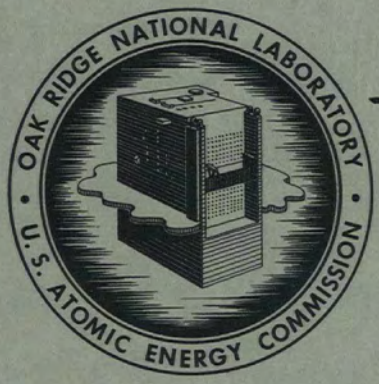
4

ORNL-2489
Chemistry-General

THERMOMETRIC (ENTHALPYMETRIC) TITRATION OF FREE ACID IN THE PRESENCE OF CERTAIN HYDROLYZABLE IONS

F. J. Miller
P. F. Thomason



OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

Printed in USA. Price 1.25 cents. Available from the

Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

ORNL-2489
Chemistry-General

Contract No. W-7405-eng-26

Analytical Chemistry Division

THERMOMETRIC (ENTHALPYMETRIC) TITRATION OF FREE ACID IN THE PRESENCE OF CERTAIN HYDROLYZABLE IONS

Francis J. Miller
Paul F. Thomason

DATE ISSUED

JUN 13 1958

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

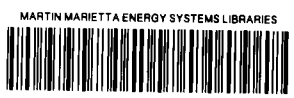


TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. ABSTRACT

For the purpose of this investigation, free acid is defined as the excess of acid over the stoichiometric amount required by the cation or cations present in the solution. The free acid is determined by titrating the sample solution with a standard base and recording the change in temperature, as detected by a thermistor, that takes place during the titration. The plot of temperature versus volume of titrant added is made automatically by use of a recording potentiometer. The end point of the titration is obtained by extrapolation of the straight-line portions of the curve.

The systems that have been studied are zirconium in hydrofluoric acid, uranyl ion in sulfuric acid, thorium in nitric acid, and uranyl ion in nitric acid. Application of the method is limited to those systems in which the heat of hydrolysis of the cation is sufficiently different from the heat of neutralization of the free acid that an end-point indication can be obtained. Free acid has not been successfully titrated by the thermometric (enthalpymetric) method in the presence of certain ions; iron(II) and (III), aluminum(III), and uranium(IV) are examples of these ions.

The method is applicable to the determination of small amounts of free acid. Test solutions that contain of the order of 0.1 meq of free acid can be titrated with a relative standard error of 1 to 2% at the 95% confidence level. The relative standard error increases to about 5% in the range of 0.01 meq.

2. INTRODUCTION

The term "free acid" is defined as the excess of acid over and above the stoichiometric amount required by the cation or cations present in a test solution. This is the definition commonly accepted at ORNL. Booman et al.[1] define it differently as "that amount of acid which would remain if the hydrolyzable ions were removed from solution."

The determination of free acid has not been a matter of great concern to many authors. There is a paucity of information on the subject in most textbooks. It is probable that many authors consider the topic to have been covered in discussions of pH.

Free acid has been determined in one of three ways; these are as follows:

(a) The most general way is by the addition of a complexing agent[8] to the test solution and subsequent titration of the free acid. The complexing agent either keeps the hydrolyzable ion in solution by formation of a nonhydrolyzable species or precipitates the hydrolyzable ion leaving in its stead in solution a neutral, nonhydrolyzable species. The oxalate ion has been the most widely used of the complexing agents, although potassium fluoride and other complexing agents have also been used.

The titration that is made after the addition of the complexing agent has been followed in various ways, for example, visually by use of indicators, by pH measurements, and by conductometric measurements.

Difficulties are inherent in the use of complexing agents. Some of these have been discussed in detail by Booman et al.[1] The complexing agent

itself must be so selected and neutralized that no excess acidic or basic compounds are introduced into the solution. The end point of a pH titration must be chosen so that a minimum bias is introduced. The choice of the end point requires considerable knowledge of the equilibria involved; this knowledge is not always available.

