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AN INVESTIGATION OF THE COLORIMETRIC METHODS FOR THE
DETERMINATION OF FLUORINE BY THE ZIRCONIUM
ALIZARIN SULFONATE METHOD

By

WILLIAM L. BREAK

A

THESIS

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN CHEMISTRY

Rolla, Missouri

[1947]

Approved by

W. S. Scherck
Chairman, Department of Chemical Engineering
and Chemistry

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INTRODUCTION

There has been a need for a rapid and an accurate method for the determination of fluorine in its compounds. Both gravimetric and volumetric methods have been studied, but both methods were time consuming or inaccurate or both.

Colorimetric methods had been studied before F. Richter¹ developed his method but none had been reported to be as satisfactory as his method. This method was investigated because it was thought that F. Richter's method would be a satisfactory colorimetric determination for fluorine in its compounds.

(1) Richter, F. The Colorimetric Determination of Fluorine in Simple and in Complex Fluorides by Means of Zirconium Alizarin Lake. Z. Anal. Chem. Vol. 124. pp. 161-216 (1942) (Translation)

REVIEW OF PREVIOUS WORK

DeBoer and Basart² described a titration of fluorine by means of a zirconium alizarin indicator lake. An excess of the lake was added. The excess lake was titrated with a standard solution of potassium fluoride. The appearance of the yellow color of the liberated alizarin indicated the end point.

One of the first colorimetric methods was developed and described by George Steiger³ of the United States Geological Survey. This method depended on the bleaching of pertitanic acid by soluble fluorides. The color of the bleached pertitanic acid was compared with a sample that had been bleached by a known amount of fluorine. The optimum pH determined for this reaction was 1.5⁴.

Treadwell and Kohl⁵ studied a potentiometric titration of fluorine. The soluble fluoride was titrated with

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- (2) DeBoer, J. H. and Basart, J. A Rapid Volumetric Determination of Fluorine Even in Complex and Insoluble Fluorides. Z. Anor. Chem. Vol. 152. pp. 213-20 (1926) (Chem. Abstracts)
- (3) Steiger, George. Analysis of Fluorspar. J. Am. Chem. Soc. Vol. 30. pp. 219-29 (1908)
- (4) Wickman, H. J. and Dahle, D. Determination of Small Amounts of Fluorine by the Steiger-Merwin Reaction. J. Assoc. of Agr. Chem. Vol. 6. pp. 612-19 (1933)
- (5) Treadwell, W. D. and Kohl, A. The Electrometric Titration of Fluorine. Helvetica Chim. Acta. Vol. 8. pp. 500-7 (1925) (Chem. Abstracts)

a standard solution of ferric chloride which contained a small amount of ferrous chloride. The ferrous chloride was added to the ferric chloride solution to give a change in potential when an excess of ferric chloride was added.

F. Pavelka⁶ first described a test for the qualitative detection of soluble fluorides. The test was made on spot paper, sensitized by dipping it in a solution of zirconium alizarin sulfonate lake and letting it dry. The suspected solution was put on the spot paper and acidified with acetic acid. The appearance of a yellow spot indicated the presence of fluorides. An attempt was made to determine the amount of fluorine present by noting the intensity of the yellow spot.

Thomson and Taylor⁷ studied the determination of fluorine in sea water. They reacted a large volume of the sea water with a zirconium alizarin lake. The color of the solution was compared to a solution that had a known amount of fluorine present.

Sanchis⁸ also determined the amount of fluorine in natural waters by modifying Thomson and Taylor's process

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- (6) Pavelka, F. A Sensitive Spot Reaction for Fluorine. Mikrochem. Vol. 6. pp. 149-51 (1928) (Chem. Abstracts)
- (7) Thomson, G. T. and Taylor, H. J. Determination and Occurrence of Fluorine in Sea Waters. Ind. and Eng. Chem., Anal. Ed. Vol. 5. pp. 87-9 (1933)
- (8) Sanchis, J. M. Determination of Fluorine in Natural Waters. Ind. and Eng. Chem., Anal. Ed. Vol. 6. p. 134 (1934)

somewhat. The solution that contained the known amount of fluorine was made as nearly as possible the same as the natural water by adding the same salts in the same concentration that the natural water contained.

Smith and Dutcher⁹ made a determination of fluorine by the use of zirconium alizarin sulfonate lake by first precipitating the natural sulfates by the addition of barium chloride. The solution was compared with a solution containing a known amount of fluorine.

F. Richter¹⁰ described a colorimetric method for the determination of fluorine by the reaction of zirconium alizarin sulfonate lake with a soluble fluoride. Two methods were described that used the lake for the reaction. Both methods were dependent on the formation of a red colloidal lake made by the addition of zirconium chloride to a solution of sodium alizarin sulfonate. Fluorine ions were reacted with an excess of the lake to liberate yellow alizarin. The solution of the lake and the fluorine ions was heated in a water bath at the boiling point of water to speed up the reaction and to coagulate the lake. The precipitate was then filtered from the sample and an excess of zirconium chloride was added to reproduce the red

(9) Smith, F. and Dutcher, H. A. Colorimetric Determination of Fluorine.
Ind. and Eng. Chem., Anal. Ed. Vol. 6. pp. 61-2 (1934)

(10) Richter, F. op. cit. pp. 161-216

colored lake. This red color was measured by means of the spectrophotometer and a calibration curve was constructed from results obtained by using varying amounts of fluorine. The red color was proportional to the amount of fluorine present. The fluoride samples were dissolved by using reagent grade hydrochloric acid and sodium tetraborate. The fluorine formed the complex fluo-borate ion with the sodium tetraborate and prevented the volatile fluorine from being lost. The formation of the fluo-borate also prevented etching of the glass.

