Spectrophotometric Determination of Copper Separated by Means of Adsorption of Its Pyrrolidinedithiocarbamate on Naphthalene

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The copper chelate of APDC was adsorbed on microcrystalline naphthalene to determine trace amounts of copper. The optimum pH range for the adsorption is 1.5—10.5. The chelate in dimethylformamide has an absorption maximum at 435 nm. Beer's law holds in the range 2.5—48 μg of copper in 10 ml of dimethylformamide. The molar absorptivity is 1.3×10^4 l·mol^{-1}·cm^{-1} and the sandell sensitivity 4.8×10^{-3} μg of copper per cm^2. Other factors such as amounts of reagent and naphthalene, shaking time, standing time and diverse ions were studied. The method can be applied to the determination of copper in Bovine Liver and human hair.

Ammonium pyrrolidinedithiocarbamate(APDC) is useful for solvent extraction and atomic absorption spectrophotometric determination of various metal ions. It was used for the extraction and spectrophotometric determination of copper by Looyenga and Boltz.[1]

We have developed a new method involving solid-liquid separation after liquid-liquid extraction, and have applied it to the determination of copper, bismuth and cobalt with APDC as a chelating agent by the naphthalene extraction method.[2] The method is based on the formation of metal chelate which is extractable quantitatively with molten naphthalene. The extract is separated from the aqueous solution and dissolved in a suitable organic solvent, the trace amounts of metal being determined spectrophotometrically.

Most metal chelates in aqueous solution can be easily adsorbed with microcrystalline naphthalene by vigorous shaking for 1 min at room temperature. The method was applied to the spectrophotometric determination of trace metals.[3,4] In the present study, APDC was used as a chelating agent for the determination of trace copper. Satisfactory adsorption of copper chelate on naphthalene is discussed in detail.

Experimental

Reagents. Standard copper solution, 5 ppm. Prepared by diluting 5 ml of standard copper solution (1000 ppm, Wako Pure Chemical Co.) to 1000 ml with water.

APDC solution, 0.2%. Prepared by dissolving 0.2 g of APDC in 100 ml of water.

Buffer Solutions. Prepared from 1 M acetic acid and 1 M ammonium acetate for pH 3—6, and from 1 M aqueous ammonia and 1 M ammonium acetate for pH 8—11.

Naphthalene solution, 20%. Prepared by dissolving 20 g of naphthalene in 100 ml of acetone.

Naphthalene, acetone, dimethylformamide, and all other reagents of analytical grade were used without further purification.

Apparatus. Absorption measurements were made with matching 10 mm glass cells on a Hitachi Model 200-20 spectrophotometer.

pH measurements were made with a Toa-Dempa HM-5A pH meter.

Naphthalene was dried with a Tabai Model K-2 drier (Tabai Mfg. Co., Ltd.).

Samples were ashed with an International Plasma Corp. low-temperature asher, IPC-1000 AN TM1640.

Procedure. Transfer 1—10 ml of 5 ppm standard copper solution to a 100-ml stoppered Erlenmeyer flask, and dilute with water to *ca.* 40 ml. Add 1.5 ml of 0.2% APDC solution and adjust pH to 5.0 with 2.0 ml of buffer solution. Mix the solution well, let stand for 10 min, add 2.0 ml of 20% naphthalene solution and shake vigorously for 1 min. Filter off on a filter paper (*e.g.*, No. 5C, Toyo Roshi Co.) placed flat on a filter plate in a funnel. Wash with water, and dry at 50—60 °C when necessary. Dissolve the crystals with dimethylformamide, dilute to 10 ml and measure the absorbance in a 10-mm cell at 435 nm against the reagent blank prepared similarly.

Results and Discussion

Absorption Spectra. Absorption spectra of the reagent blank and the copper chelate in naphthalene–dimethylformamide solution are shown in Fig. 1. The copper chelate has an absorption maximum at 435 nm where there is practically no absorption due to the reagent blank. Thus, 435 nm was chosen as

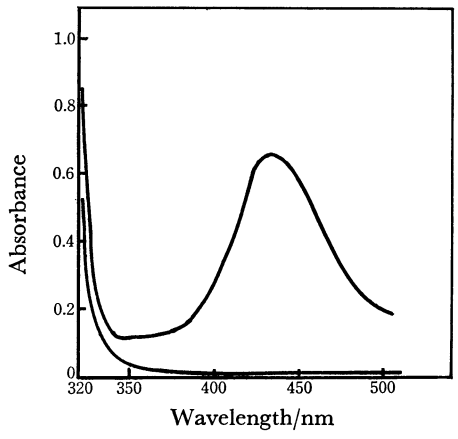

Fig. 1. Absorption spectra of APDC and copper complex in naphthalene–DMF solution.
Cu: 25 μg; 0.2% APDC: 1.5 ml; pH: 5.3; digestion time: 10 min; 20% naphthalene: 2.0 ml; shaking time: 1 min; reference: water; (1) reagent blank, (2) copper complex.

the most suitable wavelength.

