[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF IDAHO]

DIPHENYLAMINE AS A QUALITATIVE REAGENT FOR ZINC

BY W. H. CONE AND L. C. CADY

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The qualitative separation of zinc from chromium by the systems of analysis in general use requires considerable time. The production of the green cobalt zincate used as a confirmatory test is dependent upon the comparative amounts of cobalt nitrate and zinc present. Properly adjusting these amounts offers considerable difficulty to inexperienced analysts. The employment of diphenylamine and diphenylbenzidine as indicators in the titration of zinc[1] suggested their utilization in a qualitative test for zinc. A 0.5% solution of potassium ferricyanide and one gram of diphenylamine dissolved in 100 cc. of glacial acetic acid are the solutions used in this test.

Method

After the separation of the iron and aluminum groups by sodium hydroxide and sodium peroxide, the filtrate containing the aluminum group is acidified with hydrochloric acid, ammonium chloride is added, and the aluminum precipitated with ammonium hydroxide. The filtrate containing the chromium and zinc is acidified with acetic acid and divided into two equal parts. One part is tested for chromium and the other for zinc. To the part to be tested for zinc, five drops of the diphenylamine acetate solution and 5 cc. of the 0.5% potassium ferricyanide solution are added. The immediate appearance of a dark brown, green or purplish-black turbidity indicates the presence of zinc.

To test for any zinc that might be carried over into the iron group, the sulfides of zinc, cobalt and nickel are stirred for a few minutes with cold, dilute hydrochloric acid and filtered. The hydrochloric acid solution is boiled until all of the hydrogen sulfide is expelled, sodium hydroxide is added to alkalinity, the solution cooled and one gram of sodium peroxide added in small portions, with stirring. The mixture is boiled to decompose the excess sodium peroxide, cooled and filtered. The filtrate containing the zinc is acidified with acetic acid and the diphenylamine acetate and potassium ferricyanide are added as above.

Knop[2] states that in the absence of iron salts no coloration is produced by bichromate in a dilute solution of diphenylamine sulfate. This was found to be true only when the amount of bichromate present was small, less than .05 mg. per cc., a blue color being produced immediately if the concentration of bichromate was .05 mg. per cc. or greater. By using diphenylamine acetate instead of diphenylamine sulfate no color

[1] Cone and Cady, THIS JOURNAL, **49**, 356 (1927).

[2] Knop, *ibid.*, **46**, 263 (1924).

was produced unless the amount of chromium present was over 10 mg. of potassium bichromate per cc. of solution. This makes it possible to test for zinc in the presence of bichromate.

The color produced is dependent upon the relative amounts of zinc and chromium present. If much chromium is present the color will vary from a brown to a brownish-black. If chromium is absent the color will vary from a green to a purplish-black, depending on the amount of zinc present. The presence of chromium may cause the solution to turn dark on long standing even in the absence of zinc.

The following table shows the colors produced by varying the amounts of zinc and bichromate. Five cc. of potassium ferricyanide solution and five drops of diphenylamine acetate solution were used in each test.

TABLE I

COLORS PRODUCED BY VARYING MIXTURES OF ZINC AND BICHROMATE IONS

Mg. Zn per cc.	Mg. $K_2Cr_2O_7$ per cc.	Color produced
0.02	None	Pale green
.02	0.5	Greenish-yellow
.02	5.0	Brownish turbidity
.04	None	Greenish-black
.04	0.5	Greenish-brown
.04	5.0	Brown
.2	None	Blue violet
.2	0.5	Black
.2	5.0	Black

All the colors in the above table were quite distinct except when 0.02 mg. of zinc and 5.0 mg. of potassium bichromate were used, but even then there was a marked turbidity as compared with a potassium bichromate solution treated in the same manner.

A small amount of zinc ferrocyanide is always precipitated, due to the reduction of some ferricyanide to ferrocyanide by the diphenylamine. However, under the conditions prevailing any such zinc ferrocyanide formed is always dark colored on settling. Diphenylamine was used in preference to diphenylbenzidine as it is much cheaper and gives equally good results.

Summary

1. The use of diphenylamine as a qualitative reagent for zinc shortens the time required for the analysis of the aluminum and iron groups.

2. The test is more delicate than the cobalt zincate test.

3. The amount of zinc present may be estimated by the depth of the color produced.

MOSCOW, IDAHO