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### Sensitized Spectrophotometric Determination of Trace Cu(II) in Cationic Surfactant Media

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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  $1.0 \mu\text{g mL}^{-1}$ .<sup>1</sup> 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  $\text{ng mL}^{-1}$ .

The determination of trace amounts of copper has received considerable attention in the battle against environmental pollution. In the determination of copper, various methods, including ICP-MS,<sup>2</sup> ion chromatography,<sup>3</sup> anodic stripping analysis,<sup>4</sup> and electrothermal atomic absorption spectrometry,<sup>5</sup> have been used. Many of these methods either are time-consuming or require complicated and expensive instruments.<sup>6</sup> Therefore, methods that can determine the low concentrations of copper rapidly and conveniently in real samples were required.

To determine trace Cu(II) with UV-visible spectrometry, various chelating agents such as sodium diethyldithiocarbamate, cuprizone, and dithizone, have been used.<sup>7</sup> The method that is based on sodium diethyldithiocarbamate and dithizone should be performed with solvent extractions that are time-consuming and tedious, have lower accuracy and precision, and usually involve harmful solvent. The sensitivity of a dithizone-based technique is  $4.52 \times 10^4 \text{ L mole}^{-1} \text{ cm}^{-1}$  as the molar absorptivity of its Cu(II) complex in carbon tetrachloride, but it requires a high degree of operator skill as the reagent is very sensitive to other metals as well. Cuprizone reacts with Cu(II) to produce a blue, water-soluble complex; however, the molar absorptivity of this complex is relatively low, at  $1.6 \times 10^4 \text{ L mole}^{-1} \text{ cm}^{-1}$  at 600 nm.

Organic micellar media are very useful in analytical applications, including the improved analyte sensitivity in UV-visible spectrometric methods<sup>8</sup> and in fluorescence methods and quenching processes.<sup>9</sup> Especially, the surfactants have been used to improve UV-visible spectrophotometric determination of metal ions with complexing agents. Generally, the metal-chelate complexes formed in the surfactant media are more stable than those formed in the absence of surfactant.<sup>10</sup>

In the present study, the rapid, convenient and simple

determination of trace copper(II) was spectrometrically performed with its 2-mercaptobenzothiazole complex in cationic cetyltrimethylammonium bromide (CTAB) media without an extraction procedure.

#### Experimental Section

**Instrumentation.** A Hewlett-Packard 8453A single beam diode array spectrometer was used to measure the absorbance of Cu(II)-2-mercaptobenzothiazole complex in CTAB media. To determine Cu(II) in the streamwater and the diluted brass samples, a HP 4500 ICP-MS spectrometer was also used. To adjust the pHs and prepare the buffer solution, a Bantex model 300A digital pH meter equipped with a combined glass and calomel electrode was used.

**Reagents and solutions.** All chemicals, such as  $\text{Cu}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$  (Aldrich Co., U.S.A) and 2-mercaptobenzothiazole (Wako Co., Japan), were analytical or guaranteed-grade reagents. Standard Cu(II) was made from  $10^{-2} \text{ M}$  stock solution. A 0.01% (w/v) cetyltrimethylammonium bromide (CTAB) (BHD Co., England) solution was prepared by dissolving 0.01 g of CTAB in a 100 mL volumetric flask with stirring; 2-Mercaptobenzothiazole solution was prepared by dissolving in ethyl alcohol to give a 0.05 M solution. Borax buffer (pH 9.0) was prepared by mixing 0.025 M borax and 0.1 M HCl. To investigate the interfering effects by various species, such as Hg(II), Bi(III), Ni(II) and so forth,  $1.0 \times 10^{-2} \text{ M}$  stock solutions were used. Deionized water prepared by a Barnstead system (Barnstead Co., U.S.A.) was used throughout all experimental procedures.

**Calibration curve.** Standard Cu(II) solutions were prepared in the range of  $5.0 \times 10^{-8} \text{ M}$ ~ $5.0 \times 10^{-6} \text{ M}$ . Several aliquots of Cu(II) standard solutions were taken in 10 mL volumetric flasks, and 0.1 mL of 0.05 M 2-mercaptobenzothiazole and 2.0 mL of 0.01% CTAB were added to each flask. Then it was filled to the mark with borax buffer solution (pH 9.0) and the calibration curve of Cu(II) was constructed by a UV-visible spectrophotometer. The regression equation was obtained with the method of least squares. Using this linear equation, we determined the correlation coefficient ( $R^2$ ) and the detection limit. 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 the blanks.<sup>11</sup>

