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Determination of Trace Amounts of Copper as the Complex with Bathocuproinedisulfonate after Enrichment in the Thin Layer of Anion-exchange Resin

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A simple and selective method for the determination of trace amounts of copper is developed. The method is based on the concentration of copper as the complex with bathocuproinedisulfonate (BCS) with the use of finely divided anion-exchange resin, collection of the resin on a membrane filter as the disk of thin layer, and determination of the colored complex in the resin phase by densitometry. The copper(I)–BCS complex in sample volumes ranging from 50—200 cm^3 was effectively concentrated by factors ranging from 2500—10000. The method was applied to tap water. Copper at ppb (μg dm^{-3}) level was successfully determined.

As well known, cuproine and its derivatives are highly selective color-developing reagents for copper.1) Among them, bathocuproinedisulfonate has been used for the direct determination of copper in the aqueous solutions.2)

Fugimoto *et al.*3) studied the resin spot test of copper and reported that copper(I) bathocuproinedisulfonate was extremely strongly fixed on the beads of anion-exchange resin. The idea of resin spot test was further extended to ion-exchanger colorimetry,4) in which the resin phase absorbance was measured directly in a 1-mm cell. Nigo *et al.*5) applied the method to the trace determination of copper as the porphyrin complex. The method of combined use of finely divided anion- and cation-exchange resins was also reported.6,7) The colored species collected in the thin layer of mixed resins were determined spectrophotometrically6) or densitometrically.7)

In the present paper, the extraction of trace amounts of copper as bathocuproinedisulfonate is studied by the use of finely divided anion-exchange resin. The determination is carried out by using densitometer and the results are compared with those obtained by the combined use of anion- and cation-exchange resins.

Experimental

Reagents. Hydrochloric acid used was of super special grade (SSG reagent, Wako). All other chemicals used were of analytical reagent grade. A stock copper(II) solution (1000 μg Cu cm^{-3}) was prepared by dissolving copper(II) sulfate pentahydrate in deionized water containing hydrochloric acid (pH *ca.* 1). The working solution (10 μg Cu cm^{-3}) was prepared by appropriate dilution. The reagents, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bathocuproine, abbreviated as BC) and disodium salt of 2,9-dimethyl-1,10-phenanthrolyl-4,7-dibenzene-*p*,*p*′-disulfonic acid (Bathocuproinedisulfonic acid, disodium salt, abbreviated as BCS) were obtained from Dojindo Lab., and used without further purification. A 1 mmol dm^{-3} ethanolic solution of BC and 0.67 mmol dm^{-3} aqueous solution of BCS were prepared. The purity of BCS, which was estimated from absorbance-mole ratio (BCS/Cu) plots, was 78%. An aqueous 10% W/V solution of hydroxylammonium chloride and 30% W/V sodium acetate solution were purified by extracting the impurity due to copper ion as the BC complex into chloroform.

Ion-exchange Resin Suspension. The macroreticular type ion exchangers, Amberlyst 15 and A-27 (Rhom and Haas Co.) were used in RSO_3H and $RN(CH_3)_3Cl$ forms, respectively. The cation-exchange resin suspension (CRS) and the anion-exchange resin suspension (ARS) were prepared according to the reported method,8) that is, the wet resin was crashed in the slurry and sieved through 3G3 glass filter. The ion-exchange capacities of CRS and ARS were determined by the conductometric titration with standard solutions of sodium hydroxide and silver nitrate. The capacities of CRS and ARS were found to be 6.72 μeq cm^{-3} and 5.11 μeq cm^{-3}, respectively. When 2 cm^3 of CRS was mixed with 3 cm^3 of ARS, both resins were almost completely coagulated and quantitatively collected on a filter paper.

Apparatus. The densitometer used was a Shimadzu Chromatoscanner CS-920 equipped with linearizer. A Shimadzu UV-visible recording spectrophotometer, type UV-240, was used for measuring absorption spectra. A Toyo KG-25 filter holder was used. The filters used were TM-1 (0.65 μm pore size, 47 mm in diameter, Toyo) or No. 5B filter paper. Micropipets were used.

General Procedure. A 50-cm^3 aliquot of sample solution containing less than 1 μg of copper was placed in a 100-cm^3 beaker. A 1-cm^3 portion of 10% hydroxylammonium chloride, 0.5 cm^3 of 0.67 mmol dm^{-3} BCS, and 1 cm^3 of 30% sodium acetate solution were added successively. The pH of final solution was about 6. The solution was stirred by means of a magnetic stirrer for 2 min and then 1.0 cm^3 of ARS was added. The mixture was further stirred for 10 min. The anion-exchange resin was then collected by filtration with suction on a membrane filter (TM-1). The copper(I)–BCS complex was thus concentrated in a disk of the thin layer with 17 mm in diameter and about 0.1 mm in thickness. The wet membrane filter was placed on a white plastic plate fixed on a scanning board in the densitometer. The absorbance was measured with or without linearizer at 485 nm by scanning the light beam in a range of 24 mm wide and 30 mm long. In the case of the mixed resin method, the combination of 2.0 cm^3 CRS and 3.0 cm^3 ARS was used and the mixed resins were collected on a filter paper of No. 5B.