(b) A pH titration may be made, without the use of a complexing agent, to a selected pH value. This is the method delineated by Jones et al.[5] A titration curve of the acid alone is made, and then the acid plus the hydrolyzable cation are titrated. It is possible by preparing a number of such curves in which the concentrations of the acid and the hydrolyzable cation are varied to preselect a pH value that will serve as an end point for the determination of free acid.

(c) The conductometric method has been proposed by Pepkowitz et al.[10] and has been studied further by Propst.[11] This method is reported to be extremely sensitive and adaptable for use with small samples of radioactive materials. The method is in routine use at the Savannah River Laboratory. Rather complicated equipment is required, and the titration time is considerable. Booman et al.[1] comment that "the conductometric titration of acid solutions gives results of questionable accuracy when precipitates are formed."

All the methods described above have peculiar advantages and disadvantages. The investigation of the thermometric (enthalpymetric) determination of free acid that is reported herein was made relative to the analysis of solutions that contained zirconium dissolved in an excess of hydrofluoric acid because no standard method seemed adaptable to the determination of free acid in this system.

Thermometric methods[4] have been known to analytical chemists since the pioneer work of Dutoit and Grobet.[3] More recently Müller[9] suggested the use of a thermistor as a heat-sensitive device to replace the Beckman thermometer, which is still being used by some workers. Linde et al.[7] adapted the use of a thermistor to automatic thermometric titrations. Jordan and Alleman[6] followed up the work of Linde et al.[7] by determining heats of chelation by thermometric titration. Jordan and Alleman[6] have preferred to call the technique "enthalpymetric" titration, a term which has greater relation to the fundamental, thermodynamic quantities upon which the technique is based. This relationship is described by the equation

$$\Delta H = \Delta F - T\Delta S \qquad (1)$$

in which

ΔH = enthalpy change, cal/mole,

ΔF = free energy change, cal/mole,

T = temperature, ^{o}K, and

ΔS = entropy change, cal/mole.

The equation indicates that a thermometric titration is sensitive not only to a reaction in which there is a change in free energy but also to one in which the entropy change is significantly large although the free-energy change is small. By consideration of thermodynamic data, if it is available, the feasibility of a thermometric titration can often be determined without experimentation.

The thermometric titration method for the determination of free acid has been evaluated experimentally for free acid in aqueous solutions in the presence of the following hydrolyzable ions: zirconium(IV), uranyl, thorium(IV), and thorium(IV) and uranyl together. A method has been prepared for issue to the ORNL Master Analytical Manual (Method Nos. 1 220005 and 9 00720005, "Free Acid in Aqueous Solutions of Hydrofluoric Acid and Zirconyl Fluoride, Thermometric Titration Method.")

3. SUMMARY

Free acid can be determined in systems that contain uranium(VI), thorium(IV), zirconium(IV), hydrofluoric acid, sulfuric acid, and nitric acid by an automatic thermometric titration with a standard solution of sodium hydroxide. Test portions that contain of the order of 0.1 meq of free acid can be titrated with a relative standard error of 1 to 2%.

Titrant is added at a constant rate by a motor-driven, Greiner microburet to the test solution that is contained in a beaker inside a Dewar flask. Stirring is accomplished by means of a spiral glass stirrer that is turned at a rate of 300 rpm by a water-cooled motor. The change in temperature of the solution is transmitted by a thermistor—d-c bridge arrangement to a Brown recording potentiometer, which plots a graph of volume of titrant added versus change in temperature. The end point is located by extrapolating the straight-line portions of the plotted curve to their intersection point.

The advantages offered by the thermometric technique for the determination of free acid are the elimination of the use of complexing agents, the elimination of pH titrations with their concomitant dependence upon colored indicators or pH electrodes, and the more positive advantage of supplying a simple, rugged apparatus that can yield good results with little effort by the operator.