**Real samples.** The streamwater was taken as a real sample after suspended matter or particles were filtered out with a glass filter (1-G-1). A 0.1000 g brass sample cleaned by acetone and deionized water was taken into a 250 mL beaker, to which was added 10 mL of 6 M HNO<sub>3</sub>. The mixture was heated in a fumehood to dissolve the brass sample completely, cooled down to room temperature, and diluted to 1000 mL in a volumetric flask. Then, 1.0 mL of this brass solution was transferred to a 1000 mL volumetric flask, which was diluted by filling to the mark and then used as the diluted brass samples. A synthetic sample was prepared so that the concentrations of Cu(II) were  $4.0 \times 10^{-7}$  M and those of Hg(NO<sub>3</sub>)<sub>2</sub>, Bi(NO<sub>3</sub>)<sub>3</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>, and Ni(NO<sub>3</sub>)<sub>2</sub> were  $2.0 \times 10^{-6}$  M. To determine Cu(II) with the method of standard addition, several 5.0 mL aliquots of the streamwater, the diluted brass and the synthetic samples were taken in 10 mL volumetric flasks. Exactly 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 mL of a standard solution containing  $5.0 \times 10^{-5}$  M of Cu(II) were also added to each flask. Then, 0.3 mL of  $10^{-3}$  M EDTA, 0.1 mL of 0.05 M 2-mercaptopbenzothiazole and 2.0 mL of 0.01% CTAB were added, and the flask was filled to the mark with borax buffer (pH 9.0).

## Results and Discussion

**Spectra and optimum conditions.** After Cu(II), 2-mercaptopbenzothiazole and CTAB were taken in a 10 mL volumetric flask so that their concentrations were  $2.0 \times 10^{-6}$  M,  $2.0 \times 10^{-4}$  M and 0.002%, respectively, the solution was diluted to the mark with borax buffer (pH 9.0). Then, the absorption spectrum of Cu(II)-2-mercaptopbenzothiazole was obtained, which is shown in Figure 1. The analytical sensitivity and the reproducibility in this spectrum were good in CTAB media. The phenomenon seems to have been caused by the electrostatic and hydrophobic interactions between

Cu(II)-2-mercaptopbenzothiazole complex and surfactant.<sup>12</sup>

The effect of pH on the absorbance of Cu(II)-2-mercaptopbenzothiazole ( $2.0 \times 10^{-6}$  M) complex in 0.002% CTAB media was investigated. Cu(II)-2-mercaptopbenzothiazole complex showed the maximum absorption at pH 8.0-10.0. From this experimental fact, we determined that Cu(II)-2-mercaptopbenzothiazole complex was quantitatively formed and well dissolved in CTAB media at this pH range. We assume that the reaction to form this complex could have competed against hydroxide precipitation above pH 10.0 and at acidic pH, as the sulfur atom in the chelating site of 2-mercaptopbenzothiazole had more affinity power with proton at a higher concentration of protons. A pH 9.0 was chosen for the following measurements.

It is known that Cu(II) combines stoichiometrically with 2-mercaptopbenzothiazole to form 1 : 2 complex.<sup>13</sup> For a metal complex to be formed quantitatively, however, one must add more chelating agent to the sample solution. We found that when 2-mercaptopbenzothiazole was added to more than 100 times a mole of Cu(II), the absorbance was high and constant.

When the concentration of CTAB surfactant exceeds its critical micelle concentration, the homogeneous micelle solution is formed at a point where Cu(II)-2-mercaptopbenzothiazole complex can be well dissolved. Due to high viscosity, the concentrated CTAB media was hard to handle, whereas those with low viscosity under diluted conditions could not form a micelle or make a homogeneous solution of complex as the polarity of aqueous solution was not lowered. With the concentration of CTAB varying from 0.0005% to 0.05% at pH 9.0, the absorbance of Cu(II)-2-mercaptopbenzothiazole ( $2.0 \times 10^{-6}$  M) complex was investigated. The maximum absorbance was obtained when the concentration of CTAB was 0.001% to 0.005%. We assumed that although the concentration of these CTAB were somewhat less than critical micelles concentration (0.0013 M, 0.047%),<sup>14</sup> Cu(II)-2-mercaptopbenzothiazole complex was homogeneously dissolved in surfactant media. Here, the selected concentration of CTAB was 0.002%.

To investigate the effect of types of surfactants, Triton X-100 as nonionic and sodium dodecylsulfate as anionic surfactant were used. In given concentration range ( $5.0 \times 10^{-8}$  M~ $5.0 \times 10^{-6}$  M), the calibration curve of Cu(II)-2-mercaptopbenzothiazole could not be obtained in 0.1% anionic sodium dodecylsulfate media. For 0.1% Triton X-100 media, the calibration curve could be constructed, but its slope was about 30 times less than that in CTAB media. Cationic surfactants have been used rather than anionic or nonionic surfactants to determine metal ions by UV-Vis spectrophotometry.<sup>15-19</sup> Because a metal ion is a cation, the electrostatic attractive interaction between a metal ion and cationic surfactant is not present, and the complex-forming process is not affected.

