Catalytic Decomposition of the Excess Reagent in the Spectrophotometric Determination of Copper(II) with *o,o'*-Dihydroxyazo Compounds

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A simple and sensitive spectrophotometric method for determination of copper(II) is described. It is based on the reaction of copper(II) with Hydroxynaphthol Blue in the weakly alkaline medium and the decomposition of the unconsumed reagent which shows an intense absorption at the wavelength, 555 nm, of the maximum absorbance of the copper(II) complex. Beer's law is obeyed over the range 0.13—1.27 ppm copper with the molar absorption coefficient of $\varepsilon_{555}=3.01\times10^4$ dm^3 mol^{-1} cm^{-1} (Sandell's sensitivity 2.11×10^{-3} μg/cm^2). A fairly large number of common ions except for nickel(II) do not interfere.

Several *o,o'*-dihydroxyazo reagents have been employed in spectrophotometric determination of metal ions,[1] but in some cases the use of the azo reagent as a spectrophotometric reagent is prevented by similarity in absorption spectrum of the metal complex and the reagent itself. In addition, the color reaction is poor in selectivity. For improving the sensitivity and selectivity of the reaction, extraction of the complex anion formed between a sulfonated azo-dye and a metal ion as an ion-pair with a quaternary ammonium cation has been investigated[2] and applied to the spectrophotometric determination of aluminium,[3] magnesium,[4] and rare earth elements.[5]

In the present paper, a new method for spectrophotometric determination of copper(II) with *o,o'*-dihydroxyazo compounds is described, in which the excess reagent and some of the colored chelates formed by interfering metal ions are decomposed by the use of the manganese(II)-catalysed discoloration reaction.[6,7] The reaction is also utilized in the catalymetric microdetermination of manganese(II) by Yamane and Fukasawa.[8]

Experimental

Reagents. Commercially available 1-(2-hydroxy-4-sulfo-1-naphthylazo)-2-naphthol-3,6-disulfonic acid, trisodium salt (Hydroxynaphthol Blue, abbreviated as HNB), 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonic acid, sodium salt (Eriochrome Black T), 1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulfonic acid, sodium salt (Calcon) and 1-(2-hydroxy-5-methylphenylazo)-2-naphthol-4-sulfonic acid (Calmagite) were obtained from Dojindo Laboratories Ltd. and used without further purification. The purity of the reagents was checked by the method described below. The solution was daily prepared by dissolving the reagent in water and concentration was corrected.

A 0.01 mol dm^{-3} standard solution of copper(II) was prepared from its sulfate and standardized by the method of the conventional chelatometric titration.

A mixture of 3 (w/w)% hydrogen peroxide and 0.2 mmol·dm^{-3} manganese(II) was freshly prepared before use by mixing the appropriate amounts of 30 (w/w)% hydrogen peroxide and 0.01 mol dm^{-3} manganese(II) chloride solutions and diluting with water.

Sörensen's buffer solution (pH 8.0—11.0), Kolthoff's buffer solution (pH 6.0—7.4) and deionized water were used.

All the chemicals except for the azo reagents used were of analytical grade.

Apparatus. A Hitachi two-wavelength and double-beam spectrophotometer 356 and a Shimadzu spectrophotometer, Model QV-50, with 10-mm glass cells were used for spectrophotometric measurements. A Hitachi-Horiba glass electrode pH-meter, Model F-5, was used for pH measurements.

The Purity of Azo Reagents. The purity of the reagent was evaluated by applying the familiar mole-ratio method to the copper(II)–dye system, where excess reagent is decomposed in the similar manner as described below. After correcting the reagent concentration, a continuous variation method was applied to the calcium(II)- or magnesium(II)-dye system to check the estimated value of the purity. It was found that the molar ratio of the dye to the metal ion is 1:1, in accordance with the results reported by several authors.[9,10] The purity was found to be *ca.* 40% for HNB, 46.5% for Eriochrome Black T, 64% for Calmagite and 45% for Calcon, and the concentration of the reagent was therefore corrected in a suitable manner.

Procedure. In a 50-cm^3 volumetric flask are taken an appropriate volume up to 20 cm^3 of the solution containing less than 63.6 μg of copper(II), 5 cm^3 of 0.4 mmol dm^{-3} HNB solution and 20 cm^3 of the buffer solution (pH 10). The solution is mixed well. After addition of 2 cm^3 of a 3% hydrogen peroxide-0.2 mmol dm^{-3} manganese(II) solution, the mixture is diluted with water to the volume and allowed to stand for 15 min. The absorbance of the solution is measured at 555 nm against water.