In the other method the fluorine was distilled as silicon tetrafluoride. An aliquot portion of the distillate was then reacted with an excess of the lake. This was done to distill the fluorine off from any interfering impurities. Both methods used the calibration curve, and both methods gave good results, but the distillation method was more applicable because no interfering materials were present.

EQUIPMENT

Colorimeter

A Klett-Summerson photoelectric colorimeter was used to make all measurements of color concentration of the solutions. The amount of light transmitted by the solution was proportional to the amount of liberated alizarin in the solution. The solutions were all diluted to the same volume to keep this variable constant. A schematic diagram is presented in figure 1 on page 6.

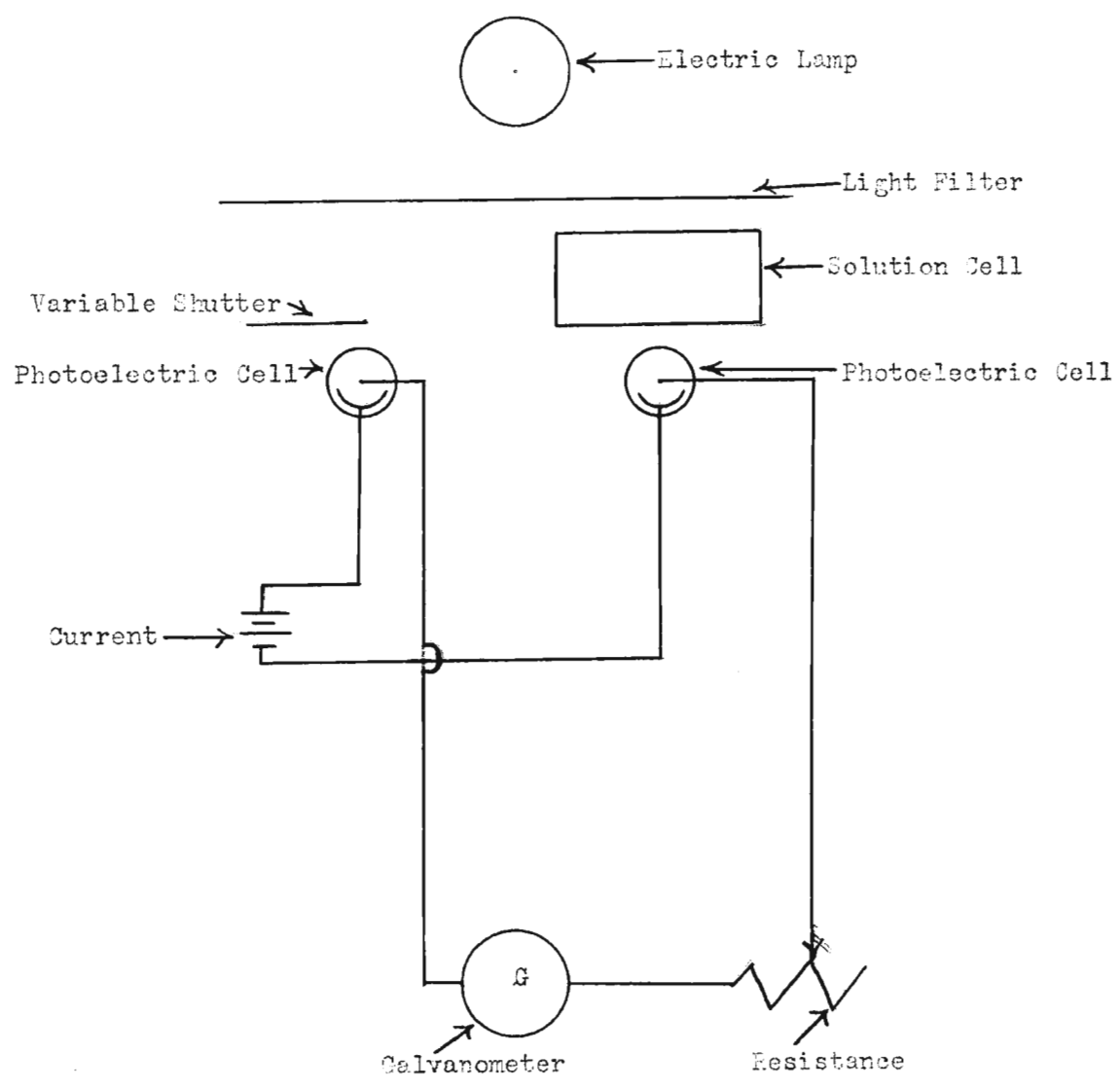
Jena G-3 Filtering Crucibles

The Jena G-3 filtering crucibles were used to filter the coagulated lake from the sample.

