Some Analytical Uses of 3-Dimethylaminopropylamine[1]

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The determination of copper based on the production of the blue color of the copper-ammonia complex is among the oldest of all colorimetric methods. This procedure has been investigated extensively by Mehlig (2, 3), Yoe and Barton (4) and Yoe and Crumpler (5). The principal disadvantages of ammonia are its odor and volatility and the dependence of the color on the ammonia concentration (2, 4).

A number of reagents of moderate sensitivity have been suggested as substitutes for ammonia, among them being triethanolamine (4) and tetraethylenepentamine (1). These reagents are two to three and one-half times as sensitive as ammonia, are less volatile, and produce a color that is independent of the amount of amine in excess.

The possibility of using 3-dimethylaminopropylamine (N,N-dimethyl-1,3-propanediamine) as a colorimetric reagent for copper has been investigated as a portion of the study of metal chelate compounds.

Experimental

A Beckman Model DU spectrophotometer was used for all absorption measurements in this investigation. Matched cells of 1.00 cm. path length were employed.

Reagent or c.p. grade salts were used for the preparation of stock solutions. The copper (II) solution was standardized by electrodeposition and the nickel (II) solution by gravimetric determination with dimethylglyoxime.

Titration indicated a purity of 99.5% for the 3-dimethylaminopropylamine, Matheson No. 7148. Stock solutions were prepared by dissolving weighed portions of the amine.

In most instances precipitation of the hydroxide occurred upon addition of the amine to the solution of a metal ion. All solutions were therefore made 2.5 M in ammonium nitrate as a buffering agent.

The color of the solutions is stable for at least three weeks.

Effect of Excess Reagent

The optical densities of solutions in which the concentration of 3-dimethylaminopropylamine is increased with the copper (II) ion concentration fixed at 50 p.p.m. and at 200 p.p.m. show that color development is independent of excess amine at high concentrations. A plateau in the curve just before complete color development similar to that observed by Crumpler with tetraethylenepentamine and copper (II) ion was noted (1).

Conformity to Beer's Law

Conformity to Beer's law by the color system is shown by the fact that a straight line resulted when the optical densities at 595 mμ for

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twelve solutions containing from 0 to 2500 p.p.m. of copper (II) ion were plotted against the respective concentrations.

Sensitivity of Color Reaction

A comparison of the sensitivities of a number of amines was reported by Crumpler (1). The specific extinction values [Extinction per centimeter per p.p.m. of copper (II) ion] at the wave length of maximum absorption are 0.00065 for ammonia, 0.0011 for triethanolamine and 0.0022 for tetraethylenepentamine. The corresponding calculations for 3-dimethylaminopropylamine give a specific extinction of 0.00084. It is seen that 3-dimethylaminopropylamine is approximately 1.3 times as sensitive as ammonia.

Use in Colorimetry

To prepare 50 ml. portions of colored solutions of the 3-dimethylaminopropylamine copper (II) ion with copper concentrations of 0 to 600 p.p.m., 10 ml. of 2% amine solution and 10 g. of ammonium nitrate should be used. For concentrations above 600 p.p.m. a greater amount of amine is necessary, about 1 ml. of 2% solution for each increment of 100 p.p.m.

The ions which interfere with this amine are those that interfere with ammonia (2). Nickel (II) ions have a greater effect than cobalt (II) ions, the reverse of their effect on the ammonia method.

Colored ions are formed by 3-dimethylaminopropylamine with nickel and cobalt ions, but the color intensity is low and therefore not promising for colorimetric purposes.

Summary

Copper may be determined colorimetrically by the use of 3-dimethylaminopropylamine provided a sufficient excess of reagent is used and ammonium nitrate is present in constant amounts to prevent precipitation of copper (II) hydroxide.

The ions which interfere with ammonia also interfere with this amine.

Literature Cited

1. CRUMPLER, T. B. 1947. Tetraethylenepentamine as a colorimetric reagent for copper. Anal. Chem. **19**:325.
2. MEHLIG, J. P. 1941. Colorimetric determination of copper with ammonia. Ind. Eng. Chem., Anal. Ed. **13**:533.
3. MEHLIG, J. P. 1942. Stability of the cupric-ammonia color system. Ind. Eng. Chem., Anal. Ed. **14**:903.
4. YOE, J. H., and C. J. BARTON. 1940. Colorimetric determination of copper with triethanolamine. Ind. Eng. Chem., Anal. Ed. **12**:456.
5. YOE, J. H., and T. B. CRUMPLER. 1935. A photoelectric colorimeter. Ind. Eng. Chem., Anal. Ed. **7**:281.