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# THE PHOTOMETRIC DETERMINATION OF ALUMINUM IN PHOSPHATE MATERIALS WITH FERRON

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# THE PHOTOMETRIC DETERMINATION OF ALUMINUM IN PHOSPHATE MATERIALS WITH FERRON

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## ABSTRACT

The ferron colorimetric method for aluminum is applied to the analysis of aluminum in phosphatic materials such as in the aluminum phosphate (leached) zone of the Florida phosphate deposits. In these deposits the major constituents are quartz, clay, and phosphate; the aluminum content varies from 2 to 30 percent $Al_2O_3$; and the phosphate content varies from about 1 to 35 percent $P_2O_5$. The ferron reaction was found to be exceptionally sensitive to small changes in pH of solutions under the usual conditions of this determination. The conditions were modified to make the reaction independent of pH in the region of 5 to 5.6. The method was purposely designed for routine use where maximum speed is the primary consideration. Although the accuracy of the method can be improved with very slight changes in operational detail, one may expect results to be within ± 3 percent of the total aluminum content of the sample.

## INTRODUCTION

Ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid) was first used by Davenport 1/ as a colorimetric reagent for the determination of aluminum.

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1/ Davenport, W. H., Jr., 1949, The determination of aluminum in the presence of iron: Anal. Chemistry, v. 21, p. 710-711.

Shapiro and Brannock 2/ have applied the reagent to the determination of aluminum in silicate rocks. Grandfield 3/ has studied the ferron reaction in considerable detail especially in its application to the analysis of complex mixtures and rocks.

We have extended the ferron method to the analysis of aluminum in phosphatic materials. The procedure developed is primarily useful for the determination of aluminum in the aluminum phosphate (leached) zone of the Florida phosphate deposits. In these deposits the major constituents are quartz, clay, and phosphate; the aluminum content varies from 2 to 30 percent $Al_2O_3$; and the phosphate content varies from about 1 to 35 percent $P_2O_5$. The procedure is applicable also to phosphate concentrates and argillaceous and silicate rocks.

Our investigations have shown the necessity of modifying the conditions under which the ferron reaction is usually carried out. For example, as generally applied the reaction is exceptionally sensitive to small changes in the pH of the solutions. It is possible to make the reaction independent of pH (in the region 5 to 5.6) by using large amounts of acetate buffer. Apparently the weak complexing action of acetate with aluminum permits a slightly smaller amount of aluminum to be in the form of ferron complex. The resulting decrease compensates for the increase in the color intensity of the ferron complex normally obtained in the pH region of 5 to 5.6 with smaller amounts of buffer.

The method was purposely designed for routine use where maximum speed is the primary consideration. Although the accuracy of the method

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2/ Shapiro, Leonard, and Brannock, W. W., 1952, Rapid analysis of silicate rocks: U. S. Geol. Survey Circ. 165, p. 8.

3/ Grandfield, Julia M., 1953, A critical study of the spectrophotometric determination of aluminum with ferron: MITG-A109, M.I.T. Mineral Engineering Lab.

can be improved with very slight changes in operational detail, one may expect results to be within ± 3 percent of the total aluminum content of the sample.

## DISCUSSION OF PROCEDURE

The sample is completely decomposed by treatment with a mixture of HF, $HNO_3$, and $HClO_4$, and most of the fluoride is removed by fuming with $HClO_4$. A 3-ml aliquot of the acid solution (containing 5 mg of sample) is transferred to a glass-stoppered test tube and 2 ml of cupferron solution added. The mixture is shaken and 10 ml of chloroform is added. The mixture is vigorously shaken and then centrifuged. A 1-ml aliquot of the aqueous layer is then transferred to a small beaker and a few milliliters of $HClO_4$ are added. The sample is then brought to fumes and evaporated until free from $HClO_4$. The chloroform extraction is made from solutions 10 percent by volume in HCl separating Zr, Ti, V, Fe, and other soluble cupferrates from aluminum which remains in the water layer. Perchloric acid is used to destroy the small amount of cupferron in the aliquot of the aqueous layer. The perchloric acid must be completely removed to permit precise control of pH in the ferron determinations.

In the removal of perchloric acid it was found that orthophosphate is converted to pyrophosphate which forms a more stable complex with aluminum leading to low results in the ferron determination. Therefore the sample is digested with a small amount of concentrated acid to convert pyrophosphate to the ortho form before completing determination. A maximum of 400 $\gamma$ of $P_2O_5$ can be tolerated in the determination of aluminum with ferron. The 1-mg sample used in the final estimation insures that phosphate concentrates can be handled without phosphate interference. With this size sample on absorbancy of 0.003 above the blank corresponds to 0.05 percent $Al_2O_3$.