Suction Flask

An eight inch test tube was placed in the suction flask to catch the filtrate. The test tube was used to facilitate the quantitative transfer of the filtrate from the suction flask to the volumetric flasks.

Fig. I A Schematic Diagram of a Photoelectric Colorimeter



REAGENTSZirconium Alizarin Sulfonate Lake¹¹

34.4 grams of zirconium oxy-chloride or 17 grams of zirconium hydroxide was weighed and transferred to a one liter Florence flask containing 170 ml. of 12N reagent grade hydrochloric acid and 700 ml. distilled water. The mixture was heated until all of the salt was dissolved. The hot solution was filtered on a dry filter paper. The filter paper was washed with 100 ml. of hot distilled water and the solution was diluted to seven liters. To this solution was added 4.2 grams of sodium alizarin sulfonate in 500 ml. of hot water and mixed thoroughly. The solution was allowed to cool to room temperature and diluted to 10 liters. This lake was allowed to stand for 14 days. The supernatant liquid was then siphoned from the slimy precipitate in the bottom of the flask. This solution was very stable and when properly stored maintained its strength for a period of 12 months.

Zirconium oxy-chloride was used in preference to zirconium oxy-nitrate for the preparation of this lake. The nitrate in the presence of strong hydrochloric acid destroyed the yellow color of any liberated alizarin by oxidation.

(11) Richter, F. Ibid. p. 162

Hydrochloric Acid

This acid was prepared by diluting one volume of concentrated reagent grade hydrochloric acid with an equal volume of distilled water. This gave an acid that was not so volatile and was used for dissolving all samples. 150 ml. of this acid was used for each liter of fluoride solution.

Sodium Tetraborate

Baker's C.P. sodium tetraborate was used to dissolve all samples and 6 grams was used per liter of solution.

Sodium Chloride Solution

This solution had 350 grams of reagent grade sodium chloride per liter of solution. This salt provided some buffering action.

Asbestos

A long fiber reagent grade Powminco asbestos was used. This asbestos was freed of iron by a concentrated hydrochloric acid extraction.

PRELIMINARY WORK

It should be possible to evaluate F. Pavelka's¹² test quantitatively if all the variables could be ascertained and some suitable colorimetric method for the measurement of the color be developed.

One of the first tasks was to determine how to get the reaction to proceed on stoichiometric basis. After some experimentation, it was found that the reaction was favored by a high concentration of hydrochloric acid. The reaction was much faster and went to completion when the acid concentration was high. The next problem was to select the proper light filter.

Selection of the Proper Light Filter

The proper light filter was determined by running samples with all conditions constant except the amount of lake used. The mixed samples were allowed to stand for 5 minutes. Then the solution was boiled for 30 minutes, cooled and filtered. The readings were taken after the filtered sample had been diluted to 100 ml.

The results indicated that light filter No. 42 was the best selection. These data are presented in table I.

(12) Pavelka, F. Op. Cit.

Table I Selection of the Proper Light Filter

Sample	1	2	3	4
Filter Number	Reading	Reading	Reading	Reading
42	478	478	520	520
54	14.1	15.8	21.9	19.1
66	negative reading	negative reading	negative reading	negative reading
Milligrams Fluorine	3.25	3.25	3.25	3.25
Milliliters Lake	7.75	7.75	8.75	8.75

