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Compounds of cobalt and dimethylglyoxime were first prepared by Tschugaeff during the course of his classical researches on the α-dioximes (1). The simplest of these compounds corresponded to the formula $[Co(NH_3)_2(DH_2)_2] X_2$, $DH_2$ representing a molecule of dimethylglyoxime and X a univalent anion. Tschugaeff prepared other compounds in which one or more of the ammonia groups were replaced by aniline or pyridine.

Braley and Hobart (2) found this reaction of cobalt, dimethylglyoxime and ammonia to be a sensitive qualitative test for cobalt but their further efforts to use the reaction for the quantitative estimation of cobalt were only moderately successful. Later Chiarottino (3) found that when benzidine was used as the base a more intense color was developed in neutral solution and the test was adapted by Scott (4) to the qualitative analysis scheme. Other bases, particularly tolidine and anisidine, can be used in place of benzidine (5).

Assuming that conditions can be found to insure their stability, the intense colors of these compounds indicate the possibility of converting this general reaction into a sensitive quantitative method for small amounts of cobalt. Nickel and iron, of course, would be expected (6) to interfere, the former by forming a precipitate with dimethylglyoxime and the latter by the pink color the reagent gives with ferrous iron. None of the known colorimetric methods for cobalt are free from interference by nickel and iron, however, and the excellent separation of iron from nickel achieved by Jones by the use of cyanide and ammonia (7) and the apparent possibility of extending it to the separation of cobalt from iron offered a possible solution at least to the interference from iron.

Selection of Organic Amine. Preliminary experiments were carried out to determine which of some twenty amines available was most suitable for the cobalt-dimethylglyoxime-amine reaction. These tests were made in neutral and in acid solution. The aliphatic amines gave little or no color. The aromatic amines gave deeper colors, and of these, the best were those having another functional group, amino-, hydroxyl-, or methoxyl-, ortho or para to the amino group.

On the basis of this, o-phenylenediamine, which yields a dark red color, was selected for the initial investigation. After considerable

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work, however, it was abandoned because conditions could not be found under which the color was either stable or reproducible.

The orange-red color with benzidine was nearly as deep as that with o-phenylenediamine. The color was found to be stable and was investigated in detail.

The Cobalt-Dimethylglyoxime-Benzidine Color. The effect of pH on the color was first studied. A series of solutions was prepared, each solution containing 5.0 ml. of a freshly prepared 0.5 per cent solution of benzidine, 4.0 ml. of a 1 per cent solution of dimethylglyoxime, and 1.00 ml. of 0.0100 M cobalt chloride. The pH was adjusted by the addition of acetic acid and sodium hydroxide and the solutions diluted to exactly 100 ml. The transmittancy of these solutions was measured using a Coleman Double Monochromator spectrophotometer. The transmittance was found to be a minimum and to be constant over the range of pH from 4.8 to 7.0. At lower and higher pH values the transmittancy increased appreciably. If the cobalt solution added was nearly neutral, a satisfactory buffer combination consisted of 10 ml. of 0.6 N acetic acid and 5 ml. of saturated sodium acetate; this gave a solution of pH about 5.2.
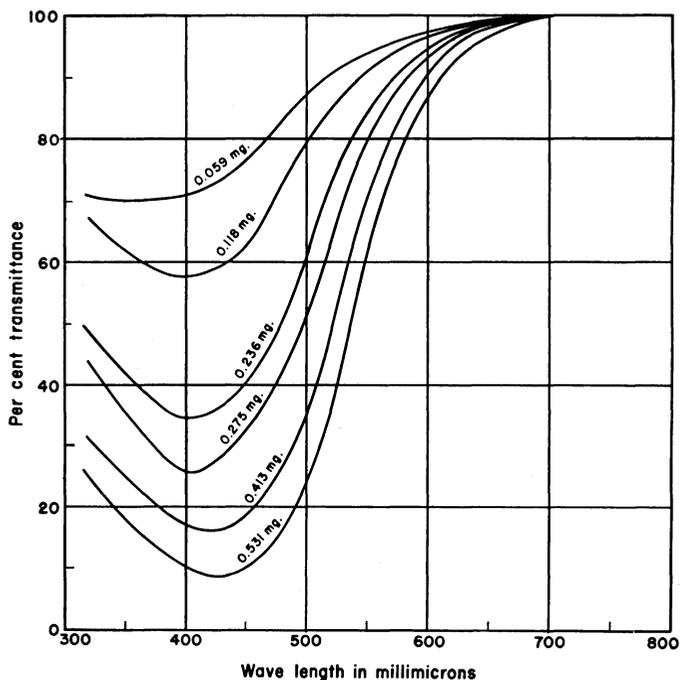


Figure 1.   Spectral Distribution Curves of Cobalt-Dimethylglyoxime-Benzidine at Various Concentrations.  Milligrams per 100 ml.

The spectral transmission curves of solutions prepared as described above but containing various amounts of cobalt was determined. The resulting curves are shown in Figure 1. The range of cobalt over which the method is applicable is from 0.02 mg. to 0.50 mg. per 100 ml. Time must be allowed for the color to develop. If the solution of the cobalt is fairly concentrated and is added directly to the reagents and the buffer before dilution, the color develops almost immediately. If, however, the reagents or the cobalt solution is diluted, the development of the color may take two to three hours. The final concentration also effects the time of development. The more dilute solutions (0.05 to 0.1 mg. in 100 ml. of final solution) were completely developed in 15 to 30 minutes even when the reagents were diluted before adding the cobalt solution. Those solutions in the neighborhood of 0.2 to 0.3 mg. of cobalt in 100 ml. of the final solution took from 2 to 4 hours if the reagents were diluted before addition of the cobalt solution.

