B-1251

Cover Page for UNCLASSIFIED Reports

OAK RIDGE NATIONAL LABORATORY

REPORT NO. ORNL-83
This document consists of 10 pages.
This is copy 7 of 117
Series A

Issued To: Training School

THIS REPORT CONTAINS NO CLASSIFIED INFORMATION

| Read By | Date | Read By | Date |
|---|---|---|---|
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |

Oak Ridge National Laboratory

(Contract No. W-7405-eng. 26)

* * * * * * *

Chemistry Division

* * * * * * *

# A Spectrophotometric Method for the Determination of Aluminum in the Presence of Iron Using Ferron.

W. H. Davenport, Jr.

* * * * * * *

July 6, 1948

Date Received: 7/12/48 Date Issued: 7/15/48

ORNL-83
Chemistry-General

DISTRIBUTION:

1. G. T. Felbeck (CACCC N.Y.-N.Y.)
2. 706-A Library
3. 706-A Library
4. 706-A Library
5. 706-B
6. Biology Library
7. Training School
8. Health Physics Library
9. Central Files
10. Central Files
11. Central Files
12. Central Files
13. Central Files
14. E. J. Murphy
15. A. M. Weinberg
16-25. W. H. Davenport, Jr.
26. E. H. Taylor
27. M. D. Peterson
28. H. Etherington
29. W. A. Johnson
30. J. R. Huffman
31. A. Hollaender (Y-12)
32. C. D. Cagle
33. S. R. Sapirie (AEC Townsite)
34. H. M. Roth (AEC Townsite)
35. AEC, Oak Ridge National Labs.
36-43. Argonne National Laboratory
44. Armed Forces Special Weapons Project
45-46. Atomic Energy Commission, Washington
47. Battelle Memorial Institute
48-57. Brookhaven National Laboratory
58-61. Carbide & Carbon Chemicals Corp. (K-25)
62-65. Carbide & Carbon Chemicals Corp. (Y-12)
66. Columbia University (Failla)
67-70. General Electric Company
71-77. Hanford Directed Operations
78. Iowa State College
79-80. Kellex Corporation
81-83. Los Alamos
84. Massachusetts Institute of Technology
85-86. Monsanto Chemical Company, Dayton
87-88. National Bureau of Standards
89. Naval Radiological Defense Labs.
90. NEPA
91-92. New York Directed Operations
93. Patent Advisor, Washington
94-108. Technical Information Division, ORDO
109. UCLA Medical Research Laboratory (Warren)
110-114. University of California Rad. Labs.
115-116. University of Rochester
117. Western Reserve University (Friedell)

# A Spectrophotometric Method for the Determination of Aluminum in the Presence of Iron Using Ferron.

## Abstract

Aluminum and ferric iron in a buffered acetate-acetic acid solution form complexes with the reagent ferron, 7-iodo-8-hydroxyquinoline-5-sulfonic acid. The absorption maxima of the two complexes are sufficiently far apart to permit spectrophotometric measurements of (a) the ferric-ferron complex at 600 mμ and (b) the ferric-ferron complex plus the aluminum-ferron complex at 370 mμ. The complexes are stable for a reasonably long period of time. The method is suitable for the accurate determination of 0 - 50 μg of aluminum in the presence of 0 - 100 μg of iron.

## Introduction

Ferron was first proposed as a reagent for iron by Yoe (1). Later Swank and Mellon (2) reported that aluminum in large concentrations (2 mg. Al/0.1 mg Fe in 100 ml.) interfered in the ferron method for iron although no visible colored complex was formed.

The author has found that this aluminum-ferron complex has a maximum absorption at 370 mμ and that at this wave length, using small concentrations of aluminum at a constant pH, the complex obeys Beer's Law. The iron-ferron complex also absorbed at this wave length but it will be shown that the amount of absorption due to the iron complex can be accurately determined. One method using hematoxylin makes use of the mixed colors obtained from the aluminum and iron lakes. However, the absorption curves for the two lakes overlap each other which means that the optical density at each absorption maximum is dependent upon the concentration of both cations. Also, the color of the aluminum lake changes quite rapidly on standing

## Experimental

### Solutions and Methods

Redistilled water was used in the preparation of all solutions.