Effect of Acid Concentration on the Reaction

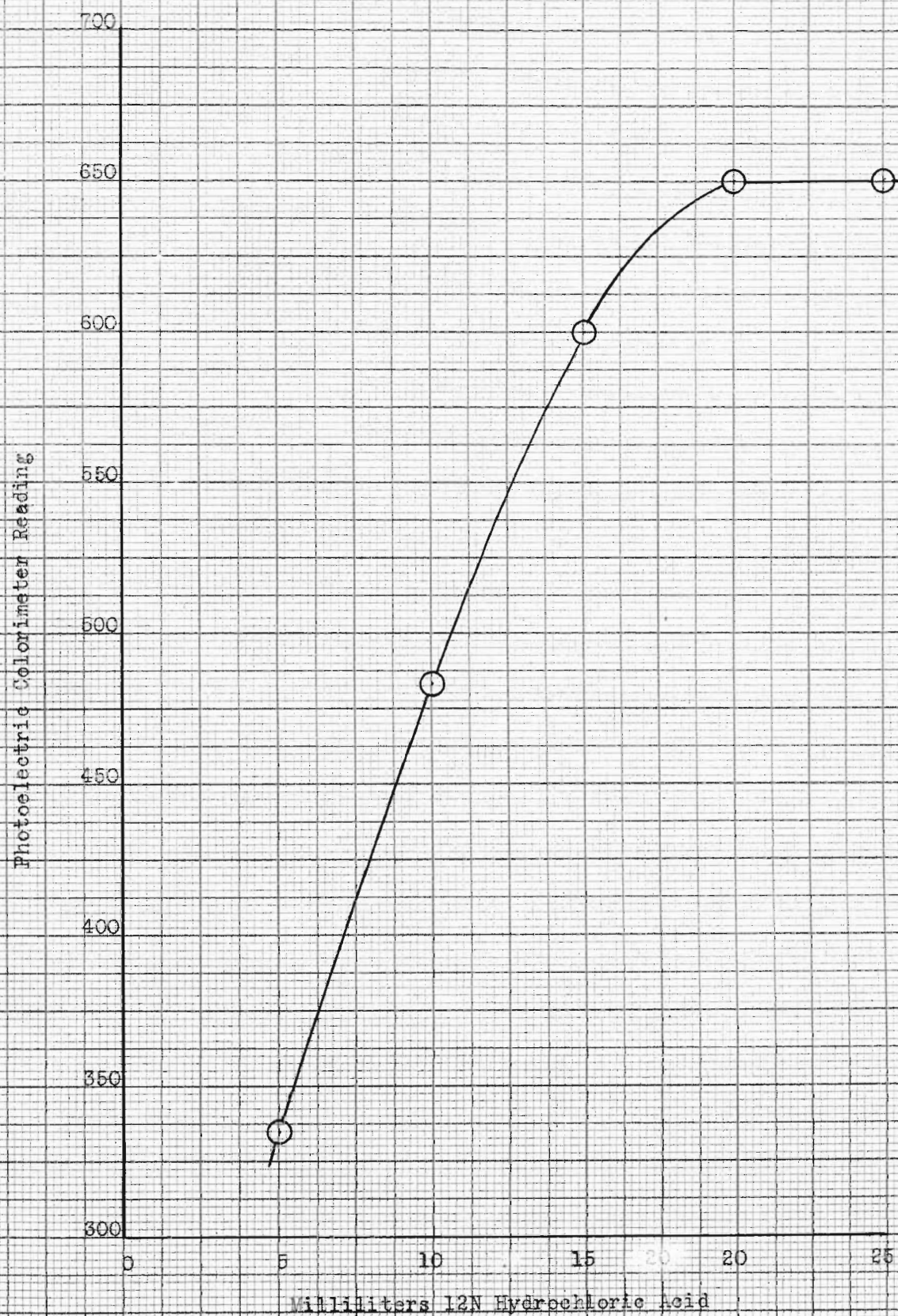
The proper concentration of hydrochloric acid was determined by maintaining all factors constant except the hydrochloric acid concentration which was varied. The mixed samples were allowed to stand for 5 minutes before boiling. Then the samples were boiled for 30 minutes and filtered. The filtered samples were diluted to 1000 ml.

The results indicated that the minimum concentration of 12N hydrochloric acid was 20 ml. per 100 ml. of reacting solution. These data are presented in table II and figure II.

Table II Effect of Acid Concentration on the Reaction

Spl.	Ml. 12N HCl	ml. NaCl	ml. Lake	mg. F.	Reading	Description
1	5	10	45	15	337	Filtrate Red
2	10	10	45	15	488	" Pink
3	15	10	45	15	600	" Orange
4	20	10	45	15	650	" Yellow
5	25	10	45	15	650	" Yellow