## EXPERIMENTAL DATA

In the experiments all solutions were made to a final total volume of 25 ml. The aluminum solution, (1 ml = 25 $\gamma$ $Al_2O_3$), made by dissolving $AlCl_3 \cdot 6H_2O$ in (1 + 99) HCl, was added first, aqueous solution of ferron next, and buffer last. Absorbancy measurements were made at 370 m$\mu$ using a slit width of 0.2 mm and 1-cm corex cells. Unless otherwise stated water was used as reference solution.

Figure 1 illustrates the effect of pH on the net absorbancy given by 50 $\gamma$ $Al_2O_3$. Different pH values were obtained by varying the proportions of 2M ammonium acetate and 2M acetic acid in the 5 ml of total buffer solution used. All solutions contained 5 ml of 0.16 percent ferron solution. Blanks were run at the corresponding pH values and the absorbancies given by the blanks were deducted from those given by the respective aluminum solutions. The same procedure was used to obtain the data plotted in figure 2 except that 2.5 ml of ferron solution was used. The data in figures 1 and 2 show that with the usual amounts of total buffer solution the ferron reaction with aluminum is very sensitive to small changes in the pH of the solution.

The data plotted in figure 3 were obtained by increasing the amount of buffer to 18 ml. On the basis of this data the pH of 5.2 was selected as optimum for this amount of buffer. A new buffer solution was made so that 5 ml of the new buffer was equivalent to 18 ml of the old buffer in terms of acetic acid and ammonium acetate contents. Five milliliters of

