastic, and rice flour CRM (certified reference material) sample using a glass column that packed benzophenone.

## 2. Experimental

### 2.1. Instrumentation and apparatus

For the determination of preconcentrated Cu(II), GBC model 903 flame atomic absorption spectrophotometer was used in following conditions: wavelength: 324.7 nm, air-acetylene flame, burner height: 12 mm, lamp current: 3.0 mA and spectral bandwidth: 0.5 nm. Cu(II) in real samples was determined directly with a HP 4500 ICP-MS spectrometer. A Bantex model 300A digital pH meter with a combined glass and calomel electrode was used to adjust the pHs of all sample solutions. CEM Microwave oven (Mars 5 model, vessel type XP 1500 Plus) was used to make the rice flour CRM samples and the plastic samples into solution samples. A glass column (10 cm×10 mm i.d.) had a glass filter (1-G-1) and a Teflon stopcock at the bottom was used to preconcentrate Cu(II) in sample solutions.

### 2.2. Reagents and solutions

All chemicals used in this experiment such as Cu(NO<sub>3</sub>)<sub>2</sub>·7H<sub>2</sub>O (Aldrich Co.) and N-benzoylphenylhydroxylamine (Aldrich Co.) were of analytical grade and guaranteed grade reagents unless otherwise specified. Cu(II) standard solution was prepared with 1000  $\mu$ g/mL stock solution by a suitable dilution. Benzophenone (Aldrich Co.) ground in an agitate mortar was used without a further purification. N-benzoylphenylhydroxylamine solution was prepared by dissolving in ethyl alcohol to give a 0.01M solution. The deionized water by a Barnstead E-Pure 3-module deionization system was used throughout all experimental procedures. The concentration of stock solution of various species used in investigating the interfering effects was 1000  $\mu$ g/mL. Rice flour certified reference materials (normal and fortified) were supplied by Korea Research Institute of

Standards and Science (KRISS)

### 2.3. Preconcentration of copper(II) in column

A 0.15 g of benzophenone was packed in glass column (10 cm×10 mm i.d.). A 1000 mL of Cu(II) sample solution was taken into a 1000 mL Erlenmeyer flask, and 8 mL of 0.01 M BPHA was added. This sample solution was adjusted to pH 9.0 with 0.1 M NaOH. And then, it was passed through the column filled with benzophenone at flow rate of 30 mL/min by controlling the stopcock in glass column simply. Cu(II)-BPHA complex retained on benzophenone was dissolved with ethyl alcohol and was collected to 10 mL volumetric flask and then filled with ethyl alcohol to the mark. Cu(II) content in the collected solution was measured on the base of Cu-free blank solution at 324.7 nm with a flame atomic absorption spectrophotometer.

### 2.4. Calibration curve and detection limit

A calibration curve was prepared in the concentration range of 5.0~120 ng/mL Cu(II) standard solution according to the procedure in experimental section 'Preconcentration of copper(II) in column' simultaneously by using several columns. The regression equation and the correlation coefficient ( $R^2$ ) of calibration curve were obtained with the method of least squares. The detection limit was obtained from the signals of twenty five blank solutions and the slope of calibration curve. The detection limit is defined as the sample concentration giving signals equal to three times the standard deviation of blank signal.<sup>19</sup>

### 2.5. Preparation of aqueous samples

The 1000 mL aliquots of the stream water (Hwangguchicheon, Suwon, Korea), the reservoir water (Botongri, Hwaseong, Korea), and the untreated wastewater (Suwon Environmental Production Office, Korea) were taken after the suspended matters or particles were filtered out with glass filter (1-G-4).

### 2.6. Preparation of diluted brass sample

To remove the impurities on the surface of the brass sample, it was washed with acetone and deionized water. A 0.1000 g brass sample was weighed accurately and transferred to a 250 mL Erlenmeyer flask, added by 10 mL of 6 M HNO<sub>3</sub>, heated in fume hood until it dissolved completely, and cooled down to the room temperature. This brass solution was transferred to 1000 mL volumetric flask and diluted by filling to the mark. A 0.5 mL aliquot of the solution was diluted further to a 1000 mL in a volumetric flask with deionized water and used as a real sample

### 2.7. Preparation of plastic sample

A 0.5 g of finely ground plastic sample was taken to a high-pressure digestion vessel. Then 9 mL of concentrated HNO<sub>3</sub> and 2 mL of H<sub>2</sub>O<sub>2</sub> were added and mixed well. Plastic sample was decomposed in CEM microwave oven (Mars 5 model) by digestion program in Table 1. The dissolved sample solution and the solution washing the digestion vessel were collected to 1000 mL volumetric flask and diluted with deionized water to the mark.

