A New Sensitive Reagent for the Spectrophotometric Determination of Copper

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A New Sensitive Reagent for the Spectrophotometric Determination of Copper[1]

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Abstract. N,N'-bis(β-1-piperazylethyl) dithiooxamide forms soluble, colored chelates with a number of the transition metal ions. This reagent might have several advantages over other substituted dithiooxamides, since both it and the chelates are water soluble. In solution the reagent acts as a dihydroxy base, deriving its basicity from the presence of the substituent piperazine rings. Potentiometric titration with hydrochloric acid yielded $K_1 = 1.70 \times 10^{-5}$ and $K_2 = 1.14 \times 10^{-5}$ for the two basic dissociation constants. In the presence of copper (II) ion this reagent forms two chelate species which were determined absorptimetrically to have the compositions Cu_2R and CuR. The latter complex, containing the metal ion and the ligand in equimolar quantities, is suitable for use in the spectrophotometric determination of copper at concentrations as low as 0.05 mg per liter. Formed under conditions of an excess of reagent in ammoniacal solution, this complex exhibits a molar absorptivity of about 18,000 at its wave length of maximum absorption. Although the reagent is not specific for copper, the simplicity of the method and its high sensitivity recommend its use in the determination of copper.

N.N'-bis(β-1-piperazylethyl) dithiooxamide $(Pz)_2DTO$, having the formula

$$\left[\underset{\text{C-NH-CH}_2\text{-CH}_2\text{-N}}{\overset{\overset{\text{S}}{\|}}{}} \, \overset{\text{CH}_2\text{-CH}_2}{\underset{\text{CH}_2\text{-CH}_2}{\diagup \diagdown}} \text{NH} \right]_2$$
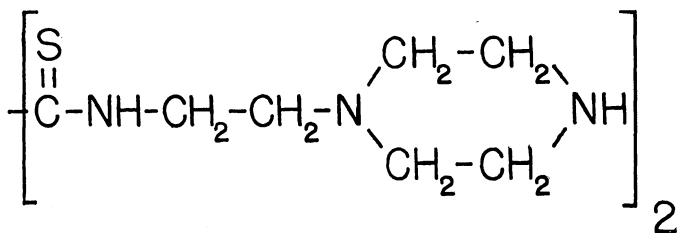
is a polyfunctional, amine-substituted thioamide which forms highly colored metal chelates with copper, cobalt, and nickel. Unlike others of the family of substituted dithiooxamides (1), however, $(Pz)_2DTO$ and its chelates with the metal ions listed above are water soluble. The purpose of this paper is to introduce the reagent and to demonstrate its applicability in the spectrophotometric determination of copper.

Experimental

A standard copper (II) solution was prepared from copper metal of known high purity.

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The (Pz)₂DTO reagent was prepared according to the general method of preparing N,N'disubstituted dithiooxamides given by Wallach (2). Slightly over two-tenths of a mole of N-(β-amino-ethyl)piperazine and one-tenth of a mole of dithiooxamide were suspended in 200 ml ethanol. The mixture was stirred and heated on a steam bath for about one hour. The reaction mixture first became a clear, dark red solution as the dithiooxamide dissolved; on further stirring and heating the solution changed from red to brown, and yellow crystals appeared on the upper walls of the flask. On cooling, the entire mixture became a solid mass of yellow crystals. The compound was then redissolved in ethanol, filtered with Norite, and again cooled. Purification was affected by recrystalization from benzene and petroleum ether on one occasion and from acetonitrile on another; the latter solvent seemed to yield a product of higher purity.
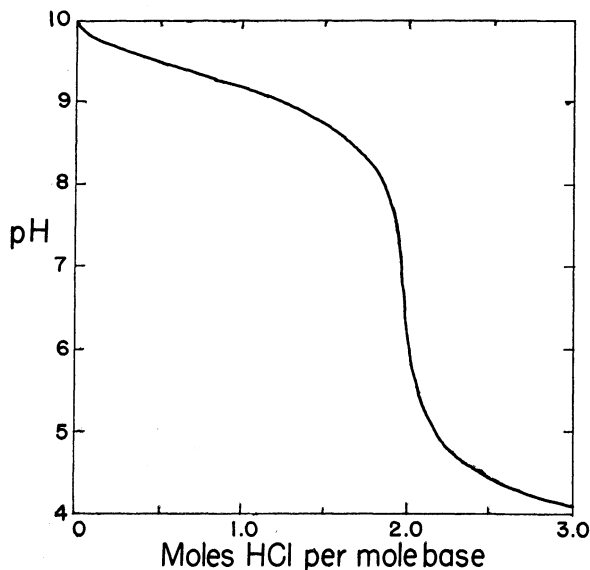

Figure 1.   Titration of .01 M (Pz)₂DTO with .01 M HCl.

