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Atomic Absorption Spectrophotometric Determination of Copper(I) After Extraction of Its Ternary Complex with 3-(4-Phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine and Tetraphenylborate into Molten Naphthalene

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A preferable atomic absorption spectrophotometric method has been established for trace determination of copper(I) *via* extraction of its ion-associated complex with 3-(4-phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine and tetraphenylborate into molten naphthalene. The optimum pH range for the extraction is 1.6—8.2. Solid naphthalene containing the copper(I) complex is separated by filtration and dissolved in *N,N*-dimethylformamide. The absorbance is measured at 324.7 nm. Beer's law is obeyed in the concentration range 2.5—80 μg of copper in 10 cm³ *N,N*-dimethylformamide solution. Ten repeat analyses on a sample containing 35 μg of copper give a mean absorbance of 0.205 with a standard deviation of 0.0017 and a relative standard deviation of 0.83%. The method has been successfully applied to determination of copper in standard reference materials and biological samples.

Numerous chromogenic reagents like 2,2′-dipyridyl- and 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine have been used for determination of copper(I) in various methods.[1-8] These reagents react with copper(I) to form water-soluble, colored complex cations, which in turn form water-insoluble, stable, ternary complexes with anions such as ClO_4^-, SCN^-, HgI_4^{2-}, $HgBr_4^{2-}$, and CdI_4^{2-}. Ternary complexes formed can be extracted into suitable organic solvents, and some metal ions or anions can thus be determined spectrophotometrically.[9]

In the present paper, 3-(4-phenyl-2-pyridyl)-5,6-diphenyl-1,2,4-triazine (PPDT) will be recommended as a reagent for extraction of copper(I) with naphthalene. PPDT forms a light brown complex with copper(I) which is partially soluble in water.[7] Perchlorate species of this complex is extremely insoluble in water and many nonaqueous solvents. Though it can be extracted into isopentyl alcohol, the color of the complex fades in a short time[7] and it is inconvenient to work with this solvent due to its unpleasant odor. These difficulties have been overcome by means of extraction with molten naphthalene.[10-14] In the presence of tetraphenylborate (TPB) anion, the Cu(I)—PPDT complex cation mentioned above forms a thermally stable, water-insoluble, ion-associated complex. This complex cannot be extracted into any organic solvents, but can easily be extracted into molten naphthalene. The extracted mixture is soluble in *N,N*-dimethylformamide, dimethyl sulfoxide, propylene carbonate, or acetonitrile, which are all miscible with water. Various conditions have been tested and a preferable method has been applied to determination of copper in some standard reference materials and biological samples.

Experimental

Reagents. Standard copper(II) solution of 5 ppm was prepared by diluting an aliquot of 1000 ppm standard copper(II) solution with distilled water. PPDT solution of 0.04% was prepared in ethanol. TPB solution of 1% was prepared in distilled water. Hydroxylammonium chloride solution of 2% was prepared in distilled water. Buffer solutions were prepared by mixing 1 M acetic acid (1 M=1 mol dm^{-3}) and 1 M ammonium acetate solution for pH 3—6 and 1 M aqueous ammonia and 1 M ammonium acetate solution for pH 8—11. *N,N*-dimethylformamide (DMF), naphthalene, and all the other reagents were of analytical-reagent grade.

Apparatus. All absorbance measurements were made with a Perkin-Elmer Model 403 atomic absorption spectrophotometer with an air-acetylene burner head. A hollow-cathode lamp for copper was obtained from Hamamatsu Photonics Ltd. Atomic absorption data were obtained in an air-acetylene mode at 324.7 nm. Measurements of pH were carried out with a Beckmann Model G pH meter.