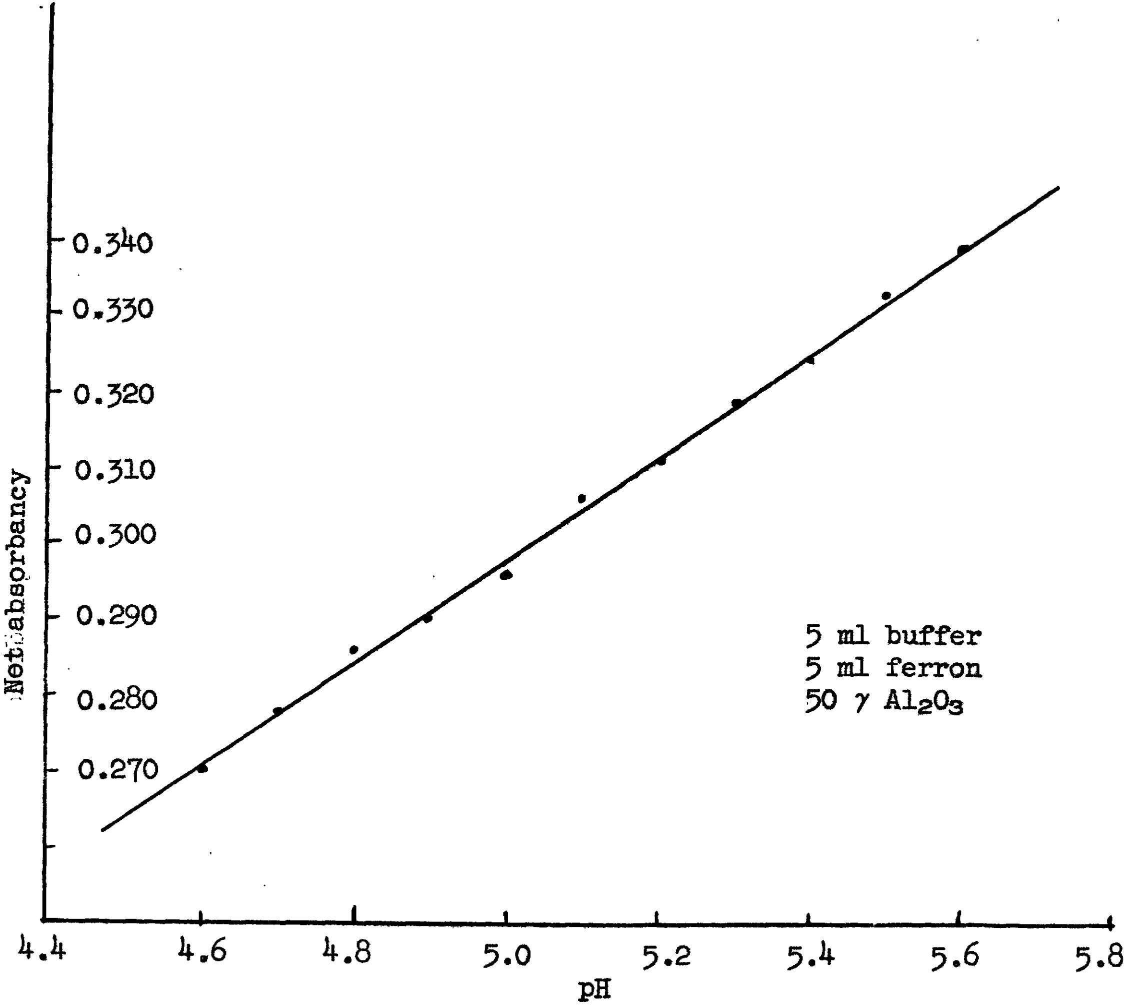

Figure 1.--Effect of pH on Al-ferron reaction (I)

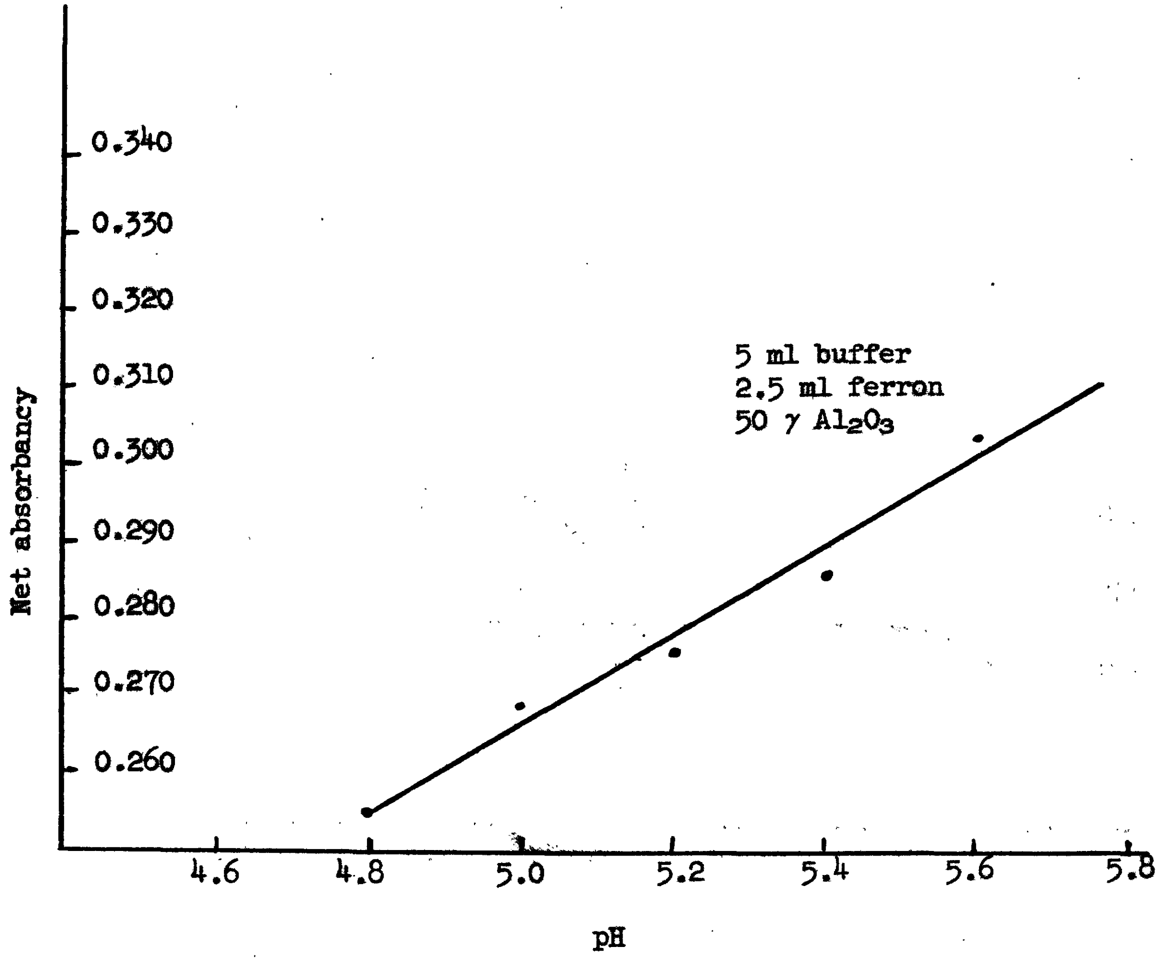

Figure 2.--Effect of pH on Al-ferron reaction (II)