The similar procedure is available for preparing the calibration graph with other dyes.

Results and Discussion

Absorption Spectra. The absorption spectra of HNB and its copper(II) complex are shown in Fig. 1. On adding hydrogen peroxide and manganese(II) after the full development of color of copper(II)-HNB complex, the HNB present in excess is rapidly decomposed by the catalytic effect of manganese(II), whereas the red-purple copper(II)-HNB complex, the absorption maximum being 555 nm, remains stable. The addition of hydrogen peroxide alone is not effective for the discoloration of the HNB solution. After standing the solution for 15 min, only approx. 5% decrease in absorbance is observed. Of the azo-dyes used, the decomposition rate of HNB is most rapid and the absorbance of the resulting solution at the wavelength of the maximum absorption of the copper(II) complex is the lowest.

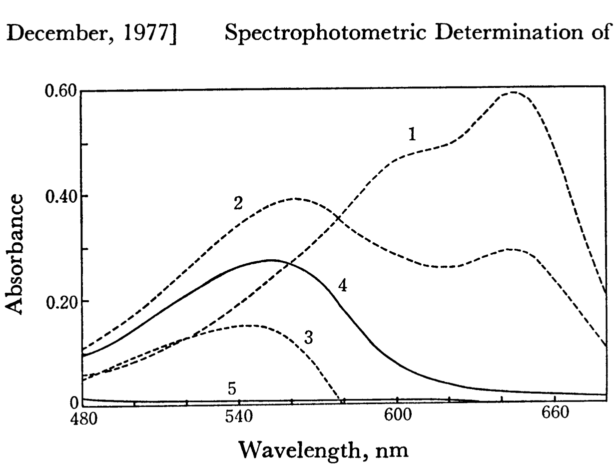

Fig. 1. Absorption spectra of copper-(II)HNB complex and HNB at pH 9.1 in the presence (——) and absence (------) of 0.12% hydrogen peroxide and 4 μmol dm^{-3} manganese (II).
1: HNB 20 μmol dm^{-3}. 2: Cu(II) 10 μmol dm^{-3}, HNB 20 μmol dm^{-3}. 3: Cu(II)-HNB complex measured against the reagent blank solution. 4: Cu(II) 10 μmol·dm^{-3}, HNB 20 μmol dm^{-3}, after decomposition of excess reagent by H_2O_2 and Mn(II). 5: The reagent blank solution corresponding to 4. The measurements were carried out after standing for 15 min.

Effect of pH. The extent of the decomposition of azo reagents is dependent on the pH of solution as shown in Fig. 2. In the pH range from 9.3 to 10.5, the reagents are almost completely decomposed after standing the solution longer than 10 min. The absorbance of the copper(II) complexes is constant in the pH range where the decomposition is almost complete.

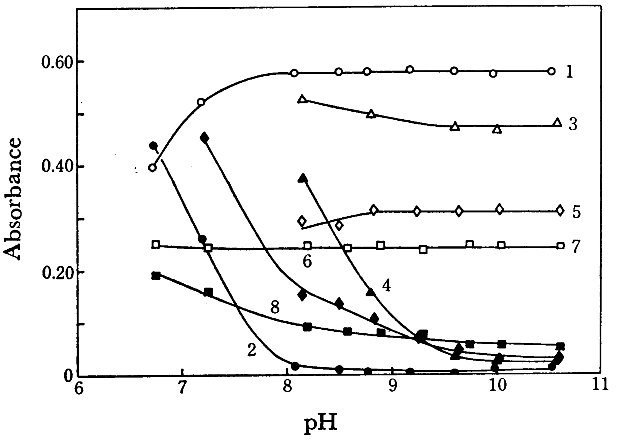

Fig. 2. Effect of pH on the absorbance of the copper(II) complexes and the reagent blank solutions after standing for 15 min in the presence of 0.12% hydrogen peroxide and 16 μmol dm^{-3} manganese (II).
1: HNB 40 μmol dm^{-3}, Cu(II) 20 μmol dm^{-3}, 555 nm. 2: The reagent blank solution corresponding to 1. 3: Calcon 44.5 μmol dm^{-3}, Cu(II) 20 μmol dm^{-3}, 545 nm. 4: The reagent blank solution corresponding to 3. 5: Eriochrome Black T 46.5 μmol dm^{-3}, Cu(II) 20 μmol dm^{-3}, 540 nm. 6: The reagent blank solution corresponding to 5. 7: Calmagite 64.5 μmol dm^{-3}, Cu(II) 12 μmol dm^{-3}, 530 nm. 8: The reagent blank solution corresponding to 7. The absorbance of the complexes was measured against the reagent blank solution.