Effect of pH. After the pH of sample solutions containing 25 μg of copper and 1.5 ml of 0.2% APDC solution had been controlled to desired values with different buffer solutions or hydrochloric acid, adsorption of the chelate was carried out. The result is shown in Fig. 2. The adsorption of the chelate starts from 2 mol dm^{-3} hydrochloric acid solution, reaches a maximum at pH 1.5, and thereafter remains constant over the range 1.5—10.5. Thus, the pH of the solution was adjusted to 5.3 for adsorption of the chelate.

Effect of Reagent Concentration. Various amounts of 0.2% APDC solution were added to the sample solution containing 25 μg of copper and 2.0 ml of the buffer solution(pH 5.3), the following procedure being the same as above. Figure 3 shows the variation in absorbance with the reagent concentration. The absorbance increases sharply with increase in the amount of reagent up to 0.1 ml of 0.2% APDC solution, becoming almost constant over the range 0.1—5.0 ml. Thus, 1.5 ml of 0.2% APDC solution was used for adsorption of the chelate.

Effect of Buffer Solution. The effect of buffer solution on the absorbance was examined. Addition of 0.5—5.0 ml of the acetate buffer solution caused practically no variation in absorbance. Thus, 2.0 ml of the buffer solution was added for adsorption of the chelate.

Effect of Digestion Time. A solution containing 25 μg of copper, 2.0 ml of the buffer solution(pH 5.3) and 1.5 ml of 0.2% APDC solution was digested at room temperature, the following procedure being the same as above. The absorbance increases with increase in digestion time up to 2 min, remaining almost constant for 2—30 min of digestion time. Thus, 10 min of digestion time was chosen for adsorption of the chelate.

Effect of Naphthalene Concentration. Adsorption of the chelate was carried out by changing the volume of 20% naphthalene–acetone solution added to the solution containing copper chelate. Figure 4 shows the effect of naphthalene concentration on the absorbance. The absorbance increases with increase in the amount of naphthalene up to 0.3 ml of 20% naphthalene solution, becoming almost constant for 0.3—5.0 ml. Thus, 2.0 ml of 20% naphthalene solution was used for adsorption of the chelate.

Effect of Shaking Time. Two ml of 20% naphthalene solution was added to the solution containing the copper chelate, and the mixed solution was shaken vigorously for 100 s. The chelate was completely collected on naphthalene by vigorous shaking for a few seconds. Shaking for 1 min was found to be satisfactory for complete adsorption.

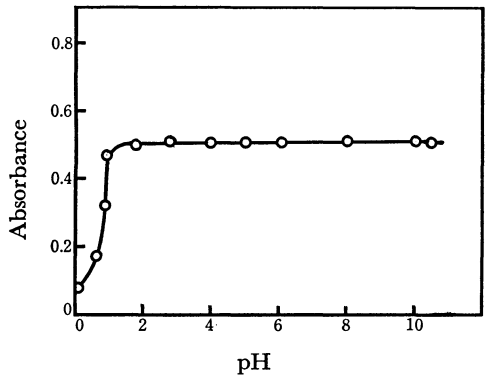

Fig. 2. Effect of pH.
Cu: 25 μg; wavelength: 435 nm; 0.2% APDC: 1.5 ml; digestion time: 10 min; 20% naphthalene: 2.0 ml; shaking time: 1 min, reference: reagent blank.

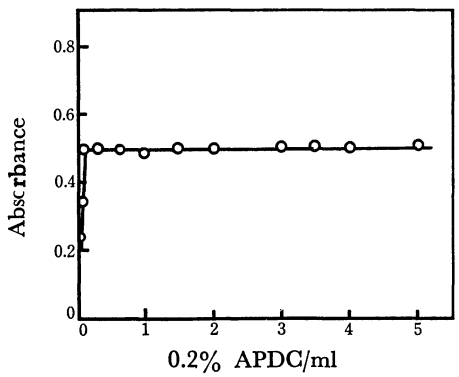

Fig. 3. Effect of reagent concentration.
Cu: 25 μg; pH: 5.3; 0.2% APDC: 1.5 ml; wavelength: 435 nm; digestion time: 10 min; 20% naphthalene: 2.0 ml, reference: reagent blank.