Titrations were performed in aqueous medium under a nitrogen atmosphere to exclude carbon dioxide; a Beckman model G pH-meter was used to follow the course of the titrations. Absorption spectra were obtained with a Cary Model 11 recording spectrophotometer. All other absorbancy measurements were made using a B. and L. Spectronic 20 grating spectrophotometer.

Chemical separations of the various mixtures of transition metal ions were accomplished by the anion exchange method of Kraus (3). The column employed contained 7 ml of Dowex

1-X8 (50-100 mesh) in the chloride form. Flow rate for the separations was maintained at 0.5 ml per minute by adjustment of the stopcock.

Reagent

When titrated with hydrochloric acid $(Pz)_2DTO$ yields a simple S-shaped neutralization curve (Figure 1) with a sharp end point break even in dilute solution. Only one break is observed, with the end point occuring at a pH of approximately 6.3; this corresponds to two equivalents of acid added per mole of reagent. The protonation constants, corresponding to the reactions

$$B + H^+ = BH^+ \quad \text{for which}$$

$$K_1 = \frac{(BH^+)}{(B)\,(H^+)}, \text{ and}$$

$$BH^+ + H^+ = BH_2^{+2} \quad \text{for which}$$
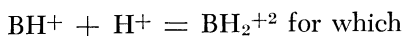
$$K_2 = \frac{(BH_2^{+2})}{(BH^+)\,(H^+)}$$

may be calculated from the data obtained from a titration curve such as that shown in Figure 1. In the above equations B represents the base, $(Pz)_2DTO$. The equation from which the constants were calculated is as follows:

$$\frac{-a}{(C_s+a)\,(H^+)} = \frac{K_1K_2(2C_s+a)\,(H^+) + K_1}{(C_s+a)}$$

In this equation C_s is the stoichiometric molar concentration of the base and a represents the quantity $[(H^+) - (OH^-) - (Cl^-)]$. Using concentration and pH data from a number of points along the neutralization curve, a graphical solution to the equation was employed to obtain the values of the two constants. By this method one obtains $K_1 = 1.70 \times 10^9$ and $K_2 = 1.14 \times 10^9$. Although these protons are not the ones involved in the formation of the chelates, they are useful in determining the ionic form of the reagent which does take part in the chelation.

The basicity of $(Pz)_2DTO$ may be more easily visualized by assuming that in aqueous solution it behaves much the same as a solution of ammonia. In this light the reactions previously discussed may be considered to be the stepwise dissociation of a di-hydroxy base. The constants for these dissociations are then obtained as follows:

$$KB_1 = K_1 \cdot Kw = 1.70 \times 10^{-5} \text{ and}$$
$$KB_2 = K_2 \cdot Kw = 1.14 \times 10^{-5}.$$

In basic solution thioamides undergo hydrolysis which results in an irreversible decomposition of the compound (4). In this respect $(Pz)_2DTO$ is no different, and due to the basic character of the substituent piperazine groups, solutions of this reagent are not stable from one day to the next. For this reason, fresh reagent solutions were prepared daily in quantities sufficient for that day's work.
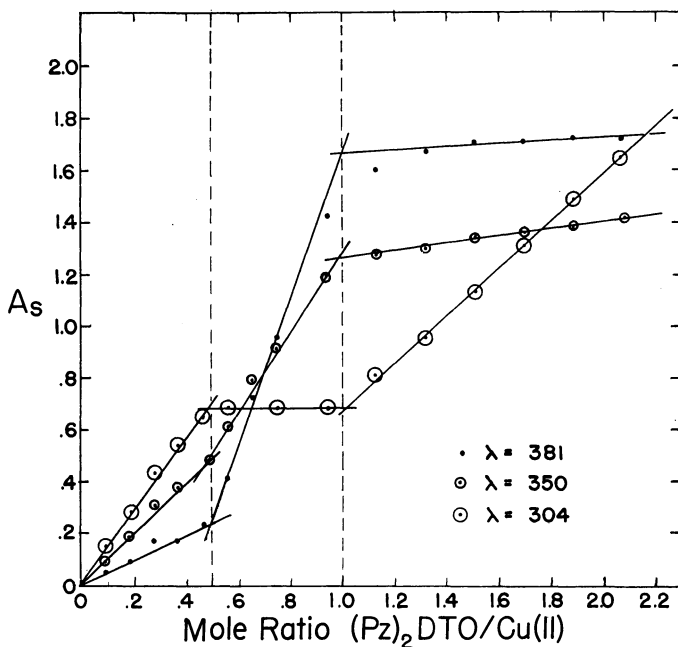