Effect of Reagent Concentration. It was found that a small excess of the reagent more than the stoichiometrically necessary amount was sufficient to develop fully the color of the copper(II) complex with each dye except for Eriochrome Black T as shown in Fig. 3. The absorbance of the copper(II)–Eriochrome Black T complex was observed to increase notably with increasing concentration of the reagent more than the equivalent amount to copper(II). The composition of the complex formed between copper(II) and the azo-dye is estimated to be 1: 1 molar ratio for each copper(II)-dye system except for the Eriochrome Black T complex.

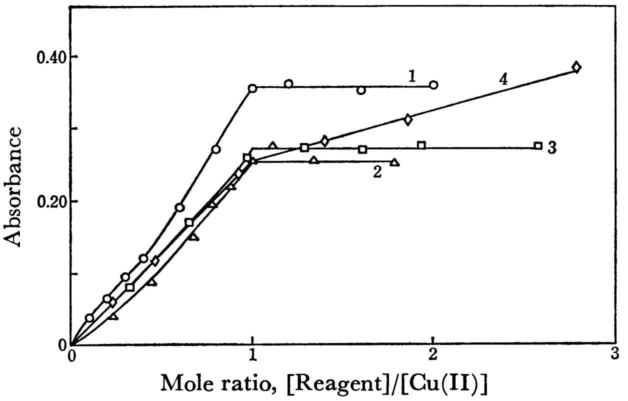

Fig. 3. Effect of the reagent concentration on the absorbance of copper(II) complex measured against water after standing for 15 min. Hydrogen peroxide 0.12%, manganese(II) 16 μmol dm^{-3}.
1: HNB, Cu(II) 12 μmol dm^{-3}, 555 nm, pH 9.1.
2: Calcon, Cu(II) 10 μmol dm^{-3}, 545 nm, pH 10.
3: Calmagite, Cu(II) 12 μmol dm^{-3}, 530 nm, pH 9.9.
4: Eriochrome Black T, Cu(II) 20 μmol dm^{-3}, 540 nm, pH 9.9.

Stability of Copper(II) Complex. The copper(II)–HNB complex after decomposing the excess reagent is sufficiently stable for practical use and the absorbance of the complex is constant at least for one hour as shown in Table 1. The addition of the hydrogen peroxide–manganese(II) solution more than 4 cm^3 is undesirable because the optical measurements are prevented by the occurrence of bubble which is adsorbed onto the wall of cell. The copper(II) complex with Calcon, Calmagite or Eriochrome Black T is somewhat unstable as compared with that of the HNB complex and the absorbance of the complexes at 12 μmol dm^{-3} copper(II) level decreases by 3—7% between 15 and 60 min.

Table 1. Stability of the copper(II)–HNB complex

Cu(II) taken μg/50 cm^3	Amount of {1.5% H_2O_2–0.2 mmol dm^{-3} $MnCl_2$} added cm^3	Absorbance at 555 nm *vs.* water after			
		15	30	45	60 min
19.0	1.0	0.174	0.173	0.173	0.172
	2.0	0.174	0.173	0.173	0.172
	4.0	0.176	0.176	0.175	0.175
38.1	1.0	0.349	0.349	0.349	0.349
	2.0	0.346	0.347	0.347	0.347
	4.0	0.350	0.350	0.350	0.350

HNB concentration 40 μmol dm^{-3}, pH 9.2.

