

Development of A Redox Speciation Method of Copper(I/II) in Environmental Water Samples by Solid Phase Extraction / Inductively Coupled Plasma Mass Spectrometry

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Abstract: We developed to a Cu(I)/Cu(II) speciation method of Cu(I)/Cu(II) using solid phase extraction (SPE) followed by inductively coupled plasma mass spectrometry (ICP-MS). In order to separate Cu(I) from Cu(II), Cu(I) and Cu(II) were complexed with bathocuproinedisulfonic acid (BCS) and ethylenediaminetetraacetate (EDTA), respectively. The Cu(I)-BCS showed a high affinity to hydrophobic solid phases such as C18, C8, tC2. On the other hand, Cu(II)-EDTA was not adsorbed on these hydrophobic solid phases. The Cu(I)-BCS adsorbed in these SPEs could be quantitatively separated by a methanol aqueous solution. When we applied this speciation method to a rain water sample, the recoveries of Cu(I) and Cu(II) were higher than 90%.

Key words : Speciation, copper, solid phase extraction, *in situ* pretreatment

1. Introduction

From the viewpoint of environmental preservation and assess of environmental risks, it is important to characterize chemical species of heavy metals in environmental samples. [1, 2] Chemical species have large effects on their bioavailabilities and fates in the environments. For example, mercury and arsenic have different toxicities to human being and animals among their organic and inorganic species.[3]

Copper (Cu) has been widely used for industrial fields. In general, Cu has two redox states, Cu(I) and Cu(II). It is widely known that Cu(II) is a major redox state in oxidative aquatic and atmospheric environments. On the other hand, Cu(I) is rarely distributed there due to its easily-oxidized property.[4] Therefore, detail distribution and fate of Cu(I) in aquatic and atmospheric environment has rarely been elucidated yet because Cu(I) usually exists in trace concentration level and is difficult to maintain its chemical state. Atomic absorption spectrometry and complicated processes such as liquid-liquid extraction have been used for conventional method of redox speciation of copper.[4]

Solid phase extraction (SPE) method is useful for *in situ* treatment in a closed system quickly and simply. Okumura *et al.* has used the SPE for *in situ* speciation of unstable species in aquatic environments and named this method as “*in situ* solid phase extraction method”.[5]

In this work, in order to separate Cu(I) from Cu(II) easily, Cu(I) and Cu(II) were complexed with BCS and EDTA, respectively. Cu(I)-BCS and Cu(II)-EDTA showed a hydrophobic and hydrophilic

property, respectively. It was expected that the different hydrophobic properties between Cu(I)-BCS and Cu(II)-EDTA was used for separation of them using hydrophobic SPE phase such as C18, C8, tC2. Concentrations of Cu(I) and Cu(II) separated by the SPE method was determined by inductive coupled plasma mass spectrometry (ICPMS). ICPMS is a powerful instrument for determination of metallic elements.

To our best knowledge, ICPMS has not been used for determination of Cu(I) yet. Thus, we investigated analytical conditions of the SPE treatment to separate Cu(I) from Cu(II) and to determine Cu in the eluants from the SPE column by ICPMS.

Materials and Methods

Apparatus

UV-visible spectrophotometric properties of Cu(I)-BCS and Cu(II)-EDTA were measured with a JASCO V-570 UV-vis spectrophotometer using a quartz cell of 10×10×40 mm³. The wavelength was scanned in the range of 200 – 600 nm and fixed at 480 nm for the analysis Cu(I)-BCS. ICPMS was a Shimadzu ICPM 8500 equipped with a quadrupole mass spectrometer. The *m/z* 63 and 65 of Cu were selected as analytical isotopes in the ICP-MS measurement. The signal obtained by the ICP-MS measurement was corrected by an internal standard method using ⁵⁹Co and ⁶⁹Ga as internal standards.

Materials

All solutions were prepared with a Milli-Q water purified with Milli-Q purification system (Nihon Millipore Kogyo). Aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol (Kanto Chemical) and hydrochloric acid (Ultrapur-100, Kanto Chemical) were mixed for preparation of the pH 7 tris-HCl buffer solution.