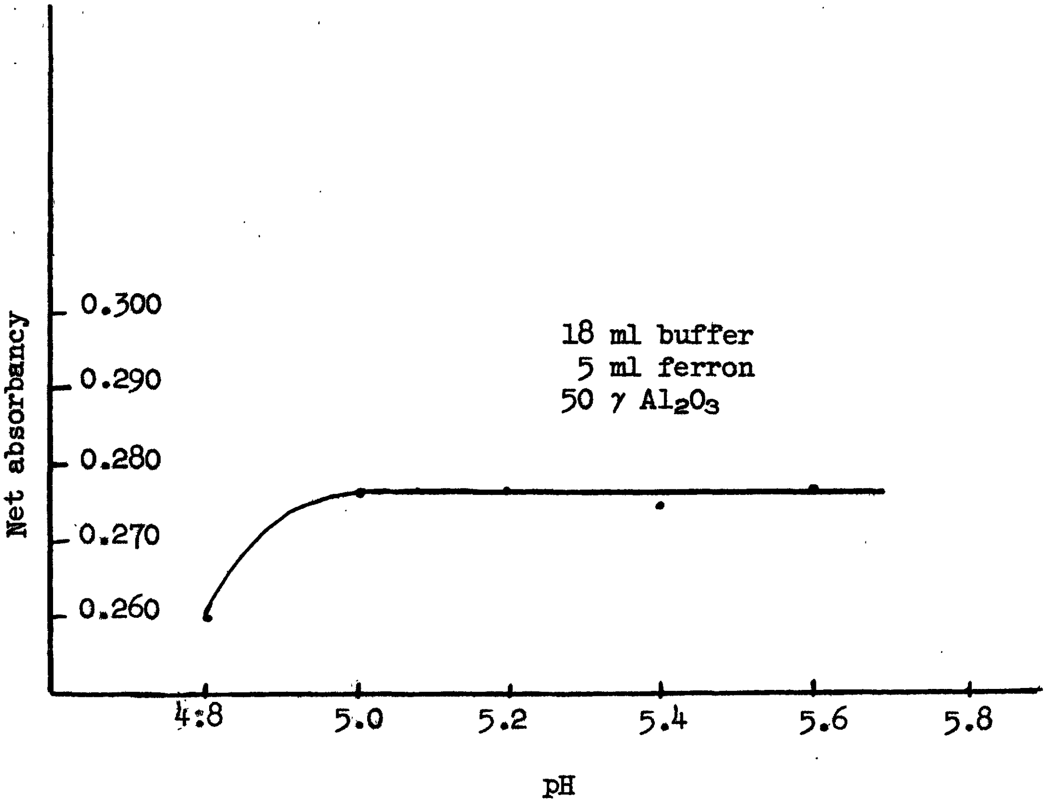

Figure 3.--Effect of pH on Al-ferron reaction (III)

the new buffer were used for all subsequent work.

The effect of ferron concentration at a pH of 5.2 is illustrated in figure 4. The nature of the curve plotted from the data suggests three possibilities: (1) that the instability constant of the aluminum-ferron complex is such as to allow some dissociation of the complex into its constituent species; (2) that aluminum forms several ferron complexes that can coexist in equilibrium in the test solution; or (3) that competition of acetate and ferron for aluminum allows only a fraction of the aluminum to be present in the form of a definite ferron complex.

On the basis of previous experiments (figs. 1, 2, and 3) it seems likely that the third explanation is the correct one. In any event 5 ml of ferron solutions was chosen as optimum in order to keep the absorbancy of the blank within reasonable limits.

The working curve in figure 5 was obtained by using the optimum conditions developed above, each solution containing 5 ml of the new buffer and 5 ml of ferron solution in a total volume of 25 ml. A blank containing all reagents was used in the reference cell. An identical curve is obtained when the results are plotted for aluminum test solutions each containing 400 $\gamma$ of $P_2O_5$. The curve deviates slightly from a straight line at about a concentration of 100 $\gamma$ $Al_2O_3$ per 25 ml of solution but is reproducible for all concentrations shown. After allowing the solution to stand for two hours the maximum change in absorbancy in this range amounted to 0.007.

The effect of phosphate is given in table 1. Two levels of aluminum (10 $\gamma$ $Al_2O_3$ and 50 $\gamma$ $Al_2O_3$) were tested varying the amount of phosphate (added as a solution of $Na_2HPO_4$) in each series. The data indicate that at least 400 $\gamma$ $P_2O_5$ can be tolerated without interference.