General Procedure. To an about 25 cm³ sample solution containing 2.5—80 μg copper(II) in a 100 cm³ tightly stoppered Erlenmeyer flask are added 2.0 cm³ of 2% hydroxylammonium chloride solution, 3.0 cm³ of 1 M ammonium acetate solution, 2.0 cm³ of 0.04% PPDT solution, and 2.0 cm³ of a buffer (pH 5.8). The solution is stirred well and 2.0 cm³ of 1% TPB solution added. After warming the solution on a water bath at about 60 °C for 5 min, 0.7 g naphthalene is added and the mixture is heated on a water bath at 85 °C to melt naphthalene completely. The solution is then shaken vigorously until naphthalene solidifies forming very fine crystals. The crystals are filtered out on a filter paper (No. 5A), washed with water and dried in an oven at 50—60 °C. The solid is dissolved in *N,N*-dimethylformamide and diluted to 10 cm³. The solution is aspirated into an air-acetylene flame to be subjected to a measurement at 324.7 nm with a copper hollow-cathode lamp.

Results and Discussion

Effect of pH. To a copper solution was added 3 cm³ of 1 M ammonium acetate solution and complex extractions were carried out at different pH with the other conditions kept the same. The optimum pH range was 1.6—8.2 (Fig. 1). Addition of 1.5—5.0 cm³

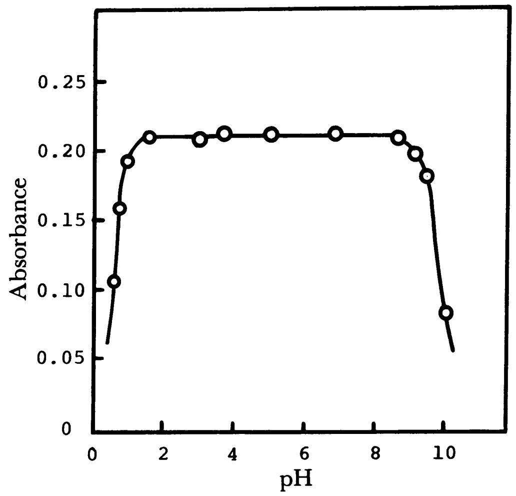

Fig. 1. Effect of pH.
Cu: 35μg; wavelength: 324.7 nm; 0.04% PPDT: 2.0 cm³; 1% TPB: 2.0 cm³; naphthalene: 0.7 g; 2% hydroxylammonium chloride: 2.0 cm³; digestion time: 5 min; shaking time: 30 s; solvent: *N*,*N*-dimethylformamide.

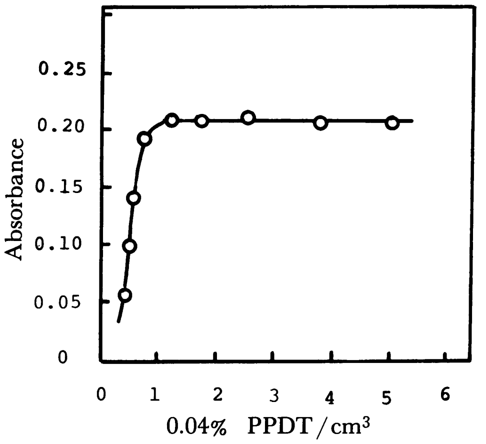

Fig. 2. Effect of PPDT concentration.
pH: 5.8; Conditions were the same as those in Fig. 1.

buffer (pH 5.8) caused virtually no variation in absorbance. Subsequent studies were conducted at pH 5.8 using 2.0 cm³ of buffer solution.

Effect of Hydroxylammonium Chloride Concentration. Varying volumes of 2% hydroxylammonium chloride solution were added to sample solutions containing 35 μg of copper. Copper(II) was completely reduced to copper(I) by addition of 0.5—5.0 cm³ of the 2% solution. For assured functioning, 2.0 cm³ of the 2% solution of reducing agent was selected.

Effect of PPDT and TPB Concentrations. Extractions were carried out at fixed pH but different PPDT concentrations. It was observed that extractions were quntitative for 1.2—5.0 cm³ of 0.04% PPDT solution. Similar studies with sodium tetraphenylborate showed that the absorbance remained constant for 0.8—4.0 cm³ of 1% TPB solution. Thus 2.0 cm³ of 0.04% PPDT solution and 2.0 cm³ of 1% TPB solution were selected for the extraction of complex (Figs. 2—3).