To investigate the stability of Cu(II)-2-mercaptopbenzothiazole in 0.002% CTAB media at pH 9.0, the absorbance of its complex was measured as the function of time. The absorbance of Cu(II)-2-mercaptopbenzothiazole remained

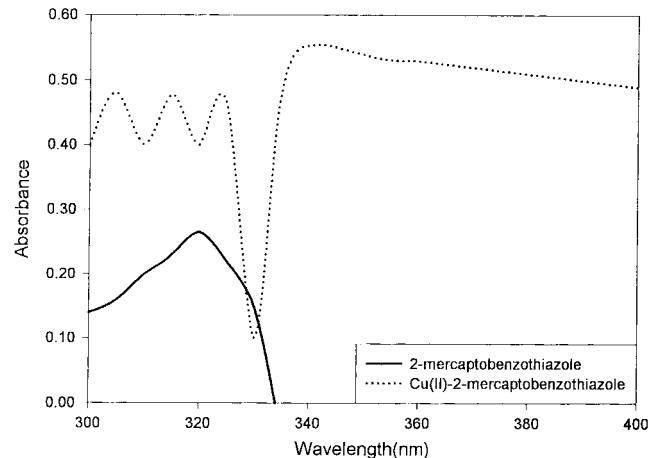


Figure 1. Spectra of Cu(II)-2-mercaptopbenzothiazole ( $2.0 \times 10^{-6}$  M) complex and 2-mercaptopbenzothiazole ( $1.0 \times 10^{-5}$  M) in 0.002% CTAB media.

**Table 1.** Tolerance limits<sup>a</sup> for diverse species in  $2.0 \times 10^{-3}$  M Cu(II) solution

Mole ratio of interfering species to Cu(II)	Interfering species
200	Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup> , NH <sub>3</sub>
100	SCN <sup>-</sup>
50	Pb(II)
25	Ni(II), Zn(II)
10	Cd(II), Co(II), CN <sup>-</sup>
5	Hg(II), Bi(III)

<sup>a</sup>Tolerance limit is the maximum mole ratio of interfering ion to Cu(II) in which the effect on the absorbance is less than 5%.

**Table 2.** Analytical data of Hg(II) in real and synthetic samples by the standard addition method

Real samples	Measured (M) <sup>a</sup>	
	This proposed method	ICP/MS
Streamwater	$9.0 (\pm 0.4) \times 10^{-7}$	$8.9 (\pm 0.4) \times 10^{-7}$
Diluted brass sample	$1.04 (\pm 0.04) \times 10^{-6}$	$1.08 (\pm 0.05) \times 10^{-6}$
Synthetic sample ( $4.00 \times 10^{-7}$ M)	$3.94 (\pm 0.07) \times 10^{-7}$	

<sup>a</sup>The average values were obtained from seven samples.

constant from the beginning of measurement to 60 minutes. After 60 minutes, the absorbance was decrease slowly (0.0007 absorbance unit/min.).

**Interference effect.** 2-Mercaptobenzothiazole combines with several metal ions such as Hg(II), Bi(III), Ni(II) and so forth to form stable and slightly a soluble metal complex in aqueous solution. So, when Cu(II) is determined with 2-mercaptobenzothiazole, the other metal ions in real samples may interfere with Cu(II) complex-forming. The possible interference effects of concomitant ions on the determination of Cu(II) were investigated under the optimum conditions given above and are shown in Table 1. Hg(II) and Bi(III) interfered with more seriously than any other ions, and unfortunately, this interference could be partially (~80%) eliminated by adding EDTA to be  $3.0 \times 10^{-5}$  M.

**Application to real samples.** A calibration curve was constructed at optimum conditions according to calibration curve procedure in Experimental Section. The dynamic range of Cu(II) was  $5.0 \times 10^{-8}$  M to  $5.0 \times 10^{-6}$  M and the regression equation was  $2.528(\pm 0.009) \times 10^5 x + 0.033(\pm 0.009)$ . The

correlation coefficient ( $R^2$ ) was 0.9981, showing a good linearity of calibration curve. Based on the signals of twenty-five blank solutions and the slope of calibration curve, it was found that the detection limit was  $3.3 \times 10^{-8}$  M (2.1 ng/mL).

The standard addition method was used to determine Cu(II) in real samples because of the incomplete release due to the interfering effects. Cu(II) in the streamwater, the diluted brass samples, and the synthetic samples were determined by this proposed technique and the results are shown in Table 2. The relative standard deviations representing the reproducibility were less than 5.0% in these measurements. Cu(II) in the streamwater and the diluted brass samples were also determined by ICP-MS spectrometry. At 95% confidence level, no difference between results from the proposed and ICP-MS methods had been established. Therefore, this proposed technique could be applied to the determination of  $\text{ng mL}^{-1}$  level of Cu(II) in real samples.

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