[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

A NEW METHOD FOR THE DETECTION AND ESTIMATION OF COBALT.

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Received December 6, 1920.

It was noted by one of us that when testing for nickel with dimethylglyoxime a brown solution always resulted when cobalt was present in the solution. This study was undertaken to determine whether this was a specific property of cobalt that might be used as a definite qualitative test and possible colorimetric quantitative method for estimating small amounts of the element.

Böttger[1] states that "cobalt salts give with dimethylglyoxime a brown colored compound." Treadwell-Hall[2] and Mellor[3] both state that when determining nickel with dimethylglyoxime not more than 0.1000 gram of cobalt should be present in 100 cc. of solution, but give no explanation.

Tschugaev[4] discusses complexes of cobalt and dimethylglyoxime with pyridine and ammonia and Matsui[5] gives a test for cobalt using dimethylglyoxime and ammonium polysulfide. In no case, however, is mention made that the brown color of cobalt dimethylglyoxime solution might be used as a qualitative test.

Materials.

Kahlbaum's cobalt and nickel carbonates ("nickel-free" and "cobalt-free," respectively) were carefully tested for impurities and used for all tests.

Experimental.

Qualitative Considerations.—It was first necessary to determine what metals give colored solutions with dimethylglyoxime under the conditions of the nickel precipitation. The following table shows the results of the test in solutions containing about 0.05 mg. of the metal per cc.

TABLE I.

Showing Result of Adding $NaC_2H_3O_2$ or NH_4OH and Dimethylglyoxime Solution to Some Metallic Solutions in Very Dilute Acid.

Metal.	Color in $NaC_2H_3O_2$ or NH_4OH solution.	On addition of dimethylglyoxime.
Nickel.....	No color	Red precipitate
Iron, ferrous....	Green solution or precipitate	Light red solution or precipitate
Ferric.....	Red solution or brown precipitate	Darkens giving red solution or precipitate
Copper, cuprous	Blue to green solution or precipitate	Dark green to brown solution
Cupric.....	Dark green solution or precipitate	Brown solution or precipitate
Cobalt.....	No color	Brown solution or precipitate

[1] Böttger, "Qualitative Analysis," 2nd edition, p. 212.

[2] Treadwell-Hall, "Analytical Chemistry," 3rd ed., **1913**, II, p. 130.

[3] Mellor, "Treatise on Quantitative Inorganic Analysis," **1913**, p. 394.

[4] Tschugaev, *J. Chem. Soc.*, **105**, 2187 (1914).

[5] Matsui, *J. Tokyo Chem. Soc.*, **39**, 459 (1918).

If, however, mineral acid be added to any of the above solutions the color of the metal in that particular acid prevails except in the case of cobalt in which the brown coloration remains, its intensity decreasing somewhat on the addition of the acid but depending principally upon the quantity of cobalt present. A solution containing 0.0005 mg. per cc. presents a very distinct color. Considerable quantities of iron or copper, of course, mask the color, but in the regular qualitative scheme these elements are removed and the filtrate resulting from the nickel confirmation gives the test directly, it being necessary only to acidify with mineral acid in order to exclude the possibility of the color being due to slight contamination with the previously mentioned elements.

Quantitative Considerations.—A Dubosq dipping colorimeter was used for all colorimetric comparisons.

The first procedure was to treat a solution of cobalt chloride according to the procedure for the determination of nickel with dimethylglyoxime as given in Treadwell-Hall[1] with slight modification. On acidifying the resulting solution with hydrochloric acid it was found that the color was not sufficiently constant for a quantitative comparison, although it works very well for a qualitative test. Acetic acid was then substituted for the hydrochloric acid, thus decreasing the hydrogen-ion concentration, when much better results were obtained. To reduce the hydrogen-ion concentration further sodium acetate was added to the slightly acid solution.

The actual method used was as follows. The cobalt, or cobalt and nickel, solution prepared as for the determination of nickel was slightly acidified and 10% sodium acetate added until the solution was practically neutral, heated to boiling, and dimethylglyoxime added in excess. (If nickel was present it was filtered off at this point.) The solution was then allowed to cool slowly and when cold comparisons were made between solutions of different strengths as standards. Because of the possible effect of excess of the dimethylglyoxime reagent or of sodium acetate these were alternately made the variable in several test solutions. Excess of sodium acetate had no effect on the accuracy while a large excess of the glyoxime reagent decreased the accuracy. This should make no difference in the determination, however, as the amount of dimethylglyoxime added in a nickel determination is based on the approximate total percentage of nickel and cobalt present, and hence a large excess of the reagent would never be present.

To show the accuracy of the results in an actual determination mixed solutions of nickel and cobalt were prepared and analyzed in this way; the results are given in the following table.

[1] *Loc. cit.*

Ni present.	Ni found.	Co present.	Dimethylglyoxime added (1% solution). Cc.	Co found.
0.0468	0.04664	0.00862	30	0.00822
0.0468	0.04657	0.00862	30	0.00822
0.0468	0.04662	0.00431	30	0.00383

Solution and washings diluted to 100 cc.; comparisons made with cobalt solutions containing 0.00431 g. of Co and 5 cc. of dimethylglyoxime reagent in 100 cc.

Many other results on other concentrations of the salts gave data comparable with the above.

While the method gives very good results for small amounts of cobalt in the presence of much larger amounts of nickel some points should be kept in mind. The solution or filtrate should be allowed to cool slowly as the intensity of color seems to vary slightly with the rate of cooling and in the sodium acetate solution copper and iron must of course be absent.

Summary.

1. It has been found that dimethylglyoxime always gives a brown colored solution with cobalt which does not disappear upon the addition of mineral acids as does the color of other metal glyoximes and hence can be used as a sensitive qualitative test for cobalt, in the absence of such interfering substances as copper and iron.

2. In the absence of the elements which give colored solutions or precipitates with sodium acetate or dimethylglyoxime (with the exception of nickel) the brown color of cobalt dimethylglyoxime is proportional to the concentration and hence can be used as a colorimetric method for this element, when the solution is prepared by use of acetic acid and sodium acetate.

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THE THERMOCHEMICAL DATA OF CADMIUM CHLORIDE AND IODIDE.

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Received December 17, 1920.

In a communication[1] relative to the thermodynamic properties of silver and lead iodides, opportunity was taken to subject the Nernst heat theorem to a careful test employing data obtained from a study of the cell combination Ag | AgI | X*N* KI solution | PbI_2 | Pb. Since the cell operated in a homogeneous liquid medium the difficulties of correction for liquid potential and osmotic work factors were eliminated and the values obtained by direct measurement could be employed in the calculations involved. This represents a marked advantage over such cases in which this procedure is not possible. The combination, however, like

[1] Taylor, THIS JOURNAL, 38, 2295 (1916).