Fig. II Effect of Acid Concentration on the Reaction



Effect of Boiling Time on the Reaction

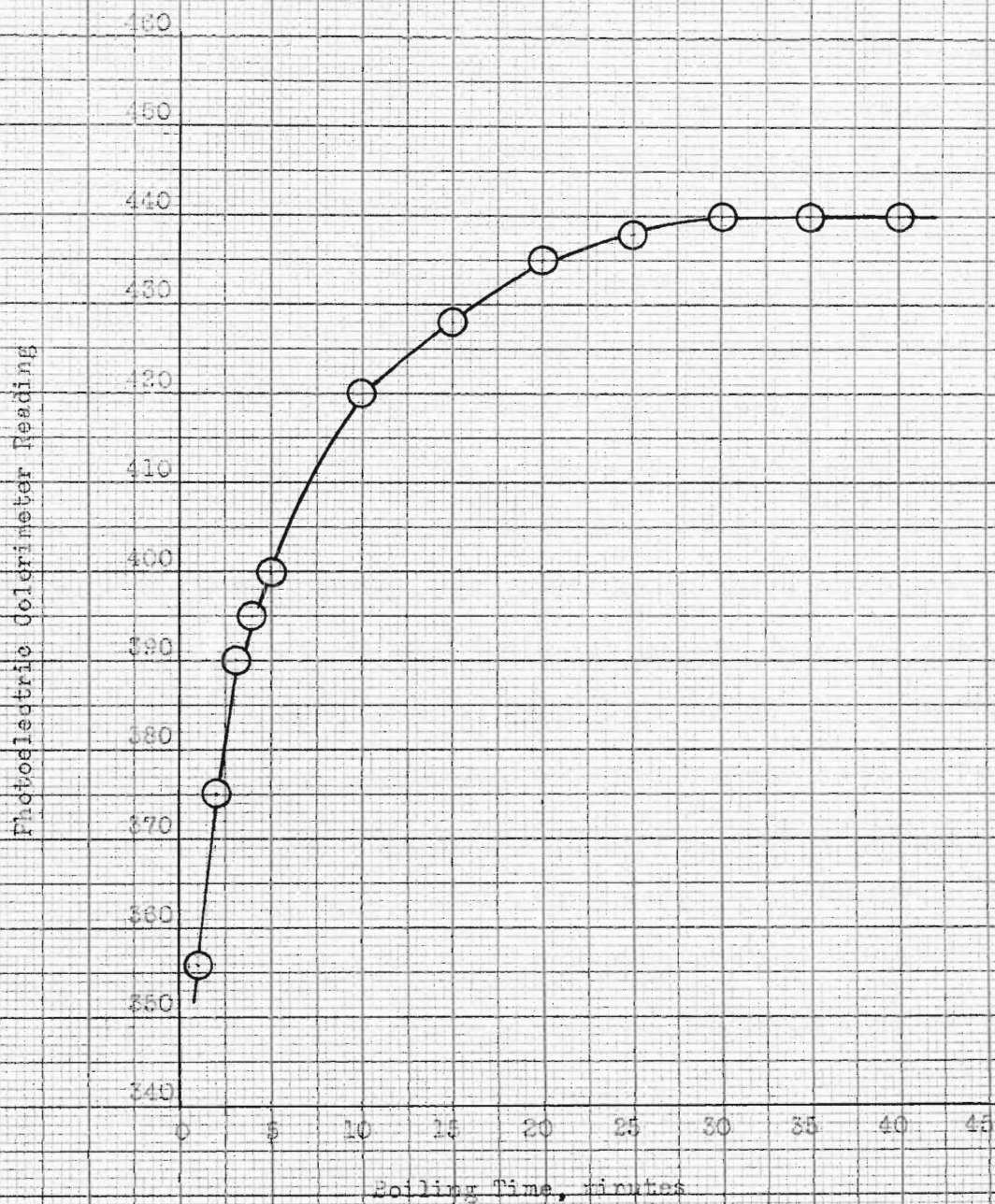
The minimum boiling time was determined by maintaining all factors constant except the length of the boiling time, which was varied 1 min., 2 min., 3 min., 4 min., 5 min., 10 min., 15 min. on up to 40 minutes. Before the samples were placed in the boiling water bath, they were allowed to stand for 5 minutes. The filtered samples were diluted to 100 ml.

The results indicated that most of the alizarin was liberated after boiling for 15 minutes but maximum liberation was not attained till the sample had been boiled for a minimum of 30 minutes. These data are presented in table III and figure III.

Table III Effect of Boiling Time on the Reaction

Spl.	mg.F.	ml.HCl	ml.NaCl	Reading	ml.H ₂ O	ml. Lake	Boiling Time
1	4	20	10	357	35	15	1 min.
2	4	20	10	375	35	15	2 "
3	4	20	10	390	35	15	3 "
4	4	20	10	395	35	15	4 "
5	4	20	10	400	35	15	5 "
6	4	20	10	420	35	15	10 "
7	4	20	10	428	35	15	15 "
8	4	20	10	435	35	15	20 "
9	4	20	10	438	35	15	25 "
10	4	20	10	440	35	15	30 "
11	4	20	10	440	35	15	35 "
12	4	20	10	440	35	15	40 "

Fig. III Effect of Boiling Time on the Reaction



CONSTRUCTION OF CALIBRATION CURVES

Two calibration curves were constructed with all factors remaining constant except the fluorine content and two concentrations of lake was used. The samples were allowed to stand for five minutes, after adding the lake, and then they were boiled for 30 minutes. The filtered samples were diluted to 100 ml. Calibration curve No. 1 had 15 ml. of lake and calibration curve No. 2 had 20 ml. of lake.

Calibration curve No. 1 was used in preference to calibration curve No. 2 because results indicated that it would give greater accuracy due to its greater slope. The slope was greater because the sensitivity of the photoelectric colorimeter was greater at lower concentrations or readings.

The results indicated that fluorine contents should be limited from 2.5 to 4.5 mgm. fluorine for curve No. 1 and 7.5 to 9.5 mgm. fluorine for curve No. 2. These data are tabulated in tables IV and V and in figures IV and V.

Table IV Construction of Calibration Curve No. 1

Spl.	mg.F.	Reading	ml.Lake	ml.HCl	ml.NaCl	ml.H ₂ O	Description
1	2.0	288	15	20	10	47.50	Filt. Pink
2	3.0	360	15	20	10	43.75	" Yellow
3	4.0	445	15	20	10	40.00	" "
4	5.0	520	15	20	10	36.25	" "
5	6.0	555	15	20	10	32.50	" "
6	7.0	560	15	20	10	28.75	" "
7	8.0	570	15	20	10	25.00	" "