The Cu(I) standard solution used in this work was prepared by reduction of Cu(II) standard solution by ascorbic acid (AA) because Cu(I) stock solution was not available commercially. A 1000 $\mu\text{mol L}^{-1}$ BCS stock solution was prepared by dissolving 0.028 g of BCS (ACROS) in 50 mL Milli-Q water. A 1000 $\mu\text{mol L}^{-1}$ of AA solution was prepared by dissolving 0.007 g of AA in 40 mL Milli-Q water. The Cu(I)-BCS solution was prepared by mixing a Cu(II) standard solution in 0.1 mol L^{-1} Tris-HCl buffer (pH 7), 1000 $\mu\text{mol L}^{-1}$ AA solution and BCS solution. EDTA solution was prepared by dissolving 10.06 g of EDTA (Doujin Chemical) in 50 mL Milli-Q water. Cu(II)-EDTA complex was prepared by mixing Cu(II) standard solution, 0.1 mol L^{-1} Tris-HCl (pH 7) and EDTA solution.

For the test of interference of the coexistence ion mentioned in the 3. 4 section, Ca^{2+} and Mg^{2+} solutions were prepared from stock solutions of atomic absorption analysis grade purchased from Kanto Chemical. Iron(II) chloride tetrahydrate as Fe^{2+} (Wako pure chemicals), Iron(III) chloride hexahydrate as Fe^{3+} (Kanto Chemicals), sodium dodecyl sulfate (SDS, Kanto Chemicals) and Triton X-100 (SIGMA) were diluted with milli-Q water. The SO_4^{2-} containing solution was prepared from dissolving sodium sulfate to water (Kanto Chemicals).

Sep-Pak C18, C8, tC2, CN, and QMA were purchased from Waters Co. Ltd. Before using, 5 mL of methanol (HPLC grade, Kanto Chemicals) and 5 mL of water were loaded for conditioning of the SPEs.

Procedure

The typical procedure of the separation of Cu(I) from Cu(II) by SPE cartridges was described as follows. The 0.5 mL of 240 $\mu\text{mol L}^{-1}$ BCS and 1 mL of 500 $\mu\text{mol L}^{-1}$ EDTA was added to 60 mL of an analytical sample containing Cu^+ and Cu^{2+} to make Cu(I)-BCS and Cu(II)-EDTA complex. The analytical solution containing Cu(I)-BCS and Cu(II)-EDTA was loaded to a SPE cartridge. In this treatment, we defined the solution passed through the SPE cartridge as "extracted solution". After loading the analytical solution, methanol-water solution was loaded to the SPE to remove components adsorbed on the solid phase. The methanol-water solution passed through the SPE was defined as "eluant solution". The adsorption rate and the recovery were calculated by determination of Cu in the analytical solution, extracted, and the eluted solution by ICP-MS. The adsorption rate was estimated as a percentage calculated from the amount of the Cu adsorbed on a column to that in the analytical solution. The recovery was estimated as a percentage of the amount of the Cu in an eluant solution to that in the analytical

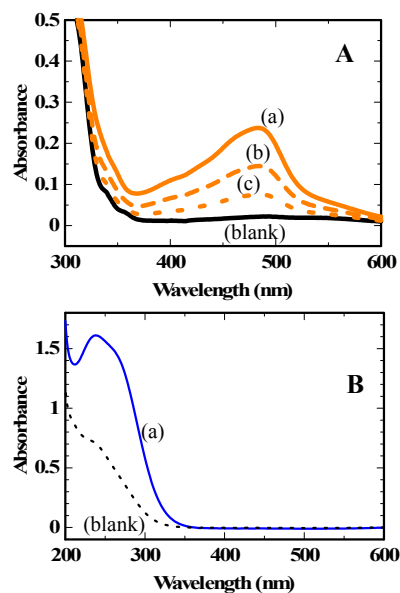


Figure. 1 UV-spectra of (A) Cu(I)-BCS complex and (B) Cu(II)-EDTA complex.