Standard aluminum solution, 1.000 mg./ ml. The solution was prepared by dissolving 1.000 g. of aluminum metal turnings, J. T. Baker Chemical Co., in 100 ml. of 1:9 hydrochloric acid and diluting to 1 liter. The final solution was standardized gravimetrically using ammonium hydroxide. A solution 10.0 µg./ml. was prepared by dilution of an aliquot of the standard.

Standard iron solution, 1.000 mg./ml. The solution was prepared by dissolving 0.100 g. of iron wire, J. T. Baker Chemical Co. #36 iron wire for standardising, in 50 ml. of 1:20 hydrochloric acid and diluting to 100 ml. A solution 10.0 µg./ml. was prepared by diluting an aliquot of the standard.

Ferron (0.2%). The reagent obtained from Eastman Kodak Company was used without further purification. An aqueous solution was prepared by dissolving 1.000 g. of reagent in 500 ml. of redistilled water.

Ammonium acetate (10%). Fifty grams of reagent were dissolved in 400 ml. of redistilled water and diluted to 500 ml.

Hydrochloric acid (1:9). C. P. Analytical grade acid was used.

Nitric acid (1:9). C. P. Analytical grade acid was used.

Buffers: The desired pH values were obtained by varying the concentration of either hydrochloric acid or nitric acid prior to the addition of 5 ml. of ammonium acetate. This procedure was followed in order to insure complete solution of aluminum and iron. In every case 5 ml. of the ammonium acetate solution and 2 ml. of the ferron solution were added. Solutions were made up to a final volume of 25 ml. and read in a Beckman spectrophotometer using 1 cm. cells.

### Spectral Absorption and Effect of pH

It can be seen from Figure 1 and Figure 2 that absorption maxima for the iron and aluminum complexes are obtained at a wave length of about 370 mµ and that at