Figure. 2.   Mole ratio plot for the copper (II)-$(Pz)_2$DTO system.

Composition of the Chelate

In basic solution $(Pz)_2DTO$ forms two species of chelates with copper (II). Figure 2 shows the plots of data obtained from a mole ratio study of this system at three selected wavelengths. Inspection of these graphs indicates that two species are of compositions represented by the mole ratios 0.5:1 and 1:1, ligand to copper (II) ion. The first of these containing copper (II) and the ligand in a 2:1 mole ratio appears in those solutions containing an excess of the metal ion and exhibits a yellowish-brown hue. The other species, having a deep green hue, is observed in those solutions with the ligand in excess. The absorption maxima of these chelates occur at 315 mμ and 381 mμ, respectively. The green complex begins to precipitate from solution at times varying from one to four hours after mixing, depending on the total ionic concentration of the solu-

tion. The brown form, however, has never been observed to precipitate. Extensive attempts to separate the brown complex by extraction and by precipitation were unsuccessful. Ion migration studies of solutions of the two species under applied potential difference indicate that the green (1:1) species is neutral and the brown (0.5:1) species is positively charged.

Chemical analysis of a sample of the green chelate confirms the composition of this species as a 1:1 molar ratio of ligand to copper (II). Gravimetric determination of the copper in the precipitated solid yields a result of 15.25% Cu; the calculated value, on the basis of $Cu(C_{19}H_{26}N_6S_2)$ is 15.15%.

The conditions necessary for the formation of the two chelates of the copper (II) − (Pz)₂DTO system are such that either one can be prepared in the absence of the other. As it is the green (1:1) complex that is of analytical interest, the remainder of this paper will be devoted to that species.

For the formation of the 1:1 Cu (II) − (Pz)₂DTO chelate, it is necessary that the concentration of ligand be in excess of the copper (II) concentration and that the solution be sufficiently basic. Figure 2 shows that a molar ratio of 2 ligands per copper (II) ion is sufficient for the complete formation of the 1:1 chelate. In these solutions the absorbancy of the chelate is not significantly sensitive to pH in the vicinity of 8.8 to 10, but in this work the solutions were maintained between the limits of pH 9 and 9.6. In practice this may be accomplished either by the use of a buffer or, if the solutions are initially acidic, by the addition of ammonium hydroxide. The full color of the chelate is slow to develop, generally requiring ten to fifteen minutes to attain maximum absorbancy. Once the color is developed, however, it is then stable until precipitation begins. Under the conditions stated, this chelate exhibits a molar absorptivity of about 18,000.

Interferences

Interferences may be generally divided into two types: those which give color reactions with the ligand, and those which form precipitates under the conditions utilized. The first group includes nickel (II), cobalt (II), and copper (I). Among the second group are those which form hydroxide precipitates in ammoniacal solution; of the commoner metals this may include iron, mercury, lead, aluminum, and manganese. Zinc, cadmium, and silver ions react with the reagent to form complexes which have a tendency to precipitate. The nature of these complexes was not investigated. In addition to the above, colored ions, such as chromate, and complexing ions, such as cyanide which destroys the chelate, should not be present in the solution.
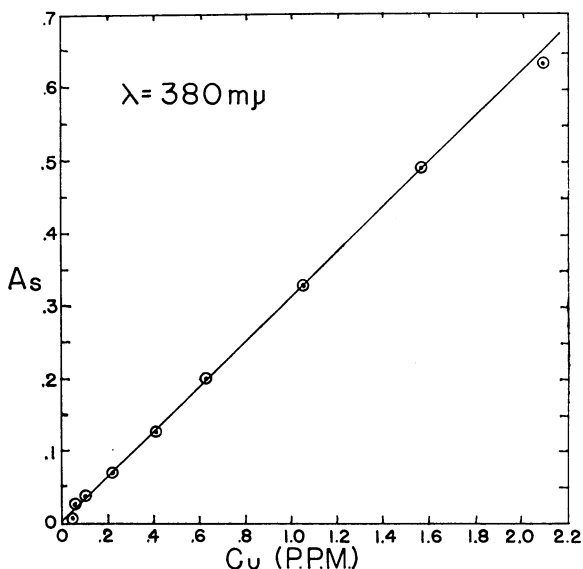
Figure 3. Calibration curve for the determination of copper (II) with (Pz)₂DTO.