(A) The UV-spectra of Cu(I)-BCS were observed in solutions containing (a) 50 $\mu\text{mol L}^{-1}$ (b) 25 $\mu\text{mol L}^{-1}$ and (c) 10 $\mu\text{mol L}^{-1}$ of Cu(I)-BCS. The spectrum of the blank was observed in a pH 7.0 Tris-HCl solution containing 240 $\mu\text{mol L}^{-1}$ BCS and 100 $\mu\text{mol L}^{-1}$ Cu(II).

(B) The UV-spectra were observed in a pH 7.0 Tris-HCl containing (a) 500 $\mu\text{mol L}^{-1}$ Cu(II) and 500 $\mu\text{mol L}^{-1}$ EDTA. The spectrum of the blank was observed in was a 500 $\mu\text{mol L}^{-1}$ EDTA solution.

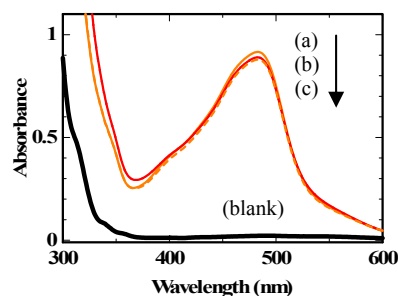


Figure.2 Stability test of the Cu(I)-BCS complex.

The UV-spectra were observed in solutions containing 250 $\mu\text{mol L}^{-1}$ Cu(II), 1 mM AA, 1 mM BCS and pH 7.0 Tris - HCl buffer solution at (a) 0 min (b) 1 hour and (c) 72 hour after preparation. The UV-spectra of the blank were observed in a pH 7.0 Tris-HCl solution containing 240 $\mu\text{mol L}^{-1}$ BCS and 100 $\mu\text{mol L}^{-1}$ Cu(II).

solution.

Results and discussion

UV-visible spectrum of Cu(I)-BCS complex and Cu(II)-EDTA complex

The UV-visible spectra of 10 - 50 $\mu\text{mol L}^{-1}$ Cu(I)-BCS was shown in Fig.1 (A). The wavelength of the maximum absorption of the Cu(I)-BCS was observed at about 480 nm. This is agreed with the result in a previous report.^[6] On the other hand, absorption of Cu(II)-EDTA did not significantly appeared in

the range (Fig. 1(B)). Cu(I)-BCS in the solution was measured. As a result, the Cu(I)-BCS formed in the mixture solution was stable for at least 3 days (Fig. 2).

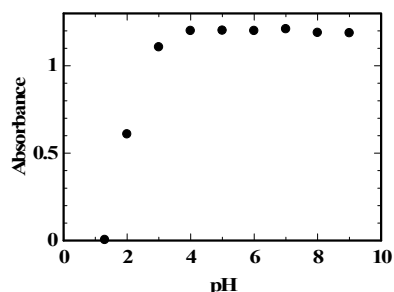


Fig. 3 Effect of pH on formation of the Cu(I)-BCS.

Analytical sample : 100 $\mu\text{mol L}^{-1}$ Cu(I)-BCS complex
Glycine- HNO_3 (pH 1.3 – 3), acetate/sodium acetate (pH 4 – 6), and Tris-HCl buffer solution (pH 7-9) were used for the pH adjustment.

The effects of pH on the Cu(I)-BCS formation were studied in the pH range 1 - 9. As can be seen in Fig.3, Cu(I)-BCS was formed over pH 4.0. Stability of the Cu(I)-BCS under air and room temperature (25 $^{\circ}\text{C}$) was checked. In the stability test, a mixture solution of 150 $\mu\text{mol L}^{-1}$ Cu(II), 1000 $\mu\text{mol L}^{-1}$ AA and 1000 $\mu\text{mol L}^{-1}$ BCS was placed under room temperature and air atmosphere and the UV-visible absorption of the

Adsorption behavior of Cu(I)-BCS to various SPE column

Adsorption behaviors of the Cu(I)-BCS and the Cu(II)-EDTA were investigated using C18, C8, tC2, CN, and QMA cartridges. Table 1 shows adsorption rates and recoveries of the Cu(I)-BCS and the Cu(II)-EDTA with each cartridge. The Cu(I)-BCS was quantitatively adsorbed on the C18, C8, and tC2 cartridges and removed by loading methanol-water solution. On the other hand, low recoveries of Cu(I)-BCS were observed with the CN and QMA. These results were due to the strong adsorption of Cu-BCS with CN and QMA, where the electrostatic adsorption of the Cu-BCS was difficult to be removed by loading methanol aqueous solution in the eluted process. On the other hand, adsorption rates and recoveries of the Cu(II)-EDTA to these SPE phase were quite low because Cu(II)-EDTA has a high hydrophobic property and could not be adsorbed on these hydrophobic solid phase.