4. EXPERIMENTAL EVALUATION OF THE THERMOMETRIC TITRATION OF FREE ACID

4.1 Apparatus

The equipment used in the series of thermometric titrations described in this report is specified in detail in Apx. I. It consists of a motor-driven microburet and associated equipment. In the initial phases of the investigation, a Micro-Metric, syringe type buret that was driven at a constant rate by the drive unit of an ORNL model Q-945 automatic titrator was used. In the later series of titrations, a Greiner microburet that had been converted by the addition of a Bodine electric motor and appropriate gears to provide a constant rate of addition was used. The Greiner microburet was mounted on a Cenco Lab-Jack that provided a means of raising or lowering the buret into or out of the solution. The use of the Lab-Jack prevented any possibility of diffusion of titrant from the buret tip during the period of temperature equilibration of the test solution.

A 300-rpm stirring motor was used to turn a spiral glass stirrer at a constant speed during the titration. It was found necessary to wind a cooling coil of 1/8-in. dia copper tubing around the stirring motor. A slow trickle of water was allowed to run through the coil while the stirring motor was in use. The cooling coil prevented the rise in temperature of the stirring motor from disturbing the titration.

The titration was carried out inside a 250-ml Dewar flask that was closed with a cork stopper. The stopper was bored with three holes that provided access for the stirrer, the thermistor, and the buret tip. A small, polyethylene beaker, which was supported by a Styrofoam block, was used as the titration vessel.

A thermistor, either a Western Electric Co's. type 14B or a Victory Engineering Corp's. type 32A1, was used as a sensitive thermometer. A thermistor is a resistor that has a large, negative temperature coefficient of resistance, that is to say, the resistance across a thermistor decreases with a rise in temperature. Consequently, if a thermistor is connected as a leg in a d-c Wheatstone bridge and the potential is read across the bridge, an indication of a change in temperature can be obtained. The compactness and simplicity of the apparatus is illustrated in Photographs 1 and 2 of Apx. I.

For experimental work, a Brown Electronik recording potentiometer that has a variable span and variable zero suppression has been used. In routine titrations, a standard Brown recording potentiometer that is equipped with a 5-mv scale is sufficient.

4.2 Procedure

The procedure used in the evaluation of the thermometric method for the titration of free acid in hydrofluoric acid solutions of zirconium is given in detail in Apx. II. The procedures used for the other systems studied were essentially the same as that given in Apx. II.

4.3 Results and Discussion

4.3.1 Free Acid in Hydrofluoric Acid Solutions of Zirconium

The heat of neutralization of hydrofluoric acid is given as -16.27 kcal/mole, which is higher than the heat of neutralization of strong acids, generally given as -12 to -13 kcal/mole. The anomalous heat of neutralization of hydrofluoric acid, a weak acid, as compared with the heat of neutralization

of strong acids was pointed out by Linde et al.[7] The anomaly is perhaps explained by the breaking of the hydrogen bonds that exist in hydrofluoric acid and the subsequent hydration of the fluoride ion. The breaking of the hydrogen bonds would, of course, require an energy input; therefore the heat evolved would be the energy supplied by the hydration of the fluoride ion less the energy required for the breaking of the hydrogen bond. The value for the heat of neutralization is taken from the Landolt-Börnstein tables.[13] From values given in Circular 500, National Bureau of Standards,[12] the heat of hydrolysis of $ZrOF_2$ can be calculated to be -4.86 kcal/mole. The pertinent equations follow:

$$NaOH + HF \rightarrow NaF + HOH \quad (-16.27 \text{ kcal/mole}) \qquad (1)$$

$$ZrOF_2 + 2\ NaOH \rightarrow ZrO(OH)_2 + 2\ NaF \quad (-4.86 \text{ kcal/mole}) \qquad (2)$$

In view of the large difference in enthalpy, a thermometric titration of the free acid in the zirconyl fluoride—hydrofluoric acid system seemed definitely feasible.