Results and Discussion

Copper(I)–BCS Complex in the Resin Phase. A trace amount of copper was quantitatively extracted to the resin phase when the amount of BCS was in excess of the stoichiometric value (Fig. 1). A constant coloration was obtained at pH above 3. Figure 2 shows the absorption spectrum of the complex in the resin phase. Although there is a general similarity between the absorption spectra of the complex in the solution and in the resin phase, but a small shift of the maximum wavelength was observed from 480 nm in the solution to 485 nm in the resin phase. The coloration was stable for at least 2 h, when the resin thin layer was kept wet with water.

The maximum fixable amounts of copper(I)–BCS complex and BCS on the resin in 1.0 cm³ of ARS were found to be 0.16 μmol and 0.57 μmol, respectively. These values were much smaller than the total exchange capacity (5.11 μeq) of the resin. The bulky ions might be fixed only on the surface of the resin particles. Since the recovery of the complex corresponding to 0.5 μg of copper was quantitative in the presence of 10 μmol of BCS, it was indicated that the copper(I)–BCS complex was much more strongly fixed on the resin than the reagent.

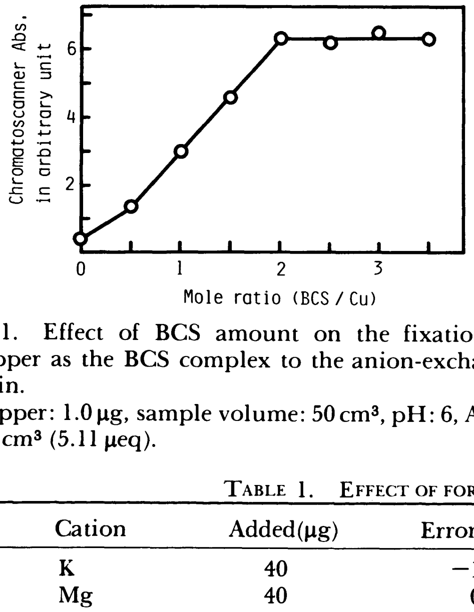

Fig. 1. Effect of BCS amount on the fixation of copper as the BCS complex to the anion-exchange resin.

Copper: 1.0 μg, sample volume: 50 cm³, pH: 6, ARS: 1.0 cm³ (5.11 μeq).

Effect of Sample Volume. The effect of sample volume was examined by the use of 1.0 cm³ of ARS. A 1.0-μg portion of copper was effectively recovered from different sample volumes ranging from 50—200 cm³. The rate of filtration was about 10 cm³ min⁻¹. The volume of resin phase was estimated to be about 0.02 cm³, and so the concentration factors were in the range of 2500—10000.

Effect of Foreign Ions. The effect of foreign ions on the determination of copper(II) was examined (Table 1). Except for iron(III), other cations and anions studied did not affect the determination of copper. Iron(III) gave a positive error, which was due to the formation of colored hydroxide. The interference by

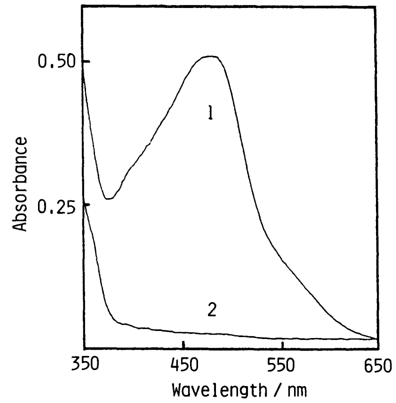

Fig. 2. Absorption spectra of copper(I)-BCS complex and reagents in the resin phase.

1: Spectrum of copper(I)-BCS complex in the resin thin layer obtained from 50 cm³ solution (pH 6) containing 2.0 μg of copper, 1 cm³ of 10% hydroxylammonium chloride, 0.3 μmol BCS, 1 cm³ of 30% sodium acetate, and 1.0 cm³ ARS.

2: Spectrum of resin thin layer obtained from 50 cm³ solution without addition of copper(II). Other components were the same as in Curve 1.

Reference: resin thin layer obtained from 50 cm³ solution containing 1.0 cm³ of ARS.