Effect of the ratio of methanol to water on elution of Cu(I)-BCS was investigated. Figure 4 shows the recovery of Cu(I)-BCS with three SPE cartridges. Cu(I)-BCS adsorbed on the C8 and tC2 could be almost recovered by use of $> 20\%$ of the methanol solution, however, that on C18 column was not completely. The low ratio of methanol to water is desirable as the eluant considering use of ICPMS for determination of Cu.^[7] Thus, we used the tC2 column and 30% methanol aqueous solution as eluant in this work.

Effects of flow rate and loaded weight of the analytical samples on adsorption of Cu(I)-BCS

First, we checked the flow rate of the analytical sample loaded to the SPE cartridge. The result was shown in Fig.5. As a result, it was found that the recovery of Cu(I)-BCS was less affected from the flow rate. The adsorption rate was almost 100% up to 10.0 mL min^{-1} .

Dependence of loaded weight of the analytical solution containing 1 $\mu\text{mol L}^{-1}$ Cu(I)-BCS on the adsorption rate was also checked. The high recovery of Cu(I)-BCS was kept over 800 g of the loaded weight.

The result indicates that tC2 cartridge has high affinity and rapid adsorption with Cu(I)-BCS.

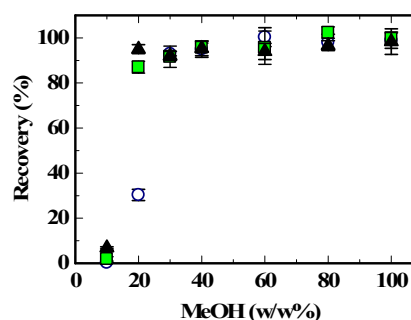


Figure. 4 Effect of the weight ratio of methanol to water as eluant on the recovery of Cu(I)-BCS.

Analytical sample : 100 $\mu\text{mol L}^{-1}$ Cu(I)-BCS complex
loaded weight of the analytical sample : 3.0 g
weight of the eluant : 3.0 g
○ : C18, ■ : C8, ▲ : tC2

The error bar was described as a standard deviation of the recovery obtained by 3-times independent analysis.

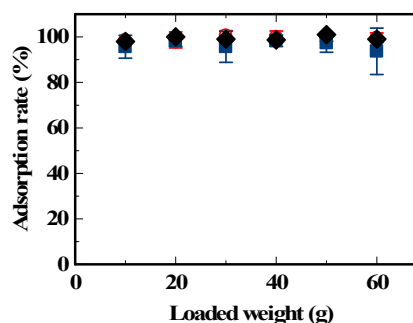


Figure. 5 Dependence of flow rate and loaded weight of the analytical solution containing 10 $\mu\text{mol L}^{-1}$ Cu(I)-BCS on the adsorption rate

Analytical sample : 1.0 $\mu\text{mol L}^{-1}$ Cu(I)-BCS complex
Flow rate : ○ : 3.0 mL min^{-1} , ■ : 7.0 mL min^{-1} , ◆ : 10.0 mL min^{-1}

Investigation of effect of each foreign ion and materials

The influences of foreign ions and materials on the adsorption of Cu(I)-BCS to the SPE cartridge was investigated. The concentrations of the foreign ions and materials were set at 10 mg L⁻¹ of Al³⁺, Ca²⁺, Fe²⁺, Fe³⁺, Mg²⁺, SO₄²⁻, 3% of Na⁺ and Cl⁻ and 0.2 mg L⁻¹ of SDS and TRITON X-100 in the existence of 1 μmol L⁻¹ of Cu(I). As a result, the adsorption rate and the recovery of Cu(I)-BCS were not affected from the foreign ions except for Al³⁺. Al³⁺ generally forms colloidal species Al(OH)₃ in neutral and alkaline pH range. Adsorption sites in the SPE may be covered by the colloidal Al(OH)₃.