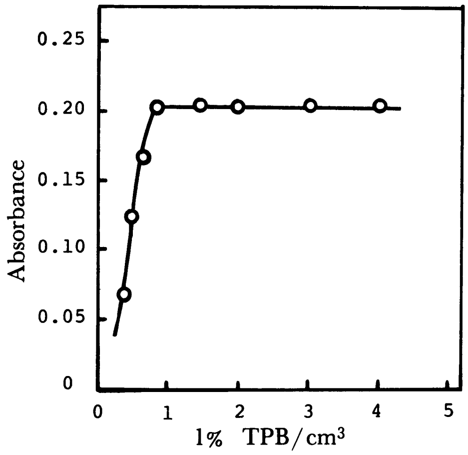

Fig. 3. Effect of TPB concentration.
Conditions were the same as those in Fig. 2.

Effect of Addition of Naphthalene. The amount of naphthalene was varied from 0.2 to 1.5 g and extractions were carried out by the general procedure. The extraction was quantitative in the range 0.3—1.5 g of naphthalene, but beyond this range, naphthalene interfered with the determination of copper due to its deposition on the burner head. Hence 0.7 g naphthalene was selected as a suitable amount.

Effect of Digestion and Shaking Times. A solution containing the Cu(I)-PPDT-TPB complex at pH 5.8 was digested at 50—60 °C. The digestion time is not critical, 1 min being sufficient for completion of the complex formation. The extraction of complex into molten naphthalene (81—85 °C) was found to be very rapid and no change was observed when the shaking time was varied from 3 to 120 s.

Effect of Electrolytes. The extraction of complex was carried out in the presence of sodium chloride, potassium nitrate, sodium acetate, ammonium acetate, ammonium chloride, or sodium sulfate (0.02—1.0 M). It was found that ammonium acetate is the most suitable for the formation and extraction of complex when its ionic strength is in the range 0.05—1.0 M. In the absence of ammonium acetate, the pH range for extraction was 3.1—8.2 and the absorbance was low, indicating a salting-out effect.

Effect of the Volume of Aqueous Phase. Since the organic/aqueous phase ratio is an important factor in such procedures, the effect of the latter on the extraction of complex was studied. The extraction is quantitative when the volume of aqueous phase does not exceed 50 cm³ (Fig. 4).

Choice of Solvent. Various organic solvents were tried to dissolve an extracted mixture of complex and naphthalene. The complex is insoluble in benzene, toluene, xylene, chlorobenzene, *o*-dichlorobenzene, nitrobenzene, chloroform, carbon tetrachloride, 1,2-dichloroethane, isopentyl acetate, diethyl ether, 1-pentanol, dioxane or isobutyl methyl ketone (IBMK), but it is soluble in dimethyl sulfoxide, propylene carbonate, acetonitrile, or *N*,*N*-dimethylformamide, which are miscible with water. Dimethyl sulfoxide and propyl-

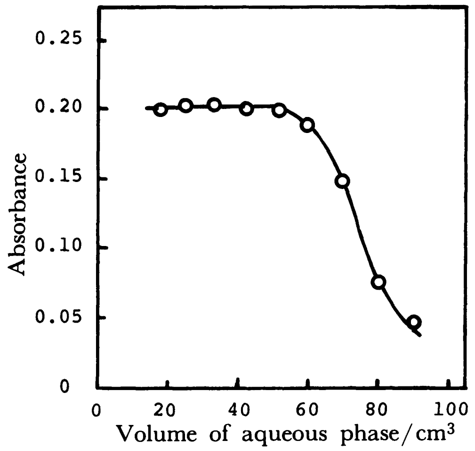

Fig. 4. Effect of volume of aqueous phase.
Cu: 35 μg; 0.04% PPDT: 3.0 cm^3; Conditions were the same as those in Fig. 2.