Much of the difficulty in checking free acid in solutions of various hydrolyzable ions arises in the preparation of standards. Zirconium proved to be no exception. First it was attempted to use an aqueous solution of $ZrOCl_2$ as a standard. Various quantities of hydrofluoric acid were added to test portions of the $ZrOCl_2$ solution, and titrations of the free acid were made. The results were unsatisfactory. From the work of Connick and McVey,[2] it is known that perchloric acid does not complex the zirconium ion. It was therefore decided to prepare a standard solution of zirconium

by taking a known amount of $ZrOCl_2$, fuming it with perchloric acid to remove the chloride ion, and then making up a solution of it to a known volume with a perchloric acid solution of strength sufficient to ensure that the zirconium present would be in an ionic form. Such a solution was prepared. The zirconium content was found by analysis to be 10.05 mg/ml. A 1/100 dilution of the stock solution was then prepared, and 5-ml aliquots were taken for titration with a standard solution of base (NaOH). The results of these titrations are presented in Table I; one of the titration curves is shown in Fig. 1. From the results of this series of titrations, it can be seen that a reasonably precise titration of the $ZrO(ClO_4)_2$ solution can be made.

TABLE I

Precision of the Results of the Titration of Free Acid in a Solution of Zirconyl Perchlorate

Test solution:

Zr concentration, 0.1005 mg/ml

Volume of test aliquot, 5.00 ml

Titrant, ~ 0.1 N NaOH

Aliquot No.	Titer Value, inches of chart travel	Deviation x 10^2	(Deviation)^2 x 10^4
1	3.60	9	81
2	3.68	1	1
3	3.65	4	16
4	3.75	6	36
5	3.78	9	81
	18.46	29	215
Average	3.69	0.058	