Fig. IV Construction of Calibration Curve No. 1

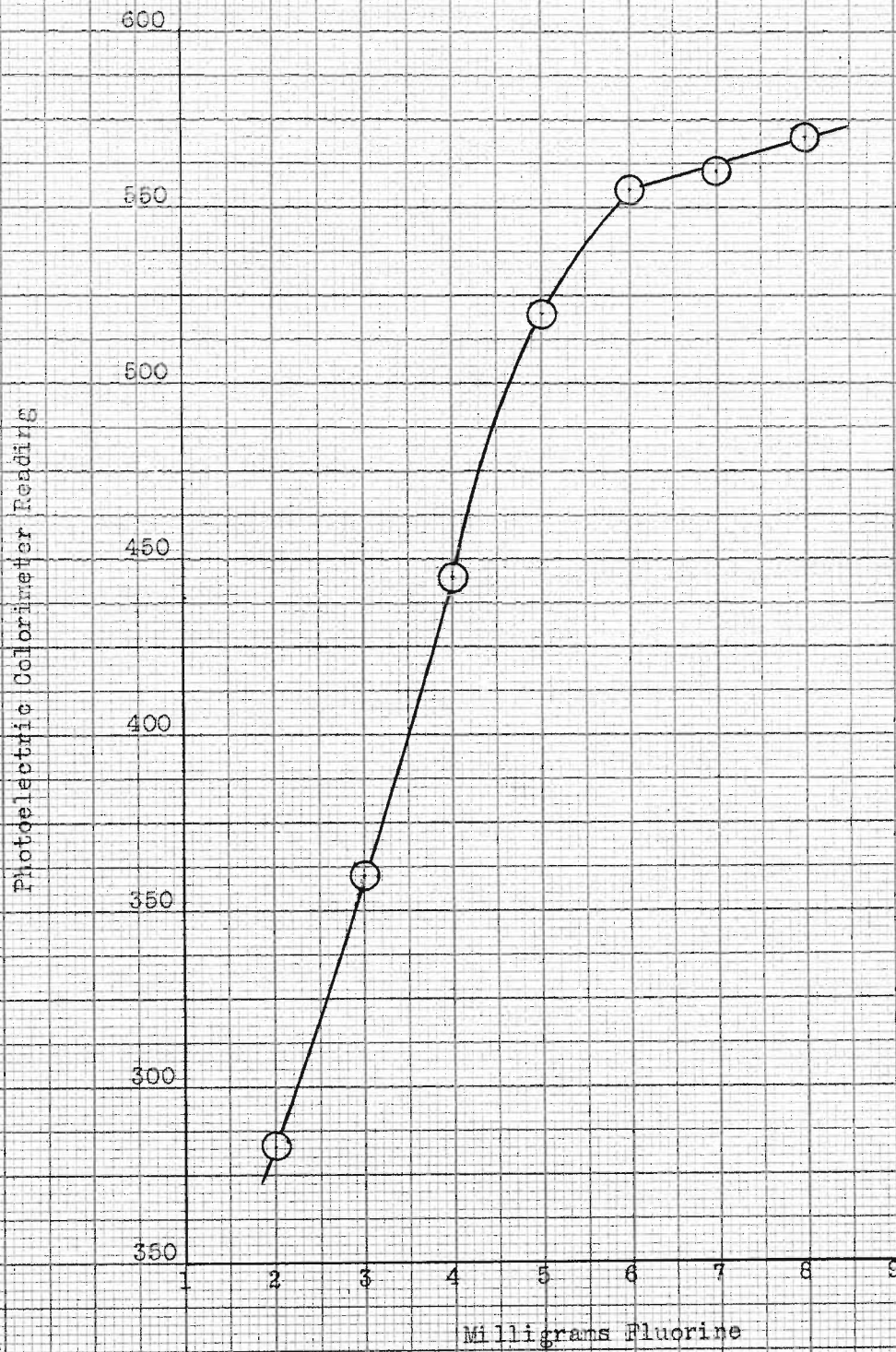
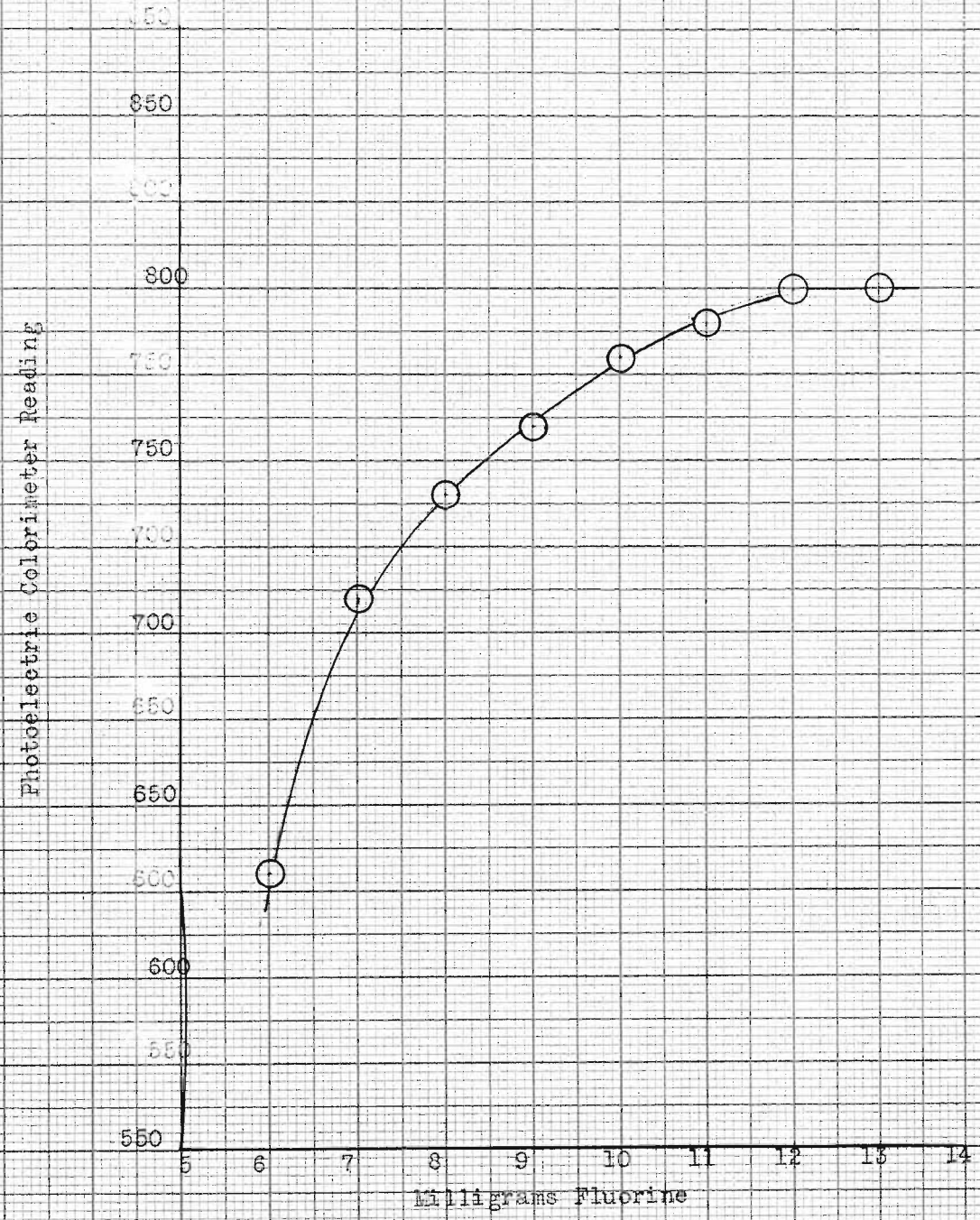