TABLE 1. EFFECT OF FOREIGN IONS ON THE DETERMINATION OF COPPER[a)]

Cation	Added(μg)	Error[b)](%)	Anion	Added(mg)	Error[b)](%)
K	40	−1.5	F^-	19	−0.1
Mg	40	0.8	Cl^-	4	−1.2
Ca	40	−2.3	Br^-	4	2.3
Ba	40	−1.4	I^-	4	4.5
Cr^{III}	40	1.9	NO_3^-	4	0.9
Mn^{II}	40	−0.6	CO_3^{2-}	4	1.2
Fe^{III}	40	71.9	SO_4^{2-}	4	4.1
Fe^{III}	4	1.9	PO_4^{3-}	4	−2.8
Fe^{III}	40[c)]	1.5			
Co^{II}	40	3.3	NaCl[d)]	Added(mol)	Error[b)](%)
Ni^{II}	40	2.4	NaCl	0.05	2.3
Zn^{II}	40	3.7	NaCl	0.10	2.4
Cd^{II}	40	2.9	NaCl	0.15	4.8
Al^{III}	40	−1.1	NaCl	0.20	2.1
Pb^{II}	40	−2.5			

a) Copper taken: 0.4 μg, sample volume: 50 cm³ b) Calculated using % Relative Error=$(A_2-A_1)/(A_1-A_0)$, where A refers to the Chromatoscanner absorbance and the subscripts 0, 1, and 2 refer to blank thin layer and thin layers without and with the foreign ion, respectively. c) A 2-cm³ portion of 0.5 mol dm⁻³ sodium fluoride was added. d) Sodium chloride solution was previously purified by extracting impurity copper as the BC complex into chloroform.

Table 2. Comparison of single resin method with mixed resin method

	Single resin method	Mixed resin method	
Resin	Amberlyst A-27	Amberlyst A-27	Amberlyst 15
Capacity of resin suspension	5.11 μeg cm^{-3}	5.11 μeg cm^{-3}	6.72 μeg cm^{-3}
Amount of resin suspension	1.0 cm^3	3.0 cm^3	2.0 cm^3
Filter	Membrane filter[a]	Filter paper[b]	
Filtration rate	10 cm^3 min^{-1}	10 cm^3 min^{-1}	
Volume of resin thin layer	0.02 cm^3	0.07 cm^3	
Concentration factor[c]	2500	700	
Calibration curve[d]	$Y=6.60X+0.39$	$Y=2.93X+3.21$	
Relative standard deviation[e]	1.4% ($n=7$)	1.7% ($n=4$)	
Standard deviation of blank value	0.02 ($n=6$)	0.06 ($n=6$)	
Limit of detection[c]	0.18 μg copper dm^{-3}	1.2 μg copper dm^{-3}	

a) Pore size: 0.65 μm, diameter: 47 mm. b) No. 5B. c) Sample amount: 50 cm^3 d) X: amount of copper in μg, Y: Chromatoscanner absorbance in arbitrary unit. The intercept at $X=0$ is the blank value including resin matrix. e) Amount of copper: 0.4 μg.

Table 3. Determination of total copper in tap water

		Single resin Method		Mixed resin method	
Sample amount (cm^3)	Copper(II) added (μg)	Copper(II) found (μg)	Concn. in tap water (μg dm^{-3})	Copper(II) found (μg)	Concn. in tap water (μg dm^{-3})
100	0.00	0.30	3.0	0.29	2.9
75	0.00	0.21	2.8	0.26	3.5
75	0.10	0.33	3.1	0.35	3.4
50	0.00	0.12	2.4	0.16	3.3
50	0.10	0.22	2.4	0.24	2.8
50	0.20	0.35	3.0	0.34	2.8
			2.78±0.33[a]		3.12±0.33[a]

a) 95% confidence limits

iron was eliminated by the addition of sodium fluoride. It was found that the copper(I)-BCS complex was quantitatively recovered even in the presence of 4 mol dm^{-3} sodium chloride.

Calibration Curve. The calibration curves obtained by the single resin method and the mixed resin method showed good linearity when the linearizer was applied. The slope of calibration curve obtained by the single resin method was about two times greater than that obtained by the mixed resin method. The results were summarized in Table 2, in which the limit of detection of copper was calculated as three times the standard deviation of the blank value.[9]

Determination of Total Copper in Tap Water. The single resin method and the mixed resin method were applied to the determination of total copper in the tap water supplied to our laboratory from a well in the University campus. After running the water for more than 20 min, the sample water was taken and acidified to pH 1. The results were summarized in Table 3. No significant difference was found between the variables (F-test) as well as between the mean values (t-test).

Comparison of the Methods. Generally, the concentration factor and thus the sensitivity of the single resin method is superior to those of the mixed resin method. However, as the mixed resins coagulate tightly with each other, the resulting thin layer is much more sturdy than that obtained by a single resin method. Therefore, it is possible to immerse the thin layer of mixed resins in the solution for making additional coloration, as successfully indicated in the determination of hexacyanoferrate(III) as Turnbull's Blue[10] and cobalt as the thiocyanate complex.[11]

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