Table 1. Decomposition conditions of microwave digestion system for plastic powder and rice flour samples

Step	Plastic Powder			Rice Flour		
	Ramping time (min.)	Temperature (°C)	Holding time (min.)	Ramping time (min.)	Temperature (°C)	Holding time (min.)
1	3.0	120	0.0	3.0	120	5.0
2	3.0	150	0.0	3.0	150	5.0
3	3.0	180	10.0	3.0	200	20.0
4	5.0	200	25.0			
Cooling		room temperature	60.0		room temperature	60.0

### 2.8. Preparation of rice flour CRM

A 1.0g of each rice flour CRM (CRM 108-01-001 (normal), CRM 108-01-002 (fortified)) was taken to a high-pressure digestion vessel. Then 7 mL of concentrated HNO<sub>3</sub> was added and mixed well. Rice flour CRM was decomposed by CEM microwave oven (Mars 5 model) using the digestion program in Table 1. The dissolved sample solution and the solution washing the digestion vessel were collected to 1000 mL volumetric flask and diluted with deionized water to the mark.

## 3. Results and Discussion

### 3.1. Optimum conditions

The pH level is an important factor according to which Cu(II) combines with BPHA to be a stable complex. The pH of 1000 mL solution containing 60 ng/mL copper(II) and adding 8 mL of 0.01M BPHA was carefully adjusted from 3.0 to 12.0 with 0.1 M HCl or 0.1 M (or 1 M) NaOH. The effect of pH on the separation of Cu(II)-BPHA complex was investigated as shown in Fig. 1. The maximum separation efficiency was in the range of pH 8.0~10. At acidic pH, it seems that the Cu(II)-BPHA complex was not formed quantitatively on account of protonation of the chelating agent. At higher pH, it is likely that Cu(II)-BPHA complex was not formed quantitatively because it competed with copper hydroxide precipitation. Hence, pH 9.0 was chosen in this experiment.

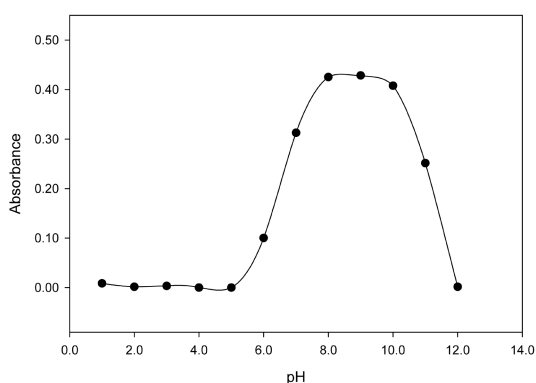


Fig. 1. Effect of pH on the separation of the Cu(II)-N-benzoylphenylhydroxylamine chelate (60 ng/mL).

To separate metal complex quantitatively, a chelating agent must be added to the sample solution more than its stoichiometric ratio. The separation efficiency in 60 ng/mL Cu(II) solution was investigated by adding moles of BPHA from 5 to 100 times moles of Cu(II). The absorbance was practically constant and maximized when mole of BPHA was above 20 times amount of Cu(II). In this experiment, moles of BPHA was used to be 20 times to that of Cu(II).

The adsorption efficiency of Cu(II)-BPHA complex onto benzophenone was investigated by varying the amount of benzophenone from 0.05 to 0.20 g. The complex was quantitatively separated at more than 0.10 g benzophenone. Above 0.20 g, however, it was difficult to use because capillary tube of flame AAS was often clogged. Thus, 0.15 g of benzophenone was used as the suitable amount.

The effect of flow rate on the adsorption of Cu(II)-BPHA was studied. This complex was quantitatively collected at the flow rate less than 30 mL/min. All subsequent experiments were performed at 30 mL/min.