Table 1. Effect of diverse ions and salts[a)]

Ion/Salt	Tolerance limit
NaI	1.5 g
NaF, Cd^{2+}	1.0 g
KSCN	300 mg
Pb^{2+}	200 mg
Mo^{6+}	40 mg
Zn^{2+}	35 mg
Ca^{2+}	25 mg
Mn^{2+}	8 mg
Mg^{2+}, W^{6+}	7 mg
Cr^{6+}	5 mg
V^{5+}	4 mg
Al^{3+}	3.5 mg[b)]
Sodium tartrate	2 mg
Sodium citrate	1.5 mg
$Na_2C_2O_4$, Hg^{2+}, Ag^+, Bi^{3+}	1 mg
KCN	700 μg
Fe^{3+}	500 μg
Co^{2+}	300 μg
Ni^{2+}	30 μg
Disodium EDTA	10 μg
Pd^{2+}	2 μg

a) pH: 5.8; 0.04% PPDT: 3.0 cm^3; 1% TPB: 2.0 cm^3; naphthalene: 0.7 g; 1 M CH_3COONH_4: 3.0 cm^3; 2% hydroxylammonium chloride: 2.0 cm^3. b) Extraction at pH 3.0.

ene carbonate are better solvents, but they are expensive and viscous. Acetonitrile may be used but the absorbance is rather low in this solvent. Hence *N,N*-dimethylformaide is preferable for dissolving the metal complex and naphthalene.

Calibration Curve. For the optimum conditions specified above, a calibration curve was constructed at 324.7 nm. It was found to be linear over the concentration range 2.5—80.0 μg of copper in 10 cm^3 of *N,N*-dimethylformamide solution. Ten repeat analyses on a sample solution containing 35 μg of copper gave a mean absorbance of 0.205 with a standard deviation of 0.0017 and a relative standard deviation of 0.83%.

Effect of Diverse Ions. Sample solutions containing 35 μg of copper and various amounts of different alkali metal salts or metal ions were prepared, and the determination of copper was carried out by the general procedure. Tolerance limits of diverse ions are given in Table 1. Naturally the method is fairly selective and may be applied to determination of copper in various complex materials.

Determination of Copper in Standard Reference Materials. A 0.05—0.5 g sample of alloy was completely dissolved in 20—30 cm^3 of hydrochroric acid (1+1) on a water bath. Then 3—5 cm^3 of 30% hydrogen peroxide were added to it. The excess of peroxide was decomposed by heating the solution on a water bath. The mixture was cooled and filtered through a filter paper. The filtrate was diluted to 500 cm^3 with distilled water in a flask. An appropriate volume of this solution was taken and the copper was determined by the general procedure. The results are given in Table 2.

Determination of Copper in Human Hair. A 10.0 g sample of human hair was taken and dissolved in 30 cm^3 of concentrated nitric acid and 3.0 cm^3 of concentrated perchloric acid by heating. This solution was cooled, filterd, and diluted to 200 cm^3 with distilled water in a standard flask. An aliquot of this solution was taken and the copper was determined by the general procedure. The results in Table 2 are in reasonable agreement with those obtained by the standard

Table 2. Analysis of copper in samples

Sample	Composition/%		Copper certified value/%	Copper content/%[a)]	
				Present method	DDTC-IBMK method
N.B.S., SRM-85b Aluminium alloy	Ni: 0.084, Mn: 0.61, Si: 0.18, Zn: 0.03, Pb: 0.021, V: 0.006,	Mg: 1.49 Cr: 0.21 Fe: 0.24 Ti: 0.022 Ga: 0.019	3.99	4.07±0.06	—
N.B.S., SRM-94c Die Casting alloy	Mn: 0.014, Sn: 0.006, Cd: 0.002, Pd: 0.006,	Ni: 0.006 Al: 4.13 Fe: 0.018 Mg: 0.042	1.01	0.983±0.013	—
Human hair (male)	—		—	0.00156±0.00004	0.00161±0.00002
Human hair (female)	—		—	0.00253±0.00003	0.00258±0.00003

a) Mean of 5 individual determinations.

DDTC–IBMK method.[15]

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