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THE ACIDIMETRIC DETERMINATION OF ALUMINUM WITH FLUORIDE AT pH 10-11

By

S. A. Hays
Analytical Section
Technical Services Division

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THE ACIDIMETRIC DETERMINATION OF ALUMINUM WITH FLUORIDE AT pH 10-11

ABSTRACT

The precipitation of potassium aluminum fluoride from an aqueous aluminate solution by potassium fluoride releases hydroxyl ion by the reaction:

$$KAlO_2 + 6KF + 2H_2O \longrightarrow \underline{K_3AlF_6} + 4KOH$$

Titration of the hydroxyl ion with standardized hydrochloric acid provides a measure of the aluminum in the sample. The solution is adjusted to a measured pH which corresponds to a point on the steepest part of the titration curve; after the addition of precipitant the suspension is back-titrated to this same pH. The base freed by the reaction, and equivalent to the aluminum content, is thus measured.

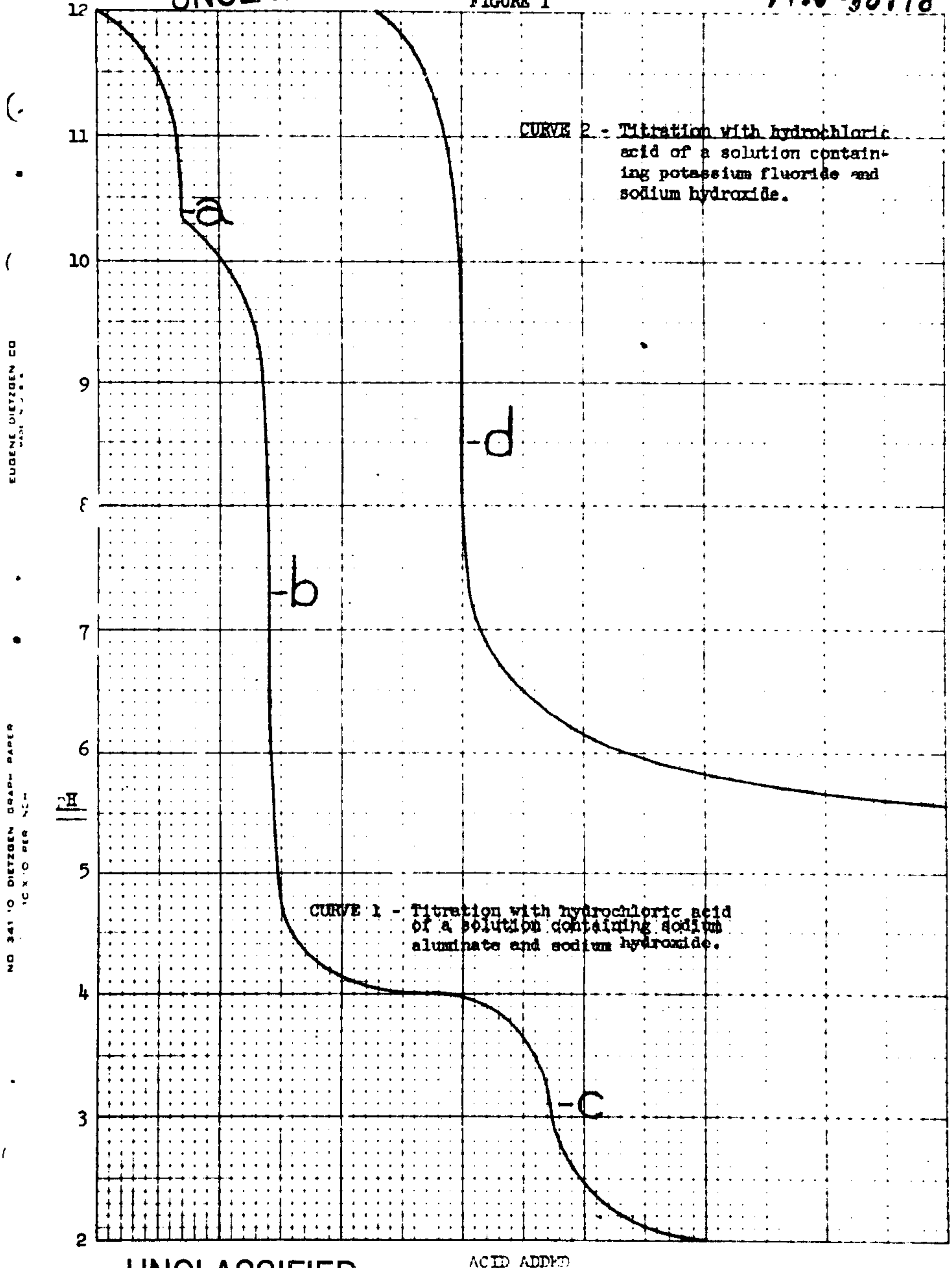
The principal advantages are simplicity and speed (five minutes per determination), a precision of ± 0.89% (at the 99% confidence level on 114 determinations by five people), and the fact that, for some types of samples, the preliminary separation required for the other acidimetric methods is unnecessary. The method is particularly advantageous for samples containing carbonate, dichromate, ammonium, uranium or iron.