N = 5 $\bar{X}$ = 3.69 S = 0.072 S.E. at 95% level, % = 2.42

N - 1 = 4 S^2 = 0.0052 S, % = 1.95

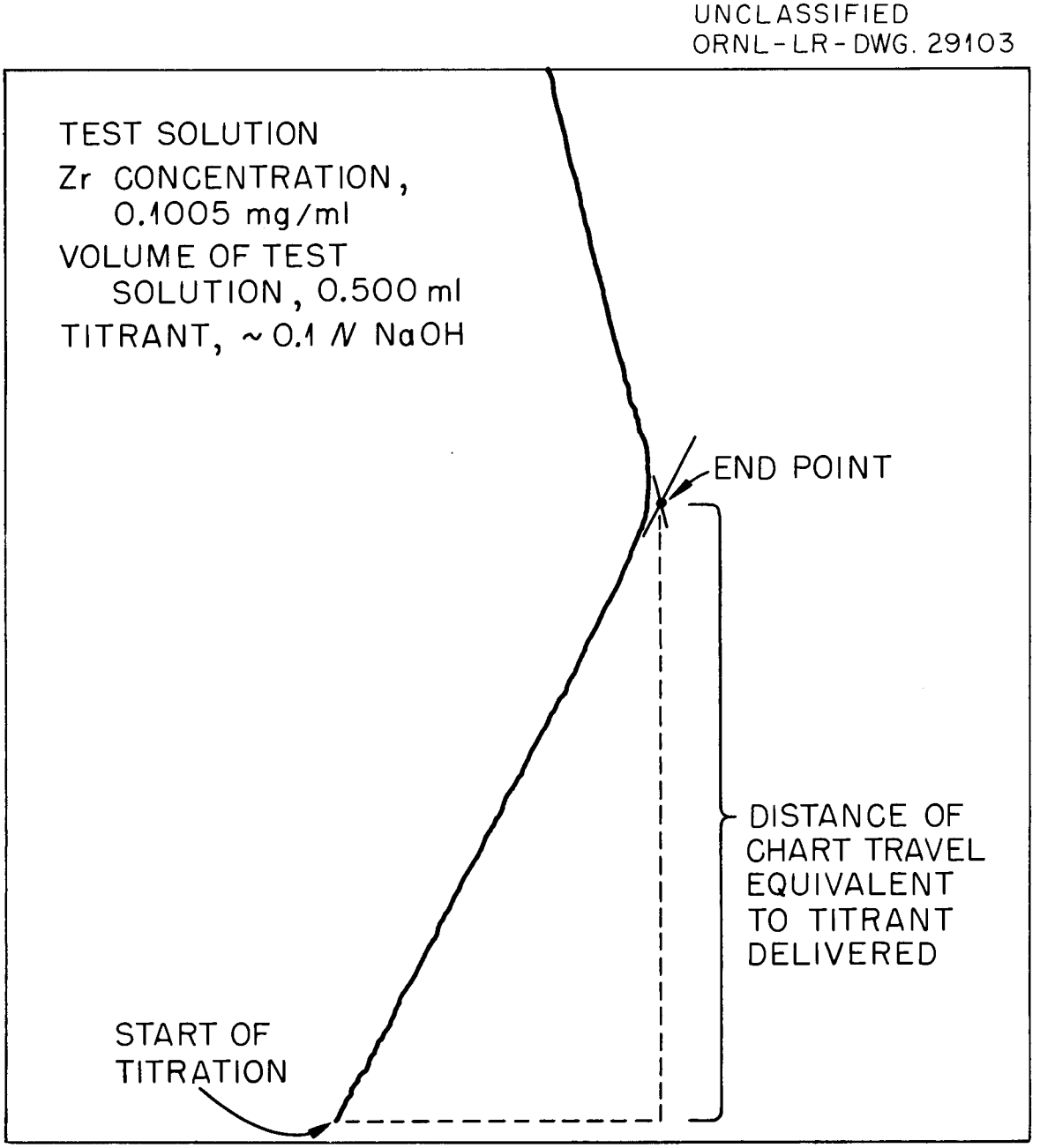


Fig. 1. Typical Curve Obtained in the Titration of Free Acid in a Solution of Zirconyl Perchlorate.

It was then decided to add different, known amounts of a standard solution of hydrofluoric acid, 0.108 N, to separate aliquots, all of the same size, of the $ZrO(ClO_4)_2$ solution for which the titer value had been obtained and to determine the free-acid content of each by thermometric titration. From a plot of the values for free acid, the recovery and bias attainable by means of the method could be estimated. The data from this experiment are given in Table II and Fig. 2; they show that the recovery of hydrofluoric acid was satisfactory and that no significant bias existed.

The results of a number of titrations of hydrofluoric acid in $ZrO(ClO_4)_2$ solution are given in Table III and Fig. 3. These titrations were made at smaller zirconium-to-HF ratios and with a smaller buret syringe than those reported in Table II. The results indicate a definite bias toward the low side for aliquots of less than 0.5 ml; for aliquots of 0.5 ml and greater, a lesser deviation toward the high side is indicated. The poorer results of Table III as compared with those of Table II are believed to have been caused by the use of the smaller buret syringe.

The results of a study of the effect of varying the amount of $ZrO(ClO_4)_2$ present on the recovery of a constant amount of HF are summarized in Table IV and Fig. 4. It can be seen from these data that the titer value for the constant amount of HF present is independent of zirconium concentration over a fairly wide range.

Uranium(IV), iron(II) and (III), and aluminum(III), when present in a test solution, act as direct interferences. No discernible inflection in the titration curve occurs between the neutralization of the free acid and the hydrolysis of these ions.

TABLE II

Results of the Recovery of Various Amounts of Hydrofluoric Acid from the Same-Sized Volumes of a Solution of Zirconyl Perchlorate

Test solution:

5.00 ml of 0.001 M $ZrO(ClO_4)_2$ solution

Indicated volume of 0.108 N HF

Titrant, 1.0115 N NaOH

Volume of buret syringe, 1.0 ml

Volume of HF Solution, ml	Titer Value, inches of chart travel	Titer Value, milliequivalents of NaOH	Milliequivalents of HF Experimental	Milliequivalents of HF Theoretical
0	3.69	-----	-----	-----
0.100	4.05	0.013	0.013	0.011
0.500	5.19	0.055	0.055	0.054
1.000	6.70	0.110	0.110	0.108