Calibration Curve and Sensitivity. The copper(II)-HNB system conforms to Beer's law in the range of 0.13 to 1.27 ppm copper with the molar absorption coefficient of 3.01×10^4 dm^3 mol^{-1} cm^{-1} at 555 nm. The molar absorption coefficient of copper(II)-Calcon and -Calmagite system is 2.59×10^4 at 545 nm and 2.04×10^4 at 530 nm, respectively. The copper(II)-Eriochrome Black T system does not obey the Beer's law. The sensitivity of the HNB method is higher than those of cuprizone method (molar absorption coefficient 1.6×10^4),[1] zincon method (2.2×10^4),[11] *N*-[2-(2-pyridylmethyleneamino)ethyl]-*N*-(2-aminoethyl)dithiocarbamic acid method (1.75×10^4),[12] Calcichrome method (8×10^3),[13] Xylenol Orange method (1.25×10^4)[14] and Sarcosine Cresol Red method (2.09×10^4),[15] but lower than those of tetraphenylporphine-trisulfate method (4.8×10^5),[16] Chromazurol S-zephiramine method (4.76×10^4)[17] and 2-bromo-4,5-dihydroxyazobenzene-4′-sulfonate-hexadecyltrimethylammonium chloride method (4.8×10^4).[18]

Effect of Foreign Ions. From the viewpoint of sensitivity and simplicity in the procedure, it seems that the HNB is most preferable among the four reagents examined in the present work. Therefore, the effect of diverse ions on the determination of copper(II) according to the above-mentioned HNB procedure was examined, as tabulated in Table 2. The cations were added as nitrates, chlorides or sulfates and anions as sodium, potassium or ammonium salts. The major interference arises from nickel(II) which reacts with HNB and produces an intense coloration. Magnesium(II), zinc(II), cadmium(II) and thorium(IV) form the similarly colored complexes, but these complexes, being unstable under the given conditions, decompose on the addition of hydrogen peroxide and manganese(II). Aluminium(III) at the 2-fold excess amount and iron(III) at the 4-fold excess amount over copper(II) are easily masked by adding a 20-fold excess amount of fluoride. The four-fold excess amount of cobalt(II) over copper(II) is masked by previously oxidizing it to cobalt(III) with hydrogen peroxide in ammoniacal buffer solution. In Table 3 are given the analytical results of copper(II) in the synthetic sample. Almost satisfactory results were obtained.

TABLE 2. EFFECT OF VARIOUS IONS

Ion added (X)	Amount μg	Copper(II) found μg	Error %	Tolerance limit X: Cu(II)
Al(III)	32	38.5	+20.3	interfere
	64	32.3[a]	+1.0	2
Ba(II)	3200	31.7	−0.9	100
Bi(III)	160	32.2	+0.6	5
Ca(II)	3200	32.1	+0.3	100
Cd(II)	960	32.6[b]	+1.9	30
Cr(III)	160	32.4	+1.3	5
Co(II)	32	62.0	+93.8	interfere
	128	32.3[c]	+0.9	4
Fe(III)	160	26.8	−16.3	interfere
	128	32.7[a]	+2.2	4
Mg(II)	3200	31.9	−0.3	100
Mn(II)	64	32.4	+1.3	2
Mo(VI)	960	31.8	−0.6	30
Ni(II)	32	54.5	+70.3	interfere
Pb(II)	320	32.4	+1.3	10
Sr(II)	1600	32.4	+1.3	50
Th(IV)	1600	33.0	+3.1	50
V(V)	64	38.1	+19.1	interfere
	320	32.8[d]	+2.5	10
Zn(II)	640	32.9	+2.8	20
Br$^-$	3200	31.8	−0.6	100
Cl$^-$	3200	32.0	0	100
F$^-$	320	31.1	−2.8	10
PO_4^{3-}	3200	32.3	+0.9	100

Copper(II) taken: 32.0 μg. Each results are the mean of three separate analyses. a) With 1.2 mg of NH_4F. b) With 80 μmol dm^{-3} of HNB. c) With 3 cm^3 of 3% H_2O_2 in ammoniacal buffer solution. d) With 3 cm^3 of 3% H_2O_2, measured after 40 min.

TABLE 3. THE ANALYTICAL RESULTS OF COPPER(II) IN A SYNTHETIC SAMPLE[a]

Copper(II) taken μg/50 cm^3	Copper(II) found[b] μg/50 cm^3	Error %	Relative standard deviation %	Number of determinations
16.0	15.9[c]	−0.6	2.5	4
	16.4	+2.5	3.2	4
32.0	31.6[c]	−1.2	1.5	4
	32.1	+0.3	2.0	4
48.0	47.2[c]	−1.7	1.5	4
	47.1	−1.9	1.0	4

a) Amount of foreign ions: Al(III) 16, Cd(II) 1.6, Cr(III) 3.5, Fe(III) 9.6, Pb(II) 2.2, Mn(II) 1.6, Zn(II) 20.8 μg in 50 cm^3. b) With 624 μg NH_4F. c) Without foreign ions.

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