The color was found to conform to Beer's Law. Figure 2 shows a plot of the log of the transmittancy versus concentration at 450 mμ.

Interfering Materials. Iron in any concentration interferes. At a pH of 5, the optimum for the formation of the color, iron forms a
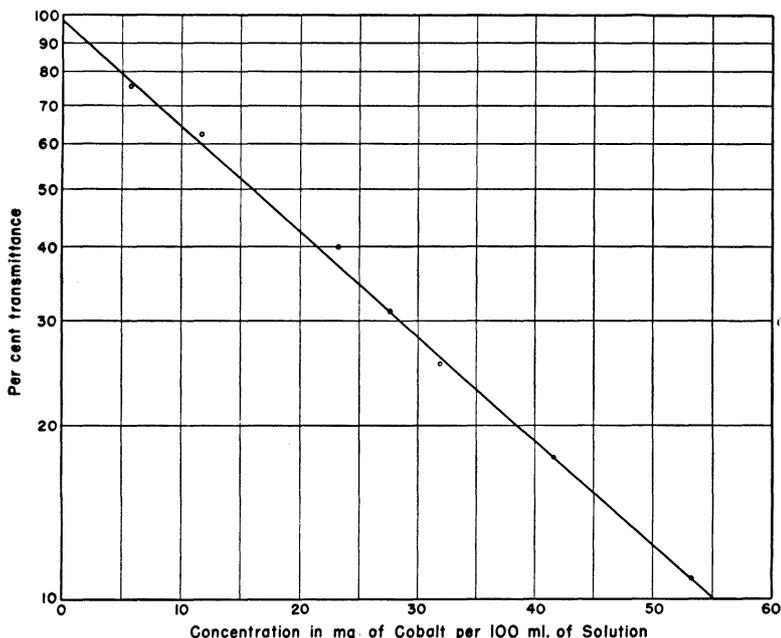


Figure 2.   Beer's Law Plot of Cobalt-Dimethylglyoxime-Benzidine.  450 mμ.

dark red compound with dimethylglyoxime which has strong absorption in the region of 450 mµ.

Copper interferes if present in amounts greater than 0.1 to 0.2 mg. of the metal by simply adding color to the solution.

Nickel does not interfere if present in amounts that remain in solution. If more than 0.8 mg. of nickel are present, a precipitate of nickel dimethylglyoxime forms when the solution is allowed to stand. This precipitate can be filtered off and the transmittancy of the filtrate measured.

Less than 2 mg. of manganese in the solution does not interfere, but with greater amounts, a precipitate forms on standing; this appears to adsorb some of the color so that a satisfactory measurement cannot be made on the filtrate.

Small amounts of trivalent chromium do not interfere, but if present to more than a few mg. adds to the color sufficiently to interfere.

Magnesium and zinc do not interfere.

Of the anions, chloride, bromide, and nitrate do not interfere, but sulfate must be absent as it yields a precipitate with benzidine.

Phosphate and oxalate prevent the formation of the color of cobalt with dimethylglyoxime and benzidine although they have no effect if added after the color has once formed. Phosphate cannot for this reason be used to eliminate the interference of iron by the formation of the colorless ferric phosphate complex.

The perchlorate and fluoride ions greatly decrease the color and must be absent. Cyanide also forms a more stable complex ion with cobalt and must be absent.

The Cyanide Separation of Cobalt from Iron. Because of the serious nature of the interference of iron with this colorimetric method for cobalt, attention was devoted to the separation of cobalt from iron by the cyanide method devised by Jones (7). This procedure involves the dropwise addition of dilute ammonium hydroxide (1:1) to the solution containing iron and cobalt in a 250 ml. volumetric flask to the point where a permanent precipitate just fails to form. To this solution is then added 2 to 5 ml. of a one per cent solution of potassium cyanide. The cobalt cyanide first formed dissolves in excess of cyanide to form the complex cobaltocyanide ion, $K_2Co(CN)_4$. The cobaltocyanide ion is a strong reducing agent and is rapidly oxidized by air or other oxidizing agent to the cobalticyanide ion, $K_3Co(CN)_6$. The iron is then precipitated by the addition of 10 ml. of dilute ammonium hydroxide (1:1) and the solution is diluted to a definite volume. The solution de-

canted through a base paper and an aliquot pipeted for analysis. In this process cobalt, copper and nickel are present in solution in the form of complex ions which are not coprecipitated with ferric hydroxide.

It appears certain that this process gives a satisfactory separation of cobalt from iron but unfortunately the cobalticyanide ion is so very stable that it precludes the formation of the color with dimethylglyoxime and benzidine. The problem then became one of finding a way to decompose the cobalticyanide ion and obtain the cobalt in a form in which it would give the color with the reagents. The first attempt to destroy the cobalticyanide ion was made by evaporating a solution of the cobalticyanide with perchloric acid. This was not satisfactory, however, because of the interference of the perchlorate ion mentioned previously. Direct treatment with nitric acid, aqua regia, hydrogen peroxide, potassium permanganate, sodium hypochlorite or potassium periodate did not destroy the complex and leave the cobalt in form suitable for the determination. Numerous attempts to destroy the cobalticyanide ion by reduction in acid solution and subsequent oxidation of the cyanide formed were also unsatisfactory. Metallic aluminum and zinc and hydroxylamine were used as the reducing agents. These were followed by treatment with nitric acid and other oxidizing agents. None of the procedures tried, however, proved satisfactory, the final color being equivalent to only about half of the cobalt actually present. From the results obtained on solutions containing iron and cobalt and containing cobalt alone, it seemed certain that the method used actually gave a complete separation and that the difficulty lay in the stability of the cobalticyanide ion or the interference in the color reaction of agents added to destroy this ion. This phase of the work was finally given up without finding an answer to the problem.

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