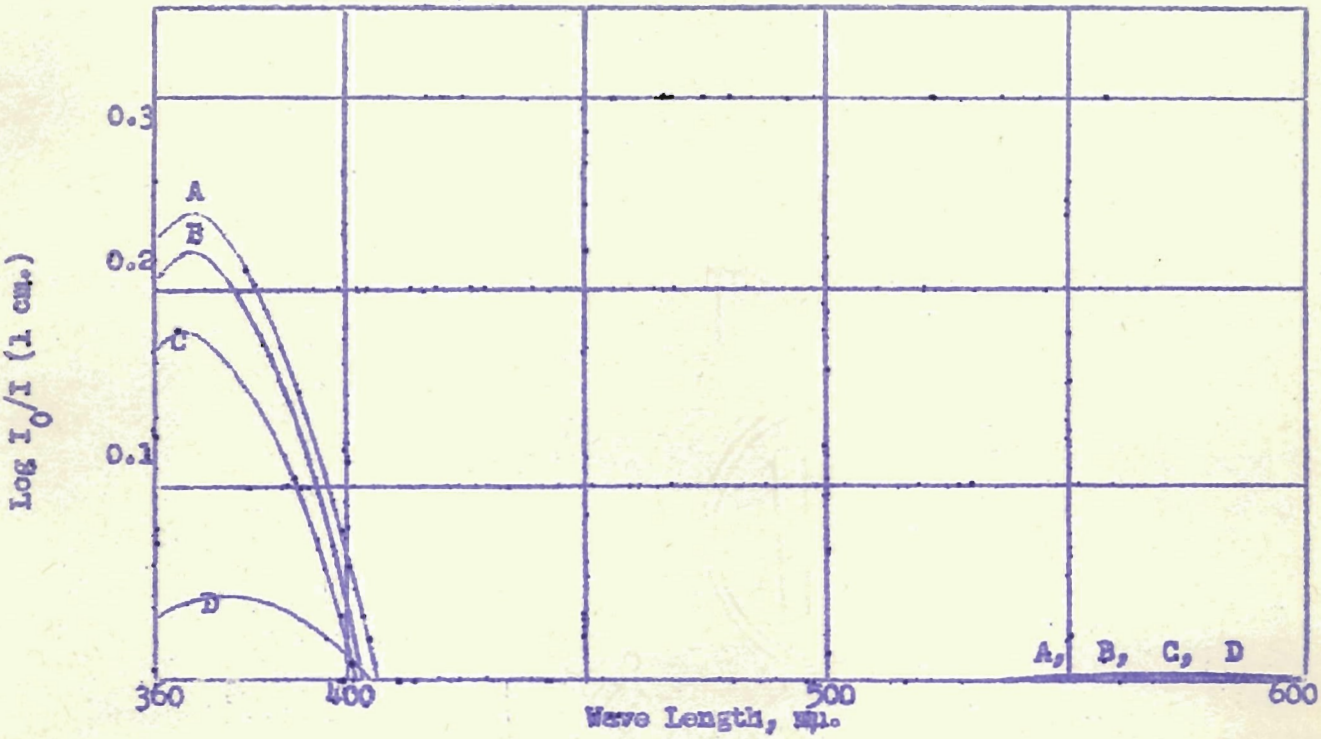


Figure 1. Effect of pH on Spectral Absorption of Aluminum-Ferron Complex in Acetic Acid-Acetate Solution
A. pH = 5.5, B. pH = 5.0, C. pH = 4.0, D. pH = 3.0
(20 μg. Al plus 2 ml. Ferron (0.2%) in 25 ml.)