Summaries are presented of the history of comparable methods and of the reasons for specificity, major types of interferences, optimum conditions, suggested procedure and advantages of this method.

ALUMINUM

The complexing tendency of aluminum and fluoride ions has been employed frequently, in combination with an acidimetric titration, in the determination of aluminum. Procedures have been published by Craig[1], Scott[2], Snyder[3], and Bushey[4], with important variations in the solution media, the end points, and the routes between end points. These variations may be indicated by reference to Figure I, which illustrates typical acidimetric titration curves of aqueous caustic solutions containing: (1) sodium aluminate, and (2) potassium fluoride. At the three breaks shown in the aluminum titration curve (1), the aluminum is

FIGURE I


12
11
10
9
8
7
6
5
4
3
2
pH
-a
-b
-c
-d
CURVE 2 - Titration with hydrochloric acid of a solution containing potassium fluoride and sodium hydroxide.
CURVE 1 - Titration with hydrochloric acid of a solution containing sodium aluminate and sodium hydroxide.
ACID ADDED
EUGENE DIETZGEN CO
NO 341 10 DIETZGEN GRAPH PAPER 10 X 10 PER INCH

principally present as aluminate ion (AlO_2^-) at (a), as an aluminum hydroxide precipitate ($Al(OH)_3$) at (b), and as aluminum ion (Al^{+++}) at (c). In curve (2) fluoride ion is predominant at (d) and both hydrofluoric acid and bifluoride ion occur below that pH.

In 1911, Craig introduced the use of fluoride to complex aluminum, thus providing a basis for use of an end point corresponding to (d) for the determination of free acid or base in samples containing aluminum. The reaction utilized was:

$$AlCl_3 + 6KF \xrightarrow{pH \sim 3} \underline{K_3AlF_6} + 3KCl$$

In 1915, Scott proposed a method for the determination of aluminum that involved the titration of duplicate samples with potassium hydroxide to the phenolphthalein end point. Prior to titration fluoride was added to one so that end points corresponding to (b) and (d) were obtained; the difference in titration was thus a measure of the aluminum.

In 1945, Snyder used barium hydroxide to neutralize an acid solution of aluminum in the presence of tartrate, and then added fluoride and titrated the liberated base with acid, using phenolphthalein for both end points, (b) and (d). The reaction utilized was:

$$Al(OH)_3 + 6KF \xrightarrow[pH \sim 8.5]{NaKC_4H_4O_6} \underline{K_3AlF_6} + 3KOH$$

In 1948, Bushey titrated a basic aluminate solution with acid from the end point (a), determined potentiometrically, to below (c), then added fluoride and back-titrated with base to (d), which was determined with phenolphthalein.