Recommended Procedure

The following method for the determination of copper with (Pz)₂DTO is proposed as the result of this investigation.

Preliminary treatment of the sample to yield a solution of copper (II) ion free from the previously mentioned interferences may be carried out by any of the standard methods or by the ion exchange method of Kraus (3). To the sample in a volumetric flask of suitable size, such that when diluted to mark the solution will contain copper at a concentration level between 0.05 and 2.0 ppm, ammonium hydroxide is added to adjust the pH to about 9 as indicated by test papers. Alternatively an ammonia-ammonium chloride buffer may be used. Four milliliters of the reagent solution, containing 0.02g (Pz)₂DTO per 100 ml, are added and the solution diluted to mark with deionized water. The absorbancy of the solution should be determined at 380 mμ not less than 10 minutes nor more than one hour after mixing. Absorbancy measurements should be made using a reagent blank in the reference cell, due to the slight interference of the reagent at this wavelength. The calibration curve shown in Figure 3 was prepared as follows: Portions of a copper (II) solution containing 0.01042 mg Cu per ml were placed in 50-ml volumetric flasks so that the final copper ion concentration would vary between .0521 and 2.082 ppm. To each flask, 2 ml of 14 M ammonium hydroxide and 8 ml of a

(Pz)$_2$DTO solution containing 0.010 g reagent in 100 ml deionized water were added. The solutions were diluted to volume with deionized water, mixed thoroughly, and allowed to stand 15 minutes before the absorbancies were determined. All solutions were compared to a reagent blank containing only the reagent and ammonia.

RESULTS AND DISCUSSION

Table 1 shows the results of a number of determinations of copper (II) with (Pz)$_2$DTO. The first five series reported are averages of two or more trials on samples containing copper only. Samples 1 and 2 contain the same amount of the metal ion, but in different volumes. By reducing the volume, a considerable improvement in accuracy was effected. A similar improvement might have been realized by the use of cells with a longer light path. However, it should be noted that in the spectrophotometric determination of microgram quantities of copper, results like those for sample 1 are not unrealistic. Samples 6 and 7 consist of the copper (II) fractions of synthetic mixtures previously separated on an anion exchange column.

Table 1. Results of determinations.

| | mg Cu | | | Error | |
	Taken	Found	Separated From	Mg	Percent
(1)	.00313	.0040	. . . .	+.0009	22.8
(2)	.00313	.00305	. . . .	-.00008	2.55*
(3)	.01042	.0106	. . . .	+.0002	1.73
(4)	.05210	.0525	. . . .	+.0002	0.77
(5)	.0783	.0779	. . . .	-.0004	0.51
(6)	.0521	.0518	.05 mg each Fe Co Ni	-.0003	0.58
(7)	.0521	.0529	.50 mg each Fe Co Ni	+.0008	1.54

* 10 ml volume; all others 50 ml.

The data indicate that satisfactory determinations of copper with very low concentrations may be carried out with this reagent. The disadvantages of the method, i.e., instability of reagent solutions, lack of selectivity, and large number of interferences, have been discussed. On the other hand, the high sensitivity of the reagent toward copper (II) ion does recommend its use in situations where the need for such sensitivity outweighs the difficulties inherent in separatory procedures. Then, too, in the absence of interfering ions the recommended procedure provides an extremely simple and rapid method for the determination of trace amounts of copper.

The determinations of cobalt (II) and nickel (II) ions are also feasible with (Pz)$_2$DTO under conditions similar to those

employed in the method for copper (II). In the author's quantitative analysis course, this reagent is being utilized for the colorimetric determination of nickel (II) following an ion exchange separation.

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