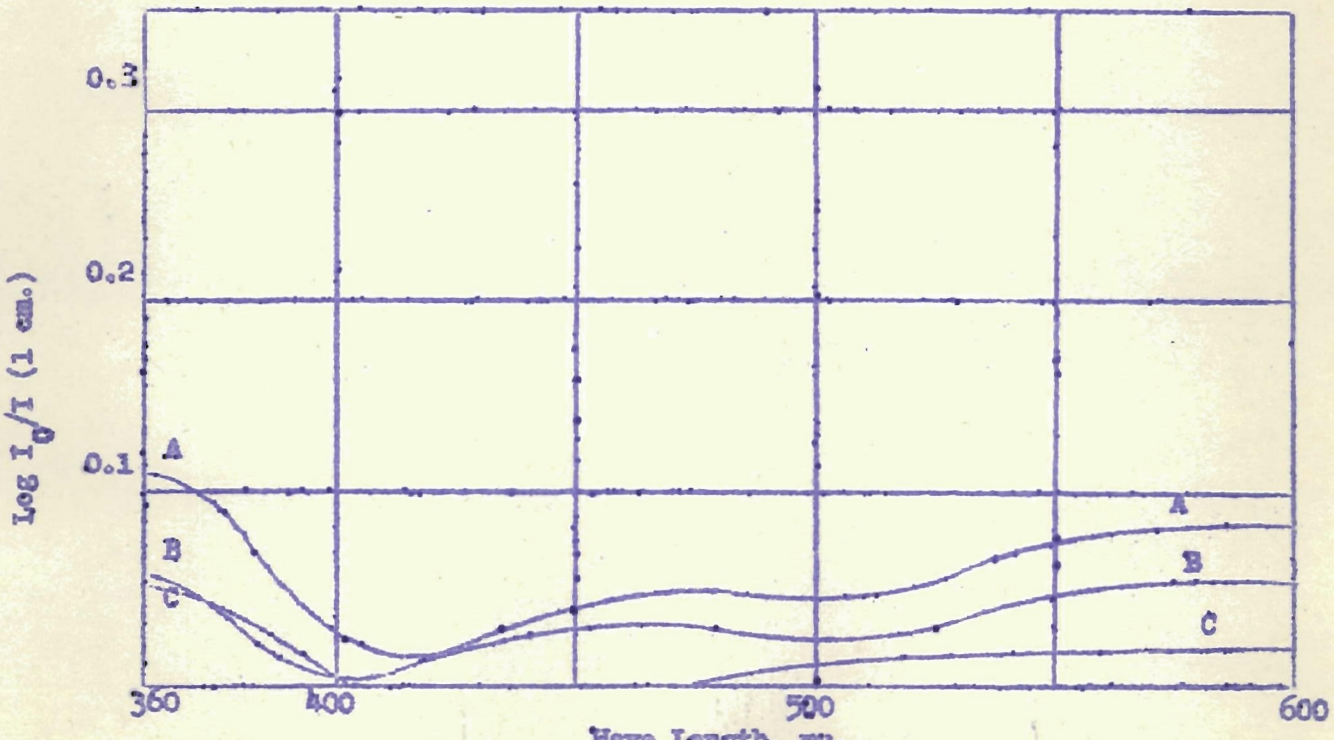


Figure 2. Effect of pH on Spectral Absorption of Iron-Ferron Complex in Acetic Acid-Acetate Solution
A. pH = 5.0-5.5, B. pH = 4.0 C. pH = 3.0
(20 μg. Fe plus 2 ml. Ferron (0.2%) in 25 ml.)

a wave length of about 600 mμ only the colored complex of iron shows absorption. The aluminum-ferron complex transmits more light than the blank between 410 mμ and 540 mμ. Maximum color development for each of the complexes was found at approximately a pH of 5.

Validity of Beer's Law

Calibration data for varying iron concentration vs. extinction at 370 mμ and at 600 mμ and for varying aluminum concentration vs. extinction at 370 mμ give the curves obtained in Figures 3 and 4. The aluminum-ferron complex does not obey Beer's Law at concentrations higher than 40 μg./25 ml. but the curve is reproducible to at least a concentration of 60 μg./25 ml. Another point to be noted is that the iron concentration vs. extinction data at 600 mμ gives a straight line plot under the above conditions, whereas Swank and Mellon (2) reported that Beer's Law was not obeyed under their conditions (pH of 2 - 3) when the ferron concentration was kept constant.

Effect of Foreign Ions

The effect of anions was not investigated. A number of cations do give positive interference. Uranium, thorium, copper, nickel, chromium, molybdenum, manganese, zirconium and zinc were found to interfere when present in a 1:1 ratio with aluminum. The degree of interference encountered when these cations are present appears in Table I. In general, those cations which form hydroxyquinolates in the pH range of the colorimetric method will interfere. Thus, magnesium, which completely precipitates with 8-hydroxyquinoline in the pH range 9.4 - 12.7 does not interfere when present in moderate amounts. Thorium which precipitates at pH 4.4 - 8.8 gives a definite positive interference in the colorimetric method.

Table I

Effect of Common Cations on the Aluminum-Ferron Complex

(20.0 µg. of Aluminum in 25 ml.)

| Ion | µg. Present in 25 ml. | Increase in Absorption at 370 mµ |
|---|---|---|
| $Cr^{+6}$ | 20.0 | 14% |
| $Cu^{++}$ | 20.0 | 100% |
| $Mg^{++}$ | 20.0 | 0% |
| $Mn^{++}$ | 20.0 | 5% |
| $Mo^{+6}$ | 20.0 | 24% |
| $Ni^{+2}$ | 20.0 | 100% |
| $Th^{+4}$ | 14.5 | 50% |
| $U^{+6}$ | 20.0 | 19% |
| $Zn^{+2}$ | 20.0 | 65% |
| $Zr^{+4}$ | 20.0 | 35% |

