

Determination of Copper after Preconcentration as Its 1-Nitroso-2-naphthol Complex onto Activated Carbon

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Copper is a gastrointestinal tract irritant but is generally not harmful to humans at low $\mu\text{g mL}^{-1}$ concentration. In surface water, however, copper can be toxic to aquatic plants and some fish at concentrations less than $1.0 \mu\text{g mL}^{-1}$.¹ Thus, copper tends to be much more of an environmental hazard than a human hazard. Most environmental, biological and alloy samples generally have a trace amount of copper at level of ng mL^{-1} .

In the determination of trace amount of copper, various methods, including ICP-MS,² ion chromatography,³ anodic stripping analysis,⁴ and electrothermal atomic absorption spectrometry⁵ have been used. Many of these methods either are time-consuming or require complicated and expensive instruments.⁶ Therefore, other methods that can determine the low concentrations of copper rapidly and conveniently in real samples were required.

Flame atomic absorption spectrometry is a simple and well available technique for the determinations of many metals in the real samples. However, its main problem is the low sensitivity for trace metals at ng mL^{-1} level. This limitation can be overcome by the use of a preconcentration procedure.

To determine trace metals in real samples, a separation and preconcentration technique is frequently required, because of the trace amount of analyte ions and the presence of interference.^{7,8} For the preconcentration and separation of copper(II) ion, various solid adsorbents such as Amberlite XAD-16 resin,⁹ silica gel,¹⁰ and benzophenone¹¹ have been used. These adsorbents have good preconcentration yields and high recovery yields for some copper(II) complexes. However, these most techniques are troublesome and time-consuming because of slow sorption and desorption process.

Solid phase extraction procedures based on sorption of metal complexes on activated carbon have also applied.¹²⁻¹⁴ Activated carbon has been widely used for many purposes both in laboratory and industrial settings, due to its ability to adsorb organic compounds and organic metal complexes.¹⁵ Enrichment of trace metals using activated carbon has been favorably performed with very high concentration factors in different matrices.¹⁵

Because activated carbon is a type of hydrophobic adsorbent which adsorbs nonpolar or little polar substances in aqueous solution, metal ions to be preconcentrated need to be transformed corresponding metal chelates¹⁶⁻¹⁸ or metal hydroxides¹⁹ which could be adsorbed on activated carbon.

Metal chelates could provide higher selectivity and high enrichment factors for such a preconcentration and separation.

The mechanism involved in the adsorption of ions as trace compounds by activated carbon is not completely known. It was assumed that the sorption is quantitative when the chelate contains systems of π -electrons in the molecule and when the centers for binding on carbon and those for the metal ions are spatially separated so that their orbitals do not have a substantial influence.²⁰

In the present work, a column separation-preconcentration method has been established for the flame atomic absorption spectrometric determination of trace amount of copper separated on activated carbon as 1-nitroso-2-naphthol complex. The proposed technique was applied for the determination of copper in stream water, ground water and diluted brass solution.

Experimental Section

Reagents and Solutions. All chemicals used in this experiment such as $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (Aldrich Co., USA) were of analytical grade and guaranteed grade reagents. Copper standard solution was made from $1000 \mu\text{g mL}^{-1}$ stock solution. 1-Nitroso-2-naphthol (Merck Co., Germany) stock solution was dissolved in ethanol (Aldrich Co., USA) to be $1000 \mu\text{g mL}^{-1}$. The activated carbon powder used as adsorbent was a granular activated carbon (20-40 mesh) supplied by Aldrich Co. (USA). About a 5 g amount of activated carbon was stirred with 500 mL of 3.0 M HCl for 1 hour, and allowed to stand for 24 h. After filtration, activated carbon was washed with deionized water until it became neutral, and was then dried at 110°C for 24 h in an oven. The deionized water prepared by a Bamstead cartridge deionization system (Bamstead, Co., USA) was used throughout all experimental procedures.

Apparatus. GBC model 903 flame atomic absorption spectrophotometer was used in following conditions: 10 cm 1-slot burner, copper hollow cathode lamp of Photron Dty. Ltd., wavelength: 324.7 nm, air-acetylene flame, burner height: 15 mm, lamp current: 3.0 mA. Copper 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 solutions. The glass column (10 cm long \times 10 mm i.d.) was sealed on one end with fritted glass filter (1-G-1) and was

packed with 0.1 g of activated carbon.

General Procedures. A 200 mL copper(II) sample solution was taken into a 250 mL Erlenmeyer flask, and 1.0 mL of $1000 \mu\text{g mL}^{-1}$ 1-nitroso-2-naphthol was added. The pH was adjusted to 10.0 using 0.1 M NaOH. After this solution was stirred for 30 minutes, it was passed through the activated carbon column at a flow rate of 3.5 mL/min. using aspirator. The desorption of Cu(II)-1-nitroso-2-naphthol was carried out by treating the activated carbon with 10 mL portion of 1 M HNO_3 in acetone. The absorbance of copper was measured on the basis of Cu-free blank solution at 324.7 nm with flame atomic absorption spectrophotometer. A calibration curve was prepared in the range of $0.005\text{--}0.4 \mu\text{g mL}^{-1}$ of copper(II).

A brass sample was prepared as follows. 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 and transferred to a 250 mL Erlenmeyer flask, added by 10 mL of 6 M HNO_3 , 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 1.0 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.

A 200 mL aliquot of stream water or ground water sample was taken after the suspended matters or particles were filtered out with glass filter (1-G-4).

