

THE DETECTION AND COLORIMETRIC DETERMINATION OF TRACES OF ALUMINUM.*

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In an investigation on the solubility of aluminum hydroxide, we wanted a very sensitive reaction for the detection and determination of traces of dissolved aluminum. The different methods described in literature were tested, however none of them could be used for our purpose. The well-known reaction of Atack¹ with alizarin—or its sulphonate is very sensitive (sensitivity about 0.2 mg. Al per liter); it appeared, however, that it gave very irregular results in making a colorimetric determination of aluminum. Therefore, different other substances were tried on their applicability as a reagent for aluminum, and we succeeded in finding an excellent reagent, namely, 1.2.5.8 oxyanthraquinone. This substance was recommended by Fr. Hahn, Wolff and Jager² as a reagent for magnesium. In alkaline solution the indicator has a violet color, in the presence of magnesium it is pure blue—(cornflower blue). By this method 1 mg. magnesium per liter, gives a distinct reaction and, if the color is compared with a blank, 0.5 mg. magnesium per liter may be detected. In studying the specific character of this reaction, we found that cobalt and nickel behave in the same way and react with the same sensitivity as magnesium.

Though the 1.2.5.8 oxyanthraquinone is a very sensitive reagent for magnesium, I prefer the titan yellow recently described by myself,³ as the latter substance also may be used for the colorimetric estimation of this metal. With aluminum solutions the 1.2.5.8 oxyanthraquinone gives in weak acid solutions a nice purple color. The indicator itself behaves as an acid base indicator at; a p_H lower than 6 it has a yellow color, if a p_H higher than 7 it is violet.

Procedure for the Reaction of Aluminum.—Indicator solution: 0.1% in alcohol.

Buffer Solutions.—A mixture of 10 volumes, 5 *N* of acetic acid and 9 volumes of 5 *N* ammonia (after tenfold dilution $p_H = 5.5-5.7$).

To 10 cc. of the solution is added 0.25–1-cc. buffer mixture and 0.3-cc. indicator solution. After 15–30 minutes the color is judged: A solution with 1 mg. Al per liter gives an intense clear violet solution; 0.5 mg. Al per liter gives a nice clear violet solution; 0.2 Al per liter gives a distinct clear violet solution; 0.1 Al per liter gives a light clear violet solution.

If the color is compared with that of a blank (without Al), the sensitivity goes to 0.02 mg. Al per liter.

Colorimetric determination is performed in the same way as the qualitative reaction; the best scale for comparison lies between 0.5 and 0.02 mg. Al per liter; the colors must be compared after standing for the same length of time, *i. e.*, 15–30 minutes.

* Scientific Section, A. Ph. A., St. Louis meeting, 1927.

¹ Atack, *Journ. Soc. Chem. Ind.*, 34 (1915), 641; compare also *Chem. Zentralk.*, 11 (1915), 491; 1 (1916), 176; I. M. Kolthoff, *Pharm. Weekbl.*, 54 (1917), 1008; Keilholz, *Pharm. Weekbl.*, 58 (1921), 1482; *Chem. Weekbl.*, 20 (1923), 193; Baldwin, *J. Amer. Water Works Assoc.*, 12 (1924), 439.

² Fr. Hahn, Wolff and Jager, *Ber.*, 57 (1924), 1394.

³ I. M. Kolthoff, *Chem. Weekbl.*, 27 (1927), No. 21.

Remarks.—1. The color of the aluminum lake develops gradually, after about 1 hour it has a maximum intensity. This maximum intensity is reached much sooner if the test-tubes are warmed after addition of the reagent at a temperature of 50° C.; the colorimetric determination may be made after five minutes standing.

2. The development of the color also depends on the p_H . The more acid the solution is, the longer it takes for the color to attain its maximum. If instead of a buffer mixture with a p_H of 5.6 another was used with a p_H of 4.8, it required about three hours before the solutions developed the maximum color intensity. Heating to a temperature of 90° C. accelerates the color development very much. At a p_H of 4.3 a solution with 0.5 mg. Al per liter gave after half an hour's standing no reaction. At a temperature of 90° C. a solution with 0.1 mg. Al, however, immediately gave a reaction, if the color is compared with that of a blank. As a matter of fact, the test-tubes used in these experiments must be of a high-grade quality, which do not respond to the test for aluminum.

3. The amount of buffer solution used is of little significance.

4. The clear solutions contain the violet aluminum lake in a colloidal state. If the color is judged after standing 10 hours, the lake is flocculate as nice violet purple flocs. Under the same conditions the blank gives a yellow-brown floc. In making a colorimetric determination it is necessary to compare, before the lake is flocculated.

5. Most metals are without influence on the reaction of aluminum. In salts of the alkali metals, alkaline earths, magnesium, zinc, manganese, nickel, cobalt, cadmium, lead and also of chromium. The presence of aluminum may be detected without difficulty. Copper has a somewhat disturbing action due to the dark blue color of a copper acetate solution; this may be corrected by the addition of an excess of sodium thiosulphate to the neutral salts, which reduces the cupric copper to the colorless cuprous copper.

Ferric iron has a disturbing action if it is present in quantities larger than 2 mg. per liter; likewise tin, antimony III and bismuth have a disturbing action, as they form precipitates, which also absorb some of the dye stuff. They can be corrected by the addition of an excess of Rochelle salt; or better, sodium tartrate. After addition of the buffer mixture and the oxyanthraquinone the solution is heated and remains clear. Due to the presence of the tartrate the sensitivity of the reaction on aluminum is somewhat decreased; in the presence of the metals mentioned 1 mg. Al per liter still may be detected. A blank should be run under the same conditions.

Summary.—1. 1.2.5.8 oxyanthraquinone is a very sensitive reagent for aluminum in weakly acid solutions.

2. Traces of aluminum can be determined in a colorimetric way with the reagent mentioned. The best concentrations for comparison are between 0.5 and 0.2 mg. Al per liter.