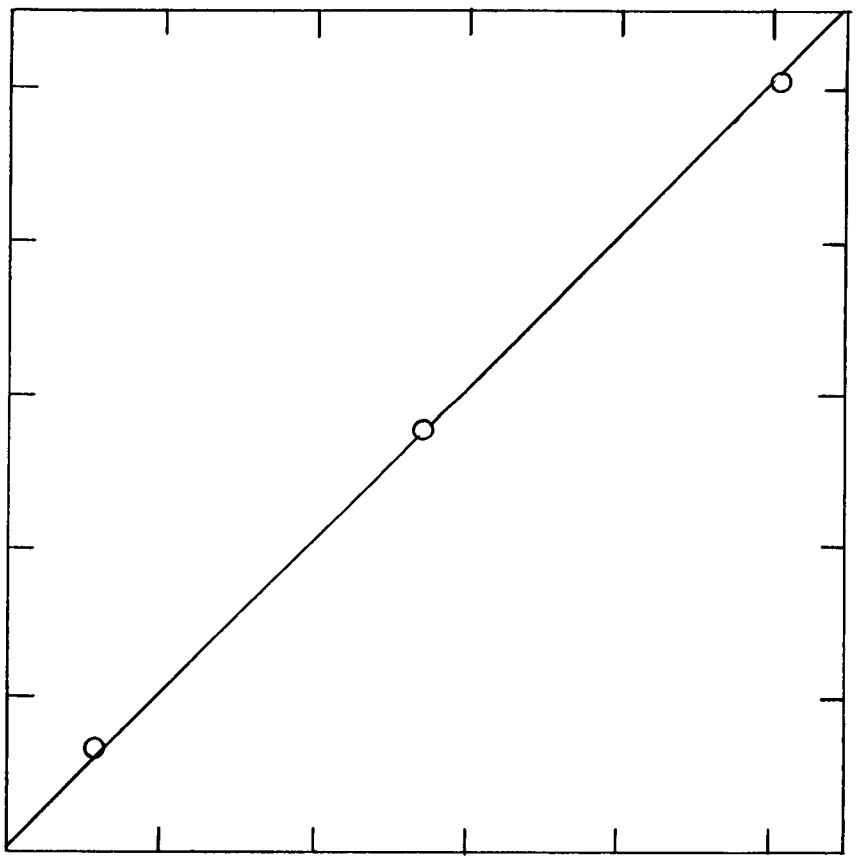


Fig. 2 Plot of the Data of Table II.

TABLE III

Effect of Varying the Concentration of Hydrofluoric Acid on the Titration of Free Acid in the Presence of a Constant Amount of $ZrO(ClO_4)_2$

Test solution,

0.100 ml of 0.001 M $ZrO(ClO_4)_2$

Indicated volume of 0.109 N HF solution

Titrant, 1.0115 N NaOH

Volume of buret syringe, 0.5 ml

Aliquot No.	Volume of HF Solution, ml	Titer Value, inches of chart travel	Titer Value, milliequivalents of NaOH	Milliequivalents of HF
1	0.100	8.08	0.0211	0.0109
2	0.200	8.25	0.0273	0.0218
3	0.250	8.50	0.0364	0.0273
4	0.500	8.95	0.0528	0.0546
5	0.750	9.65	0.0783	0.0819
6	0.800	10.02	0.0874	0.0874
7	1.000	10.25	0.1001	0.1092
8	-----	7.50	------	------