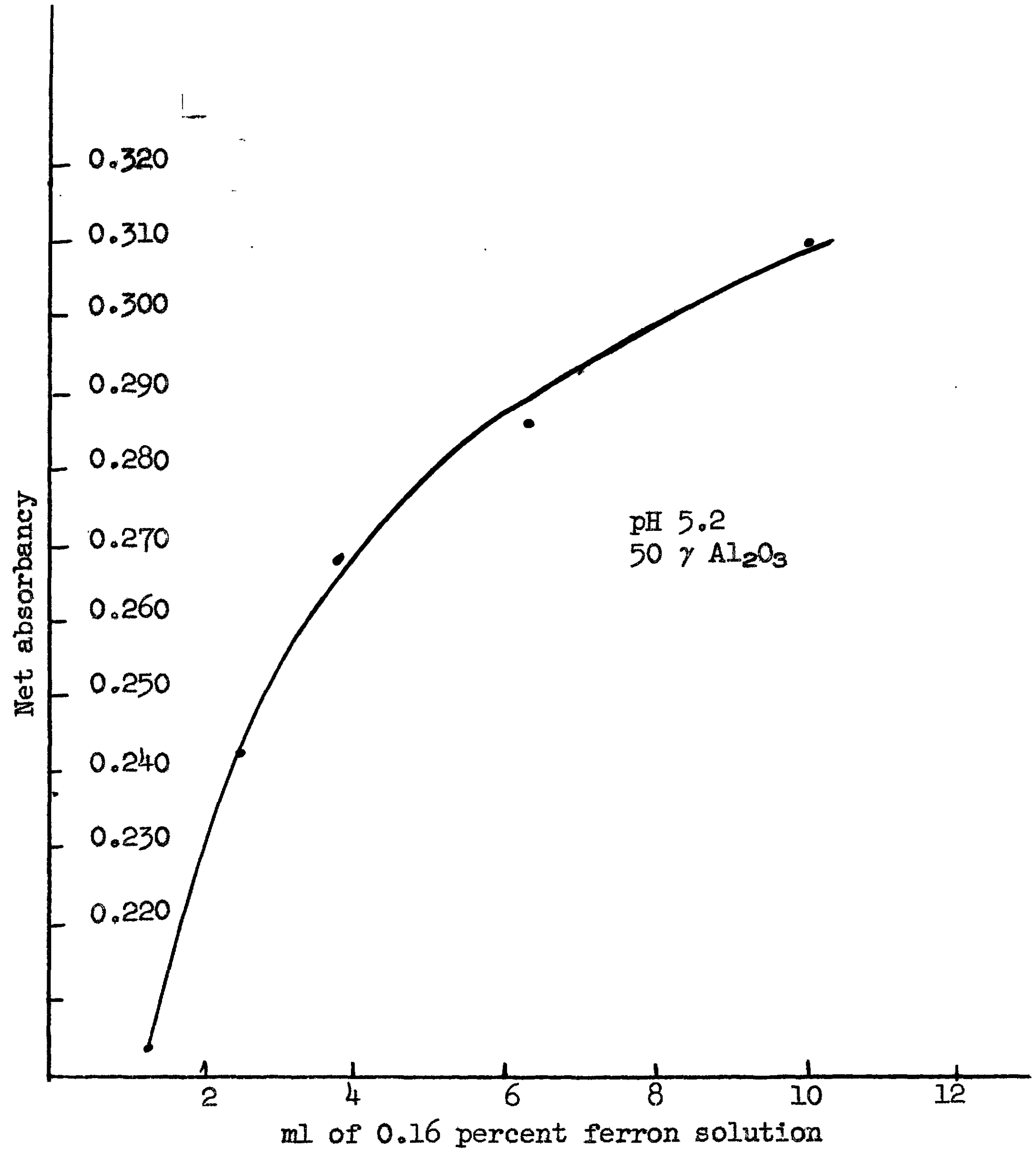

Figure 4.--Effect of ferron concentration on Al-ferron reaction.