Procedure

Transfer to a 25 ml. volumetric flask, 5 - 10 ml. of a nearly neutral sample solution containing aluminum, iron or both, having a total concentration of 10 - 60 micrograms. Add, in the following order, 1 ml. of HCl (1:9), 1 ml. of $HNO_3$ (1:9) (to convert all iron to the ferric state) 5 ml. of ammonium acetate (10%), and 2 ml. of ferron (0.2%). Dilute to 25 ml. and read the extinction in Beckman 1 cm. cells at the wave lengths 600 mµ and 370 mµ. Determine the total iron present from Curve A, Figure 4, the calibration curve for iron at 600 mµ. The contribution of this concentration of iron to the total extinction measurement at 370 mµ may be determined from Curve B, Figure 4. Subtract this value from the total extinction. The concentration of aluminum present which is responsible for the remainder of the total extinction at 370 mµ is calculated from Figure 3.

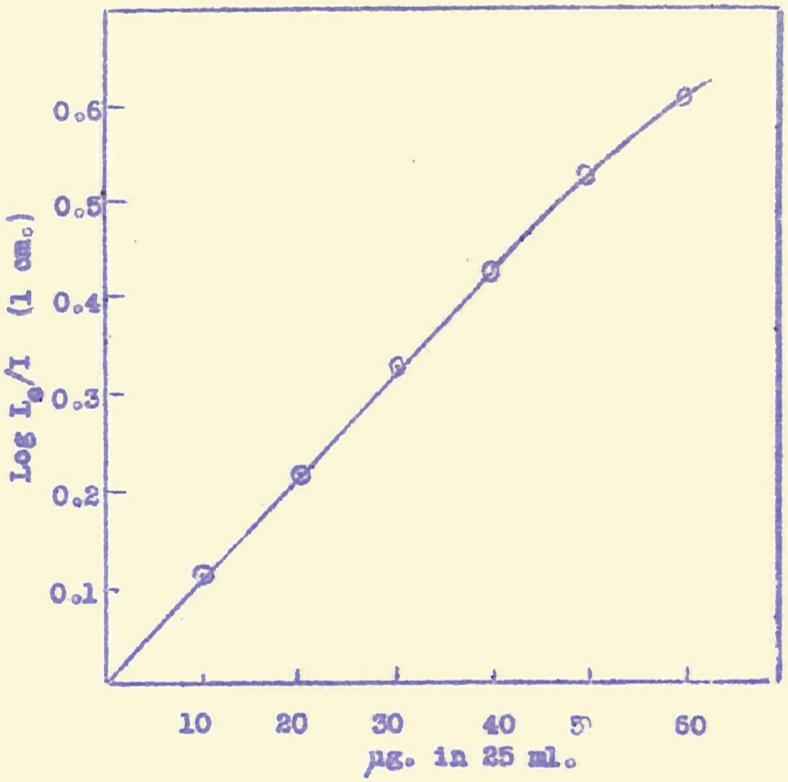


Figure 3. Aluminum Calibration Curve
370 mµ. pH=5.0, 2ml. Ferron (0.2%)