Table V Construction of Calibration Curve No. 2

Spl.	mg.F.	Reading	ml.Lake	ml.NaCl	ml.HCl	ml.H ₂ O	Description
1	6.0	630	20	10	20	27.50	Filt. Pink
2	7.0	710	20	10	20	23.75	" Orange
3	8.0	740	20	10	20	20.00	" Yellow
4	9.0	760	20	10	20	16.25	" "
5	10.0	780	20	10	20	12.5	" "
6	11.0	790	20	10	20	8.75	" "
7	12.0	800	20	10	20	5.00	" "
8	13.0	800	20	10	20	1.25	" "

Fig. V Construction of Calibration Curve No. 2



PROCEDURE USED IN ANALYZING SAMPLES

The same procedure was used in analyzing samples as was used in constructing the calibration curves. The size of the sample, that was weighed for analysis, was determined by its fluorine content and a sample of material was weighed so that the fluorine content would fall in the correct range of the calibration curve. If the range of the fluorine content was not known, a preliminary analysis was sometimes necessary.

The samples were dissolved with 150 ml. of 6N hydrochloric acid and 6 grams of sodium tetraborate. The solutions then were diluted to 1000 ml. and an aliquot portion was analyzed. The aliquot samples were placed in a 125 ml. Erlenmeyer flask and the required amounts of reagents were added. The samples were allowed to stand for five minutes and then they were placed on the hot plate and brought to a boil as quickly as possible. At the first sign of boiling the flasks were transferred to a boiling water bath and boiled for exactly 30 minutes. They were then cooled rapidly with running water, filtered, and diluted to 100 ml. All samples had 20 ml. of 12N hydrochloric acid, 10 ml. of sodium chloride, and 15 ml. of lake and enough water to dilute the sample to 100 ml.

Analysis of Synthetic Samples

A series of synthetic samples were made by blending varying amounts of reagent grade calcium carbonate with reagent grade calcium fluoride. These samples were ground with an agate mortar and pestle to insure homogeneous mixing. The samples were then analyzed by the proposed procedure with the aid of the calibration curve and these analyses compared with the theoretical percentage of calcium fluoride.

The results of these analyses indicate that the procedure was satisfactory.

A sample of sodium fluoride was analyzed by use of this calibration curve and found to be satisfactory on sodium fluoride. The sample analyzed was found to have 99.94% sodium fluoride. The purity was 99.63% sodium fluoride as reported by other methods.

These data are presented in table VI.