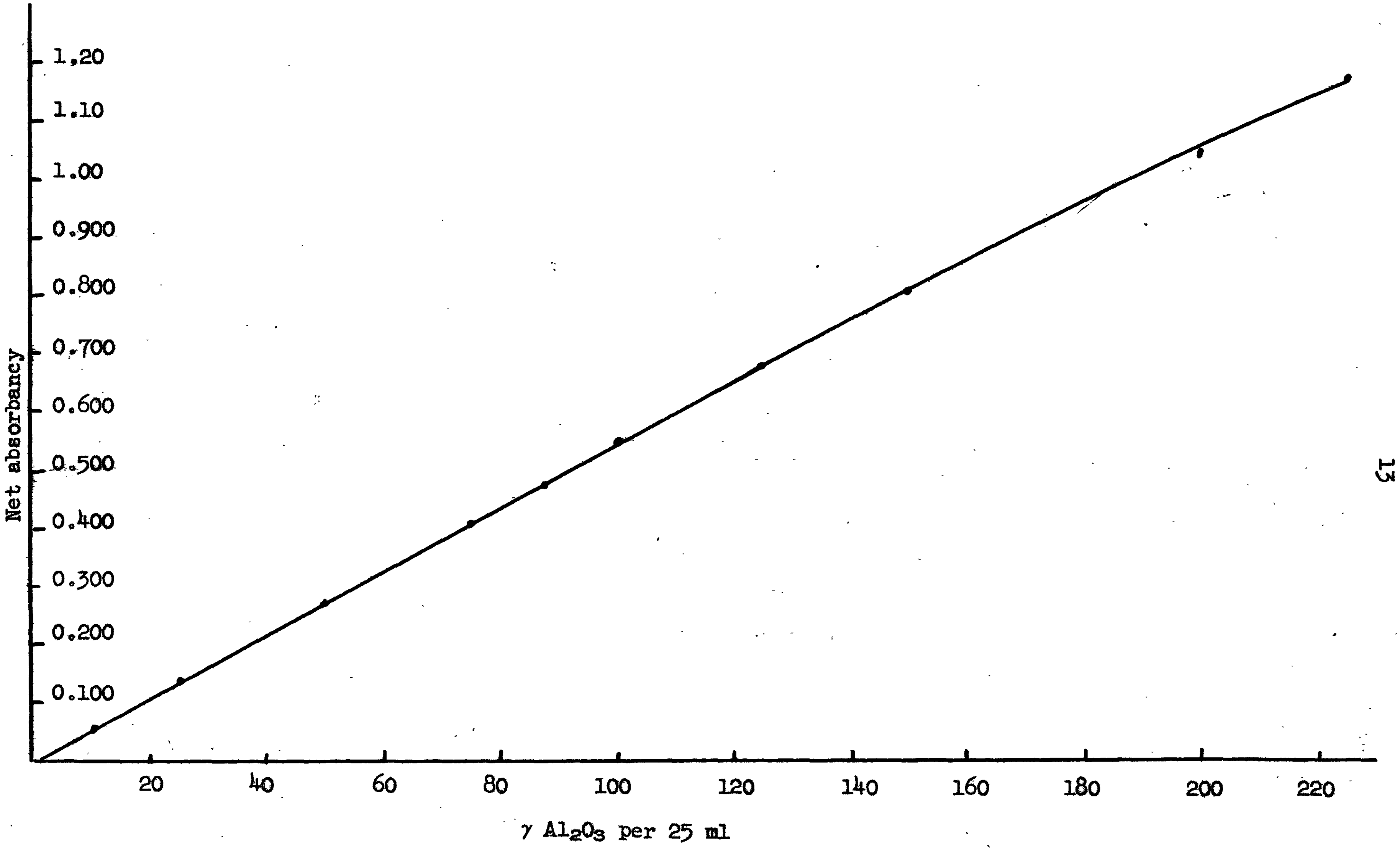

Figure 5.--Working curve

Table 1.--Effect of phosphate on the Al-ferron reaction.

| $Al_2O_3$ taken $\gamma$ | $P_2O_5$ taken $\gamma$ | Absorbancy (immediately) | Absorbancy (after 40 minutes) |
|---|---|---|---|
| 10 | 0 | 0.061 | 0.062 |
| 10 | 40 | 0.061 | 0.063 |
| 10 | 200 | 0.060 | 0.061 |
| 10 | 400 | 0.061 | 0.062 |
| 10 | 800 | 0.050 | 0.052 |
| 10 | 2000 | 0.044 | 0.048 |
| 10 | 4000 | 0.044 | 0.048 |
| 50 | 0 | 0.284 | 0.283 |
| 50 | 40 | 0.283 | 0.284 |
| 50 | 200 | 0.284 | 0.284 |
| 50 | 400 | 0.283 | 0.283 |
| 50 | 800 | 0.244 | 0.270 |
| 50 | 2000 | 0.230 | 0.260 |
| 50 | 4000 | 0.190 | 0.238 |

The interference of $P_2O_5$ decreases if the solutions are allowed to stand for some time before their absorbances are measured (table 1).