The present method, devised primarily to avoid preliminary separations of carbonate, iron, and uranium, employs the reaction:

$$KAlO_2 + 6KF + 2H_2O \xrightarrow{pH > 10.5} \underline{K_3AlF_6} + 4KOH$$

A basic aluminate solution is neutralized with acid to point (a), fluoride is added, and the liberated base is titrated with acid to point (d), with both end points determined potentiometrically.

It is desirable to decrease the time required for routine control analyses and to avoid errors resulting from the difference in pH of the two potentiometric breaks, (a) and (d). Therefore, instead of determining the two potentiometric breaks for each sample, the sample is simply adjusted to a predetermined pH - located about 0.3 of a pH unit above the inflection point (a) - and titrated back to the same pH after addition of fluoride. This method is therefore particularly suited to autotitraters based on a preset pH end point. An empirical factor is necessary. On a series of standards, the factor obtained was 3.891 moles of acid per mole of aluminum instead of the theoretical four.

The reactions in this method are relatively specific because:

1. Both end points are at the same pH. The errors from other neutralization reactions which occur between end points of different pH are greatly reduced.

2. At a pH above 10.5 many cations which would otherwise react with fluoride are precipitated and do not so react; ferric iron provides an example of this situation. Many ions, such as acetate, carbonate, dichromate and ammonium, which act as buffers at lower pH's, have little effect at a pH above 10.5.

3. Aluminum forms complexes at a fluoride concentration considerably below that required for most other elements. Therefore, it is possible to control the fluoride concentrationso that aluminum precipitates quantitatively without appreciably precipitating most other constituents. In acidic solutions, however, the fluoride concentration required for precipitation of iron or uranium is so low that adequate control is possible only by actually titrating with the fluoride. From pH 3 to 10, unless tartrate is present, the analytical results are unsatisfactorily low and variable when fluoride is added to the precipitated aluminum hydroxide. The aluminate ion, however, requires about 0.3$\underline{M}$ fluoride ion for complete precipitation, so that sufficient control of the concentration can be readily achieved, without varying the amount of potassium fluoride reagent added.

The major types of interferences encountered in this method are:

1. Some other fluorides may precipitate and cause high results. For example, the weight of uranium (VI) in the sample may exceed that of aluminum by tenfold with no apparent effect, but at twentyfold the results are about one percent high, and at 200-fold results average

35% high. This effect may be reduced by careful control of fluoride concentrations, or eliminated by a preliminary partial separation. Some cations, such as magnesium, whose hydroxides are slightly soluble at pH 10.5, and which form insoluble fluorides, may have to be precipitated or complexed before the titration.

2. Coprecipitation of aluminum with ferric hydroxide or similar precipitants gives low results. The error is approximately linear and is low by about 0.03 grams aluminum per gram of iron. If the sample contains over 0.2 grams of iron per gram of aluminum, a preliminary partial separation is necessary for accurate results.

3. Substances such as phosphate which buffer the solution at the end points will reduce the slope of the titration curve.

4. The salting effect of high concentrations of any salt, such as sodium chloride, interferes by increasing the pH of the aluminate break, so that the slope of the titration curve at the end point is reduced. Titrating at a high temperature has the same effect. Therefore, buffers, salting agents, or high temperatures unfavorably affect the precision and sensitivity, although they should not alter the accuracy.

The optimum conditions for this method are:

1. The end point pH should be chosen to be only slightly (about 0.3 pH units) above the potentiometric break; this provides nearly the maximum change of pH per increment of acid. Since the pH of the break increases with concentration of aluminum, the sample used to find the break should contain as much aluminum as any sample later used with the pH thus determined.

2. The sample size should be varied as necessary to keep the weight of aluminum present fairly constant (preferably within a factor of two) and to utilize the major part of the buret volume. The weight desired depends primarily upon the volume of the solution chosen for the first end point. A concentration of about 0.4 grams of aluminum per liter at the first end point is suggested although 5 to 0.05 g/l gave satisfactory results. The fluoride concentration is more easily controlled at the lower aluminum concentrations. In the presence of some buffers, results may be improved by choosing the dilution of sample which minimizes the

buffering effect. High concentrations are undesirable if large amounts of other precipitates will also be formed.