Table VI Comparison of Analysis of Synthetic CaF_2 Samples to the Theoretical

Spl.	Percentage Composition	% Found	Grams CaF_2 Present	Grams CaF_2 Found	Grams Deviation	Weight of Spl.
1	10.04	10.03	0.04109	0.04105	-0.00004	0.4093
2	20.03	20.52	0.04108	0.04208	+0.00100	0.2051
3	29.99	29.98	0.04108	0.04107	-0.00001	0.1370
4	40.03	40.03	0.04107	0.04107	-0.00000	0.1026
5	49.98	49.85	0.04108	0.04097	-0.00011	0.0822
6	59.91	59.88	0.04109	0.04107	-0.00002	0.0686
7	70.00	70.50	0.04067	0.04096	+0.00029	0.0581
8	79.93	79.72	0.04106	0.04105	-0.00001	0.0515
9	89.98	89.89	0.04112	0.04107	-0.00005	0.0457
10	100.00	99.97	0.04109	0.04107	-0.00002	0.0411

ANALYSIS OF NATURAL FLUORSPAR

A natural occurring sample of fluorspar was blended with varying amounts of chemically pure calcium carbonate and ground with an agate mortar and pestle to insure homogeneity of the samples. These samples were put into solution by the use of 150 ml. of 6N hydrochloric acid and 6 gms. of sodium tetraborate and the solution was diluted to 1000 ml. An aliquot portion of the solution was run with 15 ml. lake, 20 ml. 12N hydrochloric acid, 10 ml. of sodium chloride solution and enough water to make 100 ml. total volume. The readings were taken on the filtered samples which had been diluted to 100 ml. after filtering.

These data are presented in table VII.

Table VII Analysis of a Natural Fluorspar

Spl.	Dilution with CaCO ₃	% Found	Dilution Factor times %
1	Pure	89.17%	1 X 89.17 = 89.17%
2	1:1	44.46%	2 X 44.46 = 88.92%
3	1:2	29.44%	3 X 29.44 = 88.32%
4	1:3	22.08%	4 X 22.08 = 89.12%

THE EFFECT OF SOME IONS ON THE REACTION

The effect of some ions on the reaction was tried. One gram of the salt was used in each sample. The samples were run the same way as in the analysis of synthetic samples.

Sample No. 1 had 1 gram of Aluminum chloride added to determine the effect of the aluminum ion on the reaction. The aluminum ion caused the lake to change from a red color to a purple color. This lake was difficult to coagulate and the filtrate remained pink when the solution had been boiled for 30 minutes. This was probably due to the stability of the lake when aluminum ion was added to it.

Sample No. 2 had one gram of sodium phosphate added to determine the effect of the phosphate ion on the reaction. The addition of the phosphate ion caused an almost immediate precipitation of the lake as a colorless gelatinous precipitate. The filtrate was an intense yellow color. This gave a high result which might have been attributed to the complete liberation of all the alizarin from the lake due to the coagulating effect of the phosphate ion.

Sample No. 3 had 1 gram of sodium sulfate added to check the effect of the sulfate ion on the reaction. This addition gave slightly higher results. This might have been due to additional buffering effect of the sodium sulfate or the coagulating effect of the sulfate ion.

Sample No. 4 had 1 gram of sodium nitrate added to determine the effect of the nitrate ion on the reaction. The lake had completely decolorized at the end of 12 minutes boiling time and was water white with no precipitate. This might have been caused by oxidation of the free alizarin.

The results indicated that some ions interfere with the reaction. The effect of other ions should be studied and the effect of different concentrations of these ions should be studied.

These data are presented in table VIII.

Table VIII The Effect of Some Ions on the Reaction

Spl.	mgm. F. Present	mgm. F. Found	Reading	Interfering Ion
1	3.8	2.5	325	Aluminum ion
2	3.8	above curve	580	Phosphate ion
3	3.8	5.0	520	Sulfate ion
4	3.8	0.0	0	Nitrate ion

CONCLUSIONS

F. Richter's colorimetric method for the determination of fluorine was investigated. The results were satisfactory for high and low fluorine contents.

It was found that the method was not applicable when interfering substances were present.

The calibration curve was constructed by using the same material that was analyzed for its fluorine content.

All conditions had to be maintained as nearly constant as possible.

SUMMARY

1. Insoluble and soluble fluorides were dissolved with hydrochloric acid and sodium tetraborate to prevent the loss of volatile hydrofluoric acid and to prevent the glass from being etched by the hydrofluoric acid.

2. An excess of zirconium alizarin sulfonate was reacted with the fluoride solutions to liberate yellow alizarin.

3. A minimum of 20 ml. of 12N hydrochloric acid was used per sample.

4. The samples were boiled for a minimum of 30 minutes, cooled under running water, filtered and diluted to 100 ml. This solution was then placed in the solution cell and read by means of the photoelectric colorimeter. The readings were proportional to the amount of fluorine present.

5. A calibration curve was made from results obtained by using varying amounts of fluorine and by keeping all other conditions constant.

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VITA

The author, William L. Break, was born November 28, 1922 at Cape Girardeau, Missouri.

His early education was at Franklin grade school where he spent eight years. The next four years were spent at the Cape Central High School where he majored in the sciences.

In 1941 he entered school at Southeast Missouri State Teachers College to take his pre-engineering work before transferring to Missouri School of Mines in 1943. At the Missouri School of Mines he majored in Chemical Engineering. After graduating in 1945, he stayed for graduate work in chemistry.