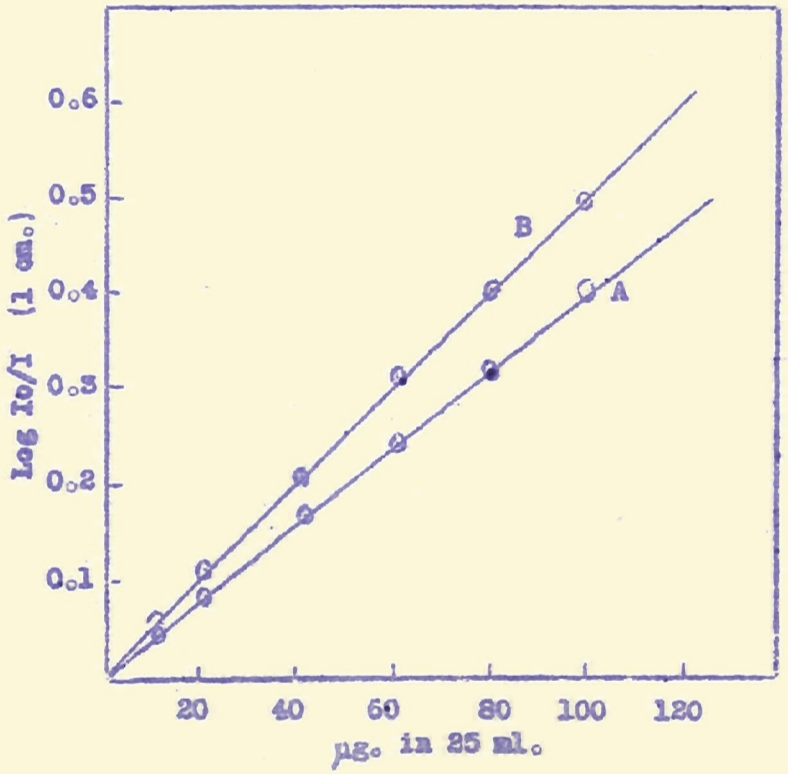


Figure 4. Iron Calibration Curve
pH=5.0, 2 ml. Ferron (0.2%)
A. 600 mµ B. 370 mµ.

## Results

A number of mixed solutions containing known amounts of aluminum and iron in varying ratios were prepared and analyzed by the ferron method. The results appear in Table II.

### Table II

### Results of Analysis of Aluminum - Iron Solutions by the Ferron Method

| | Present | | Found | |
|---|---|---|---|---|
| Sample No. | Al µg./25 ml. | Fe µg./25 ml. | Al µg./25 ml. | Fe µg./25 ml. |
| 1 | 10.0 | 20.0 | 9.5 | 19.5 |
| 2 | 20.0 | 20.0 | 20.0 | 20.5 |
| 3 | 30.0 | 20.0 | 29.0 | 20.5 |
| 4 | 20.0 | 10.0 | 19.2 | 10.0 |
| 5 | 20.0 | 20.0 | 20.0 | 20.0 |
| 6 | 20.0 | 30.0 | 19.2 | 30.5 |
| 7 | 10.0 | 10.0 | 9.6 | 10.0 |
| *8 | 10.0 | 80.0 | 9.2 | 78.0 |
| *9 | 40.0 | 10.0 | 39.0 | 10.0 |
| *10 | 20.0 | 40.0 | 19.5 | 40.0 |

*Absorption did not change after standing 24 hours.

## Summary

Aluminum in a buffered acetate solution at a pH 5 forms a complex with ferron which obeys Beer's Law for amounts of aluminum in the range 0 - 40 µg./25 ml.

The interference due to iron may be accurately determined by spectrophotometric measurements of the same solution at another wave length.

The complexes of aluminum and iron are stable for at least 24 hours. Cations which form hydroxyquinolates in slightly acid media give positive interference in the colorimetric method. In the presence of these interfering cations, a

preliminary separation of aluminum and iron is necessary. The method is applicable to the direct determination of traces of aluminum in water solutions and soil extracts.

## Acknowledgements

The author wishes to thank H. L. Heaphill and P. F. Thomason of this laboratory for constructive criticisms.

## Literature Cited

(1) Yoe, J Am. Chem. Soc., 54, 4139 (1932).

(2) Swank and Mellon, Ind. and Eng. Chem. Anal. Ed., 9, 406 (1937).

(3) Knudson, H. W., Meloche, V. W., and Juday, C., Ind. Eng. Chem. Anal. Ed., 12, 715 (1940). Hatfield, W. D., Ind. Eng. Chem. 16 233 (1924). Steenkamp, J. L. J. S. African Chem. Inst. 13, 64 (1930).