3. Before adjusting the sample with acid to the first end point, sufficient concentrated sodium hydroxide is added to the samples to raise the pH to 12 or above in order to insure complete solution of the aluminum hydroxide formed at lower pH values. Thorough stirring throughout the procedure is essential, especially if large amounts of any precipitates - particularly ferric hydroxide - are present. After the pH and volume are adjusted to the chosen values, the exact pH is read immediately before the addition of the measured quantity of potassium fluoride. Then the solution is promptly titrated, as rapidly as accurate buret drainage permits. There is no appreciable lag in the pH readings for pure aluminum salt samples, and it is not difficult to approach the end point rapidly without overshooting.

4. The pH and volume at the first end point should be duplicated carefully for precise results. The pH is recorded to hundredths just before addition of potassium fluoride, and the second end point is calculated by interpolation to the same pH. (However, a variation of either 20% in the volume or of 0.20 pH units changes the results less than 1%.)

5. The titrant should be relatively concentrated to avoid dilution errors. Although considerable variation is feasible to utilize an accurate buret size, the buret volume should not exceed one fourth of the volume of the solution being titrated.

6. The potassium fluoride reagent should be concentrated to avoid dilution errors and to reduce blank corrections. It should be stored in a Lucite, Polythene, or paraffin-lined container, and carefully adjusted with acid or base until it gives a low blank in regular titrations with no sample. Daily blank determinations are advisable.

7. The concentration of fluoride required for quantitative precipitation increases with pH. Therefore, the amount of reagent used should also be modified if the concentration of aluminum at the first end point is changed five or tenfold.

The following method is suggested:

Reagents

Standardized 1/3N hydrochloric acid, saturated sodium hydroxide solution, and a 60% solution of potassium fluoride dihydrate.

Apparatus

5 ml. buret, pH meter with calomel and glass electrodes (preferably blue glass for high pH), and an efficient mechanical or magnetic stirrer.

Notes

1. Standardize the pH meter - preferably with a buffer of pH 10-11.
2. A complete procedure without sample is used for blank determinations.
3. Treat the electrodes and stirrer occasionally with dilute hydrochloric acid.

Procedure

1. Dilute a sample, containing 5-11 mg. of aluminum, to 10-20 ml. in a 50 ml. beaker.
2. Add saturated sodium hydroxide to pH 12-13.
3. Add acid to pH 11.1-11.5.
4. Dilute to 25 ml.
5. Add acid to the proper pH, about 0.3 above the inflection point (a).
6. Record the exact pH and add 2 ml. of potassium fluoride.
7. Titrate with standardized 1/3N hydrochloric acid back to the recorded pH.

Calculations

$$\frac{(\text{ml. of HCl-Blank})\ (\text{N of HCl})\ (26.97)}{(\text{factor})\ (\text{ml. of sample})} = \text{grams of aluminum per liter}$$

The factor (empirical) may be determined from standards. A value of 3.891 was obtained in this work.

Microdeterminations

The method was easily adapted to microdeterminations of 0.06 to 0.5 mg. aluminum. A hundred microliter Gilmont ultramicroburet with 1N acid, a Beckman 290-7 glass electrode, and 1N sodium hydroxide were used. The volume at the first end point was two ml., requiring 75 microliters of a 37% potassium fluoride solution. Additional reduction of sample is feasible if required.

The advantages of this method are:

1. A precision of 0.89%, at the 99% confidence level, was obtained by five people in a control laboratory on 114 determinations of samples containing 5 to 11 mg. aluminum.

2. A complete determination of a dissolved sample requires only five minutes, unless a preliminary separation is required.

3. Samples of concentrations as low as 0.05 grams of aluminum per liter are suitable for titrations without preliminary evaporations.

4. The reaction of aluminum with fluoride in this method is relatively specific. There is no interference from amounts of many other elements, such as iron or uranium, which usually necessitate a preliminary separation. Even if interferences do exceed the permissible limits, relatively simple separation procedures are applicable, since only a partial removal is necessary.

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