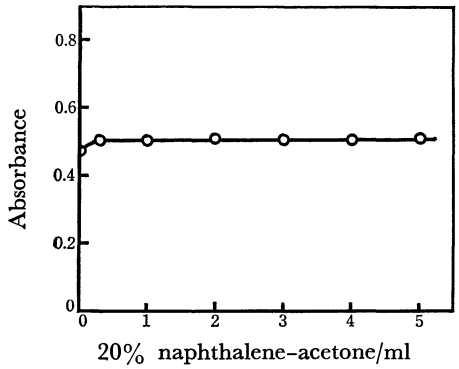

Fig. 4. Effect of naphthalene concentration.
Cu: 25 μg; wavelength: 435 nm; pH: 5.3; 0.2% APDC: 1.5 ml; digestion time: 10 min, reference: reagent blank.

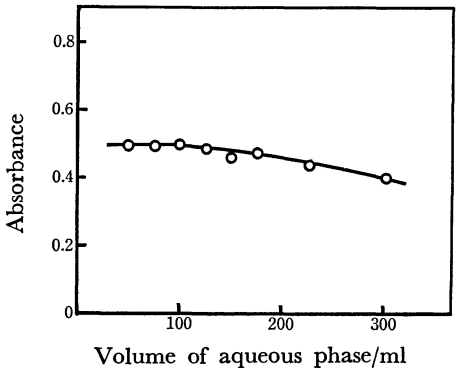

Fig. 5. Effect of volume of aqueous phase.
Cu: 25 μg; wavelength: 435 nm; pH: 5.3; 0.2% APDC: 5.0 ml; 20% naphthalene: 3.0 ml; shaking time: 5 min; reference: reagent blank.

Effect of Volume of Aqueous Phase. The volume of aqueous phase was varied between 50 and 300 ml while other factors were kept constant. Figure 5 shows the effect of volume of aqueous phase on the absorbance. The absorbance was almost constant up to about 100 ml, but decreasing gradually with increase in the volume of aqueous phase. For volumes exceeding 80 ml, the adsorption of the chelate on naphthalene was carried out by using a larger volume of the reagent solution, shaking for a long time and digesting at 40—50 °C. In this series of tests, 5.0 ml of the reagent solution was taken ; the mixed solutions were shaken for 10 min and digested for 20 min, 3.0 ml of 20% naphthalene solution being used.

TABLE 1. EFFECT OF DIVERSE ALKALI SALTS

Alkali metal salt	Amount added (mg)	Absorbance (435 nm)
—	—	0.500
Na_2SO_4	100	0.495
Na_2SO_4	500	0.500
NaCl	100	0.496
NaCl	500	0.498
NH_4Cl	100	0.495
NH_4Cl	500	0.498
$Na_2C_2O_4$	100	0.511
$Na_2C_2O_4$	300	0.518
$Na_2C_2O_4$	500	0.512
$NaH_2PO_4 \cdot 2H_2O$	100	0.501
$NaH_2PO_4 \cdot 2H_2O$	500	0.506
$Na_2HPO_4 \cdot 12H_2O$	100	0.515
$Na_2HPO_4 \cdot 12H_2O$	500	0.521
Na_2CO_3	100	0.500
Na_2CO_3	300	0.501
Na_2CO_3	500	0.493
KNO_3	100	0.509
KNO_3	500	0.513
Na_2SO_3	100	0.507
Na_2SO_3	500	0.526
CH_3COONa	100	0.505
CH_3COONa	500	0.502
KBr	100	0.519
KBr	500	0.520
Sodium tartrate	100	0.515
Sodium tartrate	200	0.518
Sodium tartrate	300	0.520
Sodium tartrate	500	0.522
Sodium citrate	100	0.509
Sodium citrate	500	0.503
KCN (pH 5.0)	100	0.498
KCN (pH 5.0)	200	0.510
KCN (pH 5.0)	300	0.495
KCN (pH 9.0)	0.04	0.000
Disodium EDTA (pH 5.0)	100	0.495
Disodium EDTA (pH 5.0)	200	0.497
Disodium EDTA (pH 5.0)	300	0.500
Disodium EDTA (pH 9.0)	0.04	0.020
Disodium EDTA (pH 9.0)	0.08	0.000

Cu: 25.0 μg; pH: 5.3.

Effect of Standing Time. A mixture of copper chelate and naphthalene was dissolved in dimethylformamide, and the effect of standing time on the absorbance was studied. The color of the chelate in naphthalene–dimethylformamide solution remained unchanged even after 10 h.

Calibration Curve. The absorbances for varying concentration of copper were measured at 435 nm against the reagent blank under the optimum conditions described above. The absorbance shows a linear relationship to the concentration of copper in the range 2.5—48 μg in 10 ml of dimethylformamide. The molar absorptivity is 1.3×10^4 $l \cdot mol^{-1} \cdot cm^{-1}$, the sensitivity being 4.8×10^{-3} μg per cm^2 for an absorbance of 0.001. Ten replicate determinations of the sample solution containing 25 μg of copper give a mean absorbance of 0.500 with a relative standard deviation of 0.89%.

