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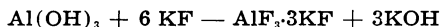
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An Extension of a Volumetric Method for Aluminum to the Determination of Milligram Quantities

WALTER N. TRUMP AND LOTHROP SMITH

Snyder (3) has given a rapid and precise titrimetric procedure for the determination of aluminum in the presence of moderate amounts of other substances. The original method was applied to samples containing from 0.025 to 0.13 gram of aluminum. In the present work it was found that, with certain modifications, the same procedure could also be used for the determination of aluminum in the range of 5 to 25 milligrams. The precision of the modified method was found to correspond to a standard deviation of about 0.1 milligram throughout this range.

The procedure described by Snyder (3) is based upon one developed by Viebock and Brecher (4), with the substitution of barium hydroxide for sodium hydroxide. The solution of the sample is neutralized with barium hydroxide until a slight precipitate of hydrated aluminum oxide forms; sodium potassium tartrate is then added, and the titration continued to the phenolphthalein end point. Potassium fluoride solution is added, and the liberated base titrated with standardized hydrochloric acid until the phenolphthalein end point is again reached. The base liberated, and hence the acid required, is a measure of the aluminum present, according to the equation (3). From 1 to 3% less than the theoretical quantity of



alkali is liberated (2, 3), so that the acid must be standardized against a known solution of aluminum under the conditions to be used in the determination.

Hale (2) and Bushey (1) confirmed Snyder's observation that neither sodium nor potassium hydroxide is satisfactory for the initial neutralization, low results being obtained. Bushey (1) obtained satisfactory results with barium hydroxide; Hale (2) pointed out that lithium hydroxide could be used where the presence of sulfates made barium hydroxide inapplicable. The presence of barium ion seems to affect the nature of the soluble aluminum tartrate complex (1). The low recovery of alkali is probably due to occlusion in the precipitated potassium fluoaluminate (1, 3).

EXPERIMENTAL

For the conversion to the smaller scale the concentrations of reagents recommended by Snyder (3) were retained, and all volumes reduced by a factor of 5. In applying the converted method, however, several difficulties were encountered. One of these was inaccuracy in locating the end point. Snyder had noted that when the liberated

base was titrated with acid the end point was not permanent, due to the slow release of occluded alkali. To overcome this he suggested adding an excess of acid and titrating back with barium hydroxide. This procedure was also used by Hale (2). However, even with the back-titration technique the end point was rather broad. This was ascribed to buffer action of the fluoride ion, as the same effect was noted in solutions containing only potassium fluoride, but was not found in solutions containing sodium chloride without any fluoride. As a possible solution to this problem the use of a different indicator was considered. Such an indicator should exhibit a transition between two colored forms in about the same range as phenolphthalein or thymolphthalein (2). No indicator fulfilling these conditions was readily available, but it was found that a suitable indicator could be prepared by mixing phenolphthalein with an inert green dye. Malachite green was used for this purpose: a useful indicator solution contained 0.4% phenolphthalein and 0.1% malachite green in 50% aqueous alcohol. The acid color of this modified indicator was light green, and the alkaline color dark red. A gray-violet color was taken as the end point.

An additional complication was introduced by the turbidity of the solution, due to precipitation of potassium fluoaluminate. This made determination of the end point of the titration by comparison with a blank solution difficult, as the color of the turbid solution could not be matched accurately with that of a non-turbid blank. Addition of gelatin, dextrin or gum arabic to the solution did not prevent precipitation of the fluoaluminate. However, it appeared feasible to produce an equal turbidity in the blank solution by the addition of a small amount of starch, most conveniently in the form of an aqueous suspension. About 0.05 gram of corn starch provided a sufficiently close match to the turbidities of solutions containing from 5 to 25 milligrams of aluminum.

On testing the procedure, thus modified, by the analysis of samples containing known amounts of aluminum, it was found that the recovery of aluminum was markedly affected by the total volume of the solution and the quantity of barium present. The most suitable values of these variables were determined empirically as 35 ml. and 0.7 millimole respectively, and the final procedure was so arranged that these values were obtained.

ANALYTICAL PROCEDURE

Reagents.—Standard aluminum chloride solution. Dissolve a weighed quantity of aluminum metal in a slight excess of 6 N hydrochloric acid, and dilute with water to a known volume such that 1 ml. of solution contains approximately 1 mg. of aluminum.

Standard hydrochloric acid. Standardize an approximately 0.3 N solution against sodium carbonate, and determine the aluminum titer by carrying out the analytical procedure with 10 to 20 ml. aliquots of the standard aluminum solution.

Standard barium hydroxide. Prepare a saturated aqueous solution and standardize against the hydrochloric acid.

Sodium potassium tartrate solution, 300 grams of the tetrahydrate per liter.

Potassium fluoride solution, 300 grams of the dihydrate per liter. Add 6 N sodium hydroxide until the solution is just alkaline to phenolphthalein.

Barium chloride solution, 0.2 N.

Indicator solution. Dissolve 0.4 gram of phenolphthalein and 0.1 gram of malachite green hydrochloride in 50 ml. of alcohol and dilute to 100 ml. with water.

Starch suspension. Shake 10 grams of corn starch briefly with 100 ml. of an aqueous solution containing 10% alcohol by volume (to inhibit bacterial decomposition).

Procedure.—Prepare a blank solution containing 6 ml. potassium fluoride solution, 6 ml. sodium potassium tartrate solution, 1 drop of indicator, 0.5 ml. of starch suspension, and water to make a total volume of 35 ml.

To a solution of the sample containing from 5 to 25 mg. aluminum and not more than 0.1 N free acid add 1 drop of indicator solution, then barium hydroxide until a slight precipitate appears. Add 6 ml. of sodium potassium tartrate solution and continue the titration with barium hydroxide nearly to the end point. Note the volume of barium hydroxide used, and add barium chloride if necessary to give a minimum of 0.7 millimole of barium. Add enough water (determined, if required, by a preliminary titration) to produce a final volume of 35 ml., then complete the titration to the end point. Introduce 6 ml. of potassium fluoride solution and titrate the liberated alkali with standard hydrochloric acid, adding about 0.1 ml. in excess. Let stand one minute, then titrate back with barium hydroxide until the color of the solution matches that of the blank. Calculate the net volume of hydrochloric acid consumed, and from the previously determined titer of the acid, the weight of aluminum present.

DISCUSSION

The procedure was tested by the analysis of solutions containing known amounts of aluminum. The results are indicated in Table I.

Table I. Analysis of Known Aluminum Chloride Solutions

Aluminum Added mg.	Number of Analyses	Mean Aluminum Found mg.	Standard Deviation mg.
5.220	10	5.273	0.086
10.44	8	10.48	0.15
15.18	8	15.23	0.056
19.91	7	19.91	0.043
25.13	8	25.04	0.15

The interferences affecting this method have been investigated by Snyder (3), and were not examined in the present study. The principal interfering ions are phosphate, sulfate and silicate. Small amounts of calcium, chromium, copper, iron, magnesium, manganese and zinc do not interfere (3).

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This paper is based on a thesis submitted by Walter N. Trump to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Master of Science, 1947.