As fluorine interferes seriously in the colorimetric determination of aluminum with ferron, no fluorine should be present. As little as 10 $\gamma$ F decreases the absorbancy of 50 $\gamma$ $Al_2O_3$ by about 0.01. The reader is referred to the paper by Grandfield [4] for data on the reaction of other elements with ferron.

## Reagents and apparatus

Standard aluminum solution A (1 ml = 0.005 g $Al_2O_3$): Dissolve 4.6535 g $KAl(SO_4)_2 \cdot 12H_2O$ in 100 ml (5 + 95) HCl. Standardize gravimetrically.

Standard aluminum solution B (1 ml = 25 $\gamma$ $Al_2O_3$): Take 5 ml (or appropriate amount) of solution A, add 1 ml HCl, and dilute to 1 liter with water.

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[4] Op. cit.

Ferron solution, 0.16 percent: Take 0.8 g of ferron and digest with 400 ml of water until dissolved. Filter into a 500-ml flask and adjust to 500 ml with water.

Cupferron solution: Dissolve 3 g of cupferron in 100 ml of water.

Buffer: Dissolve 412 g of ammonium acetate in about 600 ml of water, and filter if necessary. Add 109 ml of glacial acetic acid, and dilute to 1 liter.

Chloroform: Reagent grade

Spectrophotometer: Beckman Model DU with 1-cm corex cells was used in this work.

## Procedure

1. Transfer a 0.3333-g sample ground to at least 80 mesh to a 35-ml platinum dish. Burn off organic matter if present.

2. Add 5 to 10 ml (1 + 1) $HNO_3$, 5 to 10 ml HF, and 5 ml $HClO_4$. Evaporate on the steam bath and then take to fumes of $HClO_4$. Fume until 1 ml of $HClO_4$ remains.

3. Add 62 ml (1 + 1) HCl, digest the solution, and filter into a 200-ml volumetric flask. Make to volume with water and mix.

4. Transfer by pipet a 3-ml aliquot into a 15-ml glass-stoppered centrifuge tube. Add 2 ml (by pipet) of cupferron solution and mix gently. Add 10 ml of chloroform and extract.

5. Centrifuge at 1100 rpm for 10 minutes with stopper in place.

6. Take a 1-ml aliquot of the clear water layer by pipet and transfer to a 30-ml beaker. Add 2 ml (1 + 1) $HNO_3$ and evaporate the solution to dryness. Add 1 ml (1 + 1) $HNO_3$ and 2.5 ml $HClO_4$ and evaporate first

on steam bath and then on hot plate until no more fumes of $HClO_4$ are evident.

7. Grasp beaker with Blair tongs and heat gently (200-300 C) over a burner until no fumes are given off. The beaker should be heated up to the lip. Cool.

8. Add 2 ml HCl, cover, and digest the solution on the steam bath for at least 10 minutes to convert pyrophosphate to orthophosphate.

9. Evaporate the solution to dryness on bath. Add 5 ml of (1 + 99) HCl. Digest. Transfer the solution to a 25-ml volumetric flask, washing beaker with water and adding rinses to the flask.

10. Add 5 ml ferron solution by pipet and then 5 ml of buffer also by pipet. Make to mark with water and mix.

11. Obtain the absorbancy of the solution against a blank containing 5 ml of (1 + 99) HCl and the same amounts of buffer and ferron to 25 ml. Absorbancy measurements are made at 370 mμ with a slit width of 0.2 mm. NOTE: Carry at least 2 blanks through the procedure and deduct the average absorbancy of the blanks from the absorbancy of the samples. The net absorbancy is related to concentration of aluminum through the working curve.

## Test of procedure

One of the important factors affecting the accuracy of the method is the reproducibility of blanks carried through the procedure. Accordingly, one blank was run daily for the period of about 5 weeks. The absorbancies given by the blanks are shown in table 2.