Choice of Solvent. Tests were made with various organic solvents in order to dissolve the mixture of the chelate and naphthalene. The chelate is soluble in organic solvents such as benzene, toluene, xylene, chlorobenzene, *o*-dichlorobenzene, dichloroethane, chloroform, nitrobenzene, acetone, acetonitrile, propylene carbonate, dimethylformamide at room tem-

TABLE 2. EFFECT OF DIVERSE METAL IONS

Metal ion	Added as	Ion added (μg)	Absorbance (435 nm)
—	—	—	0.500
Pb^{2+}	Nitrate	10	0.505
Pb^{2+}	Nitrate	50	0.510
Pb^{2+}	Nitrate	100	0.503
Bi^{3+}	Nitrate	10	0.510
Bi^{2+}	Nitrate	50	0.508
Bi^{2+}	Nitrate	100	0.517
Mg^{2+}	Chloride	10	0.506
Mg^{2+}	Chloride	50	0.509
Mg^{2+}	Chloride	100	0.504
Ca^{2+}	Chloride	50	0.498
Ca^{2+}	Chloride	100	0.501
Zn^{2+}	Nitrate	10	0.507
Zn^{2+}	Nitrate	50	0.499
Zn^{2+}	Nitrate	100	0.509
Fe^{3+}	Chloride	10	0.530
Fe^{2+}	Chloride	50	0.821
Ni^{2+}	Chloride	10	0.529
Ni^{2+}	Chloride	50	0.553
Ni^{2+}	Chloride	100	0.589
Co^{2+}	Chloride	10	0.568
Co^{2+}	Chloride	50	0.758
Cd^{2+}	Chloride	10	0.504
Cd^{2+}	Chloride	50	0.498
Cd^{2+}	Chloride	100	0.500
Cr^{6+}	Dichlomate	10	0.494
Cr^{6+}	Dichlomate	50	0.499
Cr^{6+}	Dichlomate	100	0.495
Hg^{2+}	Chloride	10	0.507
Hg^{2+}	Chloride	50	0.499
Hg^{2+}	Chloride	100	0.504

perature. It undergoes decolorization in dioxane and MIBK.

Effect of Diverse Ions. Sample solutions containing 25 μg of copper and various amounts of diverse alkali metal salts or metal ions were prepared, the effect of diverse interfering salts and metal ions on copper determination being studied. The pH of solution was adjusted to 5.3. The results are given in Tables 1 and 2. The following species gave no interference: Na_2SO_4, NaCl, NH_4Cl, $Na_2C_2O_4$, $NaH_2PO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 12H_2O$, Na_2CO_3, KNO_3, Na_2SO_3, CH_3COONa, KBr, sodium tartrate, sodium citrate, KCN, EDTA, Cd^{2+}, Pb^{2+}, Bi^{3+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Cr^{6+}, Hg^{2+}· Fe^{3+}, Ni^{2+}, and Co^{2+} gave interference.

From the results we see that the present method gives the same molar absorptivity, sensitivity, precision and selectivity as those by the chloroform method.[1] The pH range for the adsorption being wider.

Analysis of Copper in Biological Sample. The method was applied to the analysis of copper in Bovine Liver(N. B. S., SRM-1577) and human hair by using spectrophotometry and atomic absorption spectrophotometry. Low-temperature ashed samples were dissolved in concentrated nitric acid on a hot plate and evaporated to dryness. The residue was dissolved with 10 ml of redistilled water. An aliquot of this sample was taken for analysis. Iron(III) was masked with triethanolamine at pH 9.0. The results of Bovine Liver and human hair for copper by the two methods are satisfactory (Tables 3 and 4).

Table 3. Analysis of Bovine Liver for copper

Sample	Certified value (μg/g)	Spectrophotometric value (μg/g)	A.A.S (direct method) value (μg/g)
N.B.S SRM Bovine Liver 1577	193±10	190	191
		193	192
		192	191
		193	190
		194	193

pH: 9.0; Naphthalene: 0.4 g; 10% triethanolamine: 1.5 ml.

Table 4. Result of analysis of human hair for copper

Sample	Spectrophotometric value (μg/g)	A.A.S (direct method) value (μg/g)
Human hair A	8.7	9.8
Human hair B	12.4	11.8
Human hair C	24.0	23.4
Human hair D	27.5	27.8
Human hair E	12.0	12.4

pH: 9.0; Naphthalene: 0.4 g; 10% triethanolamine: 1.5 ml.

References

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