### 3.2 Effect of coexisting species

Preconcentration procedures for trace metal ions can be strongly affected by the matrix constituents of the samples, because it was assumed that they prevent the Cu(II)-BPHA complex from forming. Various ions were used for the investigation of their interference effects on 60 ng/mL Cu(II) solution at

Table 2. Tolerance limit\* for diverse species in 60 ng/mL Cu(II) solution at pH 9.0

Concentration of species ( $\mu\text{g/mL}$ )	Interfering species on Cu(II)
200.0	Na <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Ca <sup>2+</sup> , CH <sub>3</sub> COO <sup>-</sup>
100.0	Mg <sup>2+</sup> , Cl <sup>-</sup> , F <sup>-</sup>
50.0	Pb(II), Mn(II), Br <sup>-</sup> , I <sup>-</sup>
10.0	Al(III), Zn(II), citrate, tartrate, oxalate
5.0	Cd(II), SCN <sup>-</sup> , thiosulfate, Sn(II), Co(II)
1.0	Ni(II), PO <sub>4</sub> <sup>3-</sup>
0.5	CN <sup>-</sup>
0.1	Fe(III)

\*Tolerance limit is the maximum concentration in which there is less than 5% effect on absorbance.

optimum conditions given above. The results of interference studies are summarized in *Table 2*.

Fe(III) and CN<sup>-</sup> interfered with more seriously than any other ions. However, the interference by these ions could be overcome sufficiently by adjusting the added volume of 0.01 M BPHA to 10 mL

### 3.3. Figures of merit

A calibration curve was constructed at optimum conditions according to the procedure in experimental section 'Calibration curve and detection limit'. The linear range of Cu(II) was 5.0~120 ng/mL, and the correlation coefficient ( $R^2$ ) was 0.9974, showing a good linearity of calibration curve. The detection limit was 2.1 ng/mL.

### 3.4. Aqueous samples

Cu(II) in the stream water, the reservoir water and the untreated wastewater sample were determined by

this proposed method and the results are shown in *Table 3*. In this determination, the relative standard deviations were less than 6.0%. Cu(II) in real samples was also determined by ICP-MS spectrometry. No difference between the results from the proposed method and the ICP-MS had been established at 95% confidence level. The recovery yields in the real samples spiked with 20 and 40 ng/mL Cu(II) were more than 93 %. Therefore, it was found that this proposed technique could be applied to the determination of Cu(II) in real aqueous samples.

### 3.5. Brass and plastic samples

Cu(II) in brass sample and plastic sample prepared by procedures in experimental section 2.6 and 2.7 was determined by this proposed method and ICP-MS, and the results are shown in *Table 4*. The concentration of Cu(II) in diluted brass sample was 32.5 ng/mL (65% in original sample), and recovery obtained from the spiked Cu(II) standard solution

*Table 3.* Determination of Cu(II) in some aqueous samples

Real samples	Spiked (ng/mL)	Measured(ng/mL)*		Recovery yield (%)
		This method	ICP-MS	
Stream water	0	36.2(±2.0)	35.1(±2.1)	
	20	55.5(±2.6)		97
	40	75.2(±3.3)		98
Reservoir water	0	25.1(±1.2)	24.7(±1.8)	
	20	44.7(±2.0)		98
	40	62.6(±3.3)		94
Wastewater	0	52.3(±2.9)	53.5(±2.9)	
	20	70.9(±3.2)		93
	40	93.2(±5.0)		102

\*The mean values in this method were obtained from 7 samples and those in ICP-MS were obtained from 5 samples.

*Table 4.* Determination of Cu(II) in the plastic sample and the diluted brass sample

Real sample	Spiked (ng/mL)	Measured (ng/mL)*		Recovery yield (%)
		This method	ICP-MS	
Plastic	0	0(±0.3)	0(±0.4)	
	20	19.2(±1.1)		96
	40	38.8(±2.0)		97
Diluted brass sample	0	32.5(±1.9)	32.2(±2.6)	
	20	51.8(±2.8)		97
	40	71.0(±3.5)		96

\*The mean values in this technique were obtained from 7 samples and those in ICP-MS were obtained from 5 samples.

Table 5. Determination of Cu(II) in certified rice flour samples (KRISS CRM)

CRM	Certified value (mg/kg)	Measured value (mg/kg)*
CRM 108-01-001(normal)	3.22(± 0.09)	3.09(± 0.15)
CRM 108-01-002(fortified)	4.59(± 0.74)	4.43(± 0.32)

\*These mean values were obtained from 5 samples

were more than 95%. In plastic sample, Cu(II) was not contained. Recovery in spiked plastic solution were above 95%.

### 3.6. Rice flour CRM sample

Cu(II) in two rice flour CRM prepared by the procedure in experimental section 2.8 was determined by this proposed method. The results are shown in Table 5. They were not different between the CRM value and the measured average value at 95% confidence level. Therefore, it was found that this proposed technique could be applied to the determination of Cu(II) in rice flour samples.

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