Results and Discussion

Optimum Conditions. The pH level is an important factor according to which Cu(II) combine with 1-nitroso-2-naphthol to be a stable complex. The pH of the 200 mL solution containing $0.15 \mu\text{g mL}^{-1}$ copper(II) and $5 \mu\text{g mL}^{-1}$ 1-nitroso-2-naphthol was carefully adjusted from 3.0 to 11.0 with 0.1 M HNO_3 or 0.1 M NaOH. The effect of pH on the separation of Cu(II)-1-nitroso-2-naphthol complex was investigated. The maximum absorbance obtained in the range of pH 9.0-10.5. At acidic pH, it seems that the Cu(II)-1-nitroso-2-naphthol complex was not formed quantitatively on account of protonation of the chelating agent. At higher pH, it is likely that Cu(II)-1-nitroso-2-naphthol complex was not formed quantitatively because it competed with copper hydroxide precipitation. Hence, pH 10.0 was chosen in this experiment.

To separate metal complex quantitatively, more chelating agent must be added to the sample solution than its stoichiometric ratio. The extraction efficiency in $0.15 \mu\text{g mL}^{-1}$ copper(II) solution was investigated by adjusting concentrations of 1-nitroso-2-naphthol from $1 \mu\text{g mL}^{-1}$ to $30 \mu\text{g mL}^{-1}$. The absorbance was practically constant when the concentration of 1-nitroso-2-naphthol was above $3 \mu\text{g mL}^{-1}$. In this experiment, the concentration of 1-nitroso-2-naphthol was used to be $5 \mu\text{g mL}^{-1}$.

The adsorption efficiency of Cu(II)-1-nitroso-2-naphthol complex onto activated carbon was investigated by varying

the amount of activated carbon as the adsorbent from 0.03 to 0.30 g. The complex was quantitatively separated at more than 0.08 g activated carbon. Above 0.20 g, however, it was difficult to use because the elution rate of sample solution was so slow. Thus, 0.10 g of activated carbon was used as the suitable amount.

The effect of flow rate on the adsorption of Cu(II)-1-nitroso-2-naphthol was studied. This complex was quantitatively collected at the flow rate in the range of 1 mL-5 mL/min. All subsequent experiments were performed at 3.5 mL/min. flow rate.

The desorption of the retained Cu(II)-1-nitroso-2-naphthol complex from the activated carbon column was investigated using various eluent agents such as 4 M HNO_3 , ethyl alcohol, 1 M NaOH, 0.1 M acetic acid and 1 M HNO_3 in acetone. Quantitative recoveries ($> 95\%$) was obtained by 1 M HNO_3 in acetone. The selected volume of eluent was 10 mL and the recommended desorption rate was 1.0 mL/min.

Interfering Effects. The possible interfering effects of concomitant ions on the determination of copper(II) were investigated under optimum conditions given above. Various ions were used for investigation of their interference effects on $0.15 \mu\text{g mL}^{-1}$ copper solution, because it was assumed that they prevent the Cu(II)-1-nitroso-2-naphthol complex from forming. The results of interference studies are summarized in Table 1. Co(II) and Ni(II) interfered with more seriously than any other ions. However the interference by these ions could be overcome sufficiently by adjusting the concentration of 1-nitroso-2-naphthol to $20 \mu\text{g mL}^{-1}$.

Applications to Real Samples. A calibration curve was constructed at optimum conditions according to general procedure described above. The linear range of Cu(II) was $0.005 \mu\text{g mL}^{-1}\text{--}0.4 \mu\text{g mL}^{-1}$. The correlation coefficient (R^2) was 0.9983, showing a good linearity of calibration curve. The detection limit is defined as the sample concentration giving a signal equal to the blank average signal plus three times the standard deviation of blanks.²¹ The detection limit obtained from the signals of twenty-five blank solutions and the slope of calibration curve, was 4.4 ng mL^{-1} .

Cu(II) in Suwon stream water, ground water and diluted brass sample were determined by this proposed method and the results are shown in Table 2. The recovery yields in the real samples spiked with 0.10 and $0.20 \mu\text{g mL}^{-1}$ Cu(II) were determined, and found to be more than 95%. In this determination, the relative standard deviations were less than 5.0%. Cu(II) in real samples were also determined by ICP-

Table 1. Tolerance limit^a for diverse ions in $0.15 \mu\text{g/mL}$ Cu(II) solution containing $5 \mu\text{g/mL}$ 1-nitroso-2-naphthol

Concentration ($\mu\text{g/mL}$)	Ions
300	Mg(II), SCN^- , $\text{C}_2\text{O}_4^{2-}$, IO_3^-
100	Zn(II), tartarate ion
50	Al(III), Fe(III), CN^-
10	Co(II), Ni(II)

^aTolerance limit is the maximum concentration in which there is less than 3% effect on absorbance.

Table 2. Analytical data of Cu(II) in real samples

Samples	Spiked ($\mu\text{g/mL}$)	Measured ($\mu\text{g/mL}$) ^a		Recovery (%)
		This technique	ICP-MS	
Stream water (Suwon)	0	0.039 (± 0.002)	0.040 (± 0.002)	
	0.10	0.135 (± 0.006)		96
	0.20	0.242 (± 0.009)		102
Ground water	0	0.038 (± 0.002)	0.040 (± 0.002)	
	0.10	0.139 (± 0.006)		101
	0.20	0.234 (± 0.008)		98
Diluted brass sample	0	0.064 (± 0.003)	0.062 (± 0.003)	
	0.10	0.162 (± 0.008)		98
	0.20	0.258 (± 0.009)		97

^aThe mean values were obtained from 7 samples in this technique and 5 samples in ICP-MS technique.

MS spectrometry. No difference between results from the proposed method and the ICP-MS method had been established at 95% confidence level. Therefore, this proposed technique could be applied to the determination of copper(II) in real samples.

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