In another series of experiments blanks were run in triplicates at various times. The maximum difference in absorbancy among the individual

Table 2.--Variations in absorbancies of blanks prepared at different times.

| Sample | Absorbancy | Sample | Absorbancy |
|---|---|---|---|
| 1 | 0.008 | 13 | 0.021 |
| 2 | 0.014 | 14 | 0.019 |
| 3 | 0.015 | 15 | 0.024 |
| 4 | 0.025 | 16 | 0.008 |
| 5 | 0.015 | 17 | 0.011 |
| 6 | 0.018 | 18 | 0.016 |
| 7 | 0.010 | 19 | 0.011 |
| 8 | 0.014 | 20 | 0.010 |
| 9 | 0.012 | 21 | 0.021 |
| 10 | 0.015 | 22 | 0.018 |
| 11 | 0.017 | 23 | 0.016 |
| 12 | 0.016 | 24 | 0.019 |

members of each set generally did not exceed 0.01. This corresponds to 2 $\gamma$ $Al_2O_3$, and on the basis of a 1 mg sample, the absolute error from this source should not exceed 0.2 percent $Al_2O_3$. If the blank readings are averaged the error is of course smaller.

The procedure was tested first on three standard samples: Bureau of Standards phosphate rock no. 120, a standard granite,[5] and a standard diabase.[5] The results are given in table 3. The standard diabase was then used for a series of tests in which various amounts of phosphate were added to the diabase according to the following scheme:

1. Solution I: A 0.3333-g sample of diabase was taken, 0.1257 g $Na_2HPO_4 \cdot 7H_2O$ was added, and the mixture dissolved according to the general procedure to prepare 200 ml of solution 16 percent by volume in HCl.

2. Solution II: A 50-ml aliquot of solution I was transferred to a 100-ml volumetric flask, 0.0314 g of $Na_2HPO_4 \cdot 7H_2O$ as solid was added,

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[5] Schlecht, W. G., 1951, Cooperative investigation of precision and accuracy in chemical analysis of silicate rocks: Anal. Chemistry, v. 23, p. 1568-1571.

Table 3.--Results on standard samples.

| Sample | Percent $Al_2O_3$ Accepted value | Percent $Al_2O_3$ Found |
|---|---|---|
| BS 120 (phosphate rock) | 0.87 | 0.82<br>0.80<br>0.81<br>0.81<br>0.82 |
| Granite | 14.1 | 14.0<br>13.9<br>14.0 |
| Diabase | 15.0 | 14.7<br>14.9<br>14.8 |

And the volume of the solution adjusted to 100 ml with (16 + 84) HCl.

3. Solution III: A 50-ml aliquot of solution I was transferred to a 100-ml volumetric flask, 0.0176 g of $Na_2HPO_4 \cdot 7H_2O$ as solid was added, and the volume adjusted to 100 ml with (16 + 84) HCl.

Five 3-ml aliquots of each solution were analyzed for aluminum according to the procedure. The aliquots taken for light absorption measurements contained the following amounts of $Al_2O_3$ and $P_2O_5$, taking 15.00 percent $Al_2O_3$ as the "true" content of $Al_2O_3$ in the diabase:

| | |
|---|---|
| Solution I | 150 $\gamma$ $Al_2O_3$, 100 $\gamma$ $P_2O_5$ |
| Solution II | 75 $\gamma$ $Al_2O_3$, 200 $\gamma$ $P_2O_5$ |
| Solution III | 37.5 $\gamma$ $Al_2O_3$, 300 $\gamma$ $P_2O_5$ |

The results are given in table 4. The results of duplicate analyses on several Florida aluminum phosphate zone samples are given in table 5.

Table 4.--Results on a standard diabase solution to which known amounts of phosphate were added.

| Sample | $\gamma$ $Al_2O_3$ in sample | $\gamma$ $Al_2O_3$ found |
|---|---|---|
| Solution I | 150 | 147 |
| | 150 | 147 |
| | 150 | 147 |
| | 150 | 148 |
| | 150 | 148 |
| Solution II | 75 | 74.5 |
| | 75 | 77.6 |
| | 75 | 73.0 |
| | 75 | 74.0 |
| | 75 | 73.2 |
| Solution III | 37.5 | 38.6 |
| | 37.5 | 36.5 |
| | 37.5 | 37.0 |
| | 37.5 | 37.0 |
| | 37.5 | 37.2 |

Table 5.--Results of duplicate analyses of aluminum phosphate zone samples.

| Sample no. | Percent $Al_2O_3$ |
|---|---|
| 1 | 2.08, 2.10 1/ |
| 2 | 2.72, 2.62 2/ |
| 3 | 3.54, 3.25 1/ |
| 4 | 6.20, 6.15 1/ |
| 5 | 1.50, 1.60 3/ |
| 6 | 8.0, 8.1 3/ |
| 7 | 20.4, 20.8 3/ |

1/ Samples analyzed on different days.
2/ Samples analyzed by different analysts.
3/ Samples analyzed concurrently by one analyst.