Separation of Cu(I)-BCS and Cu(II)-EDTA under the optimum condition and its application to rain water sample

Separation of Cu(I)-BCS and Cu(II)-EDTA under the optimum experimental condition was tested. As a result, the recoveries of Cu(I)-BCS and Cu(II)-EDTA were 98 ± 2% and 99 ± 2%, respectively, when a 60 g of the analytical solution containing 0.05 μmol L⁻¹ Cu(I)-BCS and 0.1 μmol L⁻¹ of Cu(II)-EDTA in the pH 7 tris-HCl buffer solution was loaded to tC2 cartridge using 2 g of the 30 % methanol as the eluant.

This method was applied to a recovery test using a rain water sample. The rain water was collected for 12 hours at the building of Department of Chemical Science and Technology, The University of Tokushima on July 21 and 22, 2009 by a plastic tank. The tank was sequentially washed by a detergent, pure water, and concentrated nitric acid prior to use. Solutions for the recovery test were prepared by the addition of Cu(I) and Cu(II) to the rain water samples. In this test, the Cu(I) and Cu(II) was spiked to be 0.05, 0.1, 0.5 μmol L⁻¹ of Cu(I) and 0.2, 0.5, 1.0 μmol L⁻¹ of Cu(II). In Table 3, the recoveries of 0.05 - 0.5 μmol L⁻¹ of Cu(I)-BCS and 0.2 - 1.0 μmol L⁻¹ Cu(II)-EDTA were higher than 92%. The relative standard deviation of the recovery in the added concentration of 0.5 μmol L⁻¹ Cu(I)-BCS was 3.6% (n=3). The detection limits was estimated as the concentration of Cu corresponding to 3-times standard deviation of a blank solution (0.1 mol kg⁻¹ HNO₃) observed by ICP-MS measurement. The detection limits of Cu(I)-BCS and Cu(II)-EDTA were 1.57×10⁻⁴ μmol L⁻¹.

Table 2 Influence of foreign ions and materials on the adsorption and recovery of the Cu(I)-BCS

Ion/Material	Concentration	Adsorption rate (%)	Recovery (%)
Al ³⁺	10 mg L ⁻¹	-	12
Ca ²⁺	10 mg L ⁻¹	100	90
Fe ²⁺	10 mg L ⁻¹	100	103
Fe ³⁺	10 mg L ⁻¹	100	100
Mg ²⁺	10 mg L ⁻¹	99	103
Na ⁺	3%	99	96
SO ₄ ²⁻	10 mg L ⁻¹	100	96
Cl ⁻	3%	99	96
SDS	0.2 mg L ⁻¹	100	91
TRITON X-100	0.2 mg L ⁻¹	99	104

Analytical sample was a solution containing 1 μmol L⁻¹ Cu(I)-BCS with each foreign ion. Loaded weight of the analytical sample : 60 g, Sample flow rate of the analytical sample : 10.0 mL min⁻¹ Cartridge : tC2, Eluant composition : Methanol/Water 30/70 (w/w%), Eluant weight : 2 g

Table 3 Recoveries of Cu(I)-BCS and Cu(II)-EDTA in a rain water sample under the optimum experimental conditions

Cu(I)		Cu(II)	
Added (μmol L ⁻¹)	Recovery (%)	Added (μmol L ⁻¹)	Recovery (%)
0.05	100	0.2	92
0.1	92	0.5	96
0.5	94	1.0	94

Conclusion

Under the optimal condition, the detection limits and recoveries of Cu(I)-BCS and Cu(II)-EDTA were 1.57×10⁻⁴ μmol L⁻¹, 94% and 96%, respectively. This speciation method can be operated using two syringes and a SPE column in a closed system by hand. Furthermore, the procedure was very simple. This method can be applied to monitoring Cu(I) and Cu(II) in aqueous environment.

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