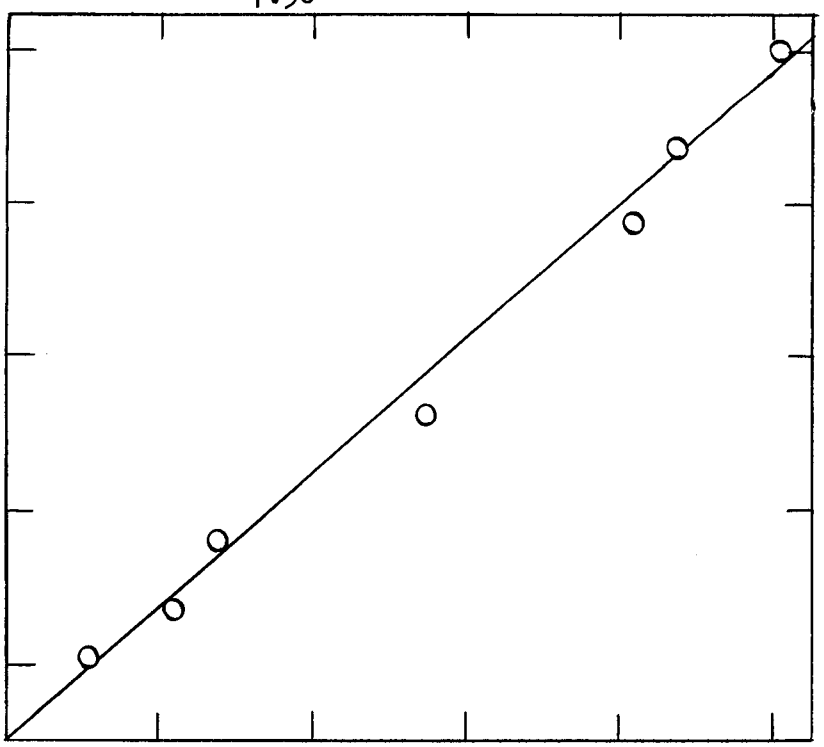


Fig. 3 Plot of the Data of Table III.

TABLE IV

Effect of Variation in the Amount of Zirconyl Perchlorate on the Recovery of a Fixed Amount of Hydrofluoric Acid

Test solution,

1.00 ml of 0.1092 N HF solution

Indicated volume of 0.001 M $ZrO(ClO_4)_2$

Water to make a final volume of 5.00 ml

Titrant, 1.0115 N NaOH

Volume of buret syringe, 0.5 ml

Volume of $ZrO(ClO_4)_2$ Solution, ml	Titer Value, inches of chart travel	Titer Value, milliequivalents of NaOH	Milliequivalents of NaOH Required by the $ZrO(ClO_4)_2$ Solution	Milliequivalents of HF*
-----	2.91	0.1059	------	0.1059
0.500	3.65	0.1329	0.1329	------
1.000	9.88	0.3596	0.2658	0.0938
0.500	6.44	0.2344	0.1329	0.1015
0.250	4.66	0.1696	0.0664	0.1031
0.200	4.47	0.1627	0.0531	0.1095
0.100	3.90	0.1420	0.0265	0.1154

* Theoretical value = 0.1092 meq.

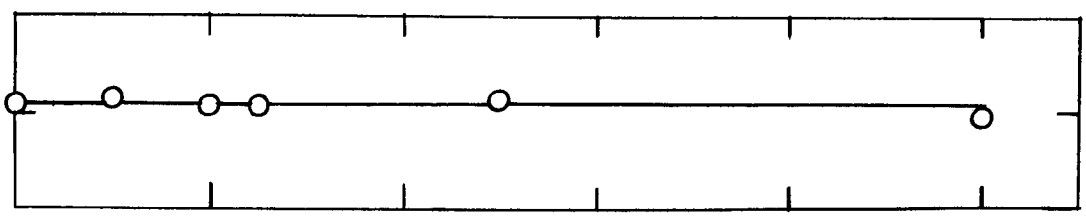


Fig. 4 Plot of the Data of Table IV.

4.3.2 Free Acid in Sulfuric Acid Solutions of Uranyl Ion

The uranyl sulfate—sulfuric acid system is another system in which the thermometric determination of free acid is feasible. The change in slope of the titration curve is remarkably sharp at the end of the free acid titration. Copper(II) may be added to the UO_2SO_4—H_2SO_4 system without precluding a successful titration, although the shape of the titration curve is altered. The hydrolysis of the copper(II) ion follows the neutralization of the free acid and precedes the hydrolysis of the UO_2^{++}. The change in the slope of the copper(II) hydrolysis curve is not as pronounced as that of the UO_2^{++} hydrolysis curve; this less pronounced change therefore presents some difficulty in the location of the end point. The results of some titrations in a system that contains UO_2SO_4, $CuSO_4$, and H_2SO_4 are given in Table V. The precision is shown to be reasonably good.

4.3.3 Free Acid in Nitric Acid Solutions of Thorium(IV) and of Thorium(IV) and Uranyl Ion

Free acid can also be determined in the $Th(NO_3)_4$—HNO_3 system by thermometric titration. This system was investigated; the results are summarized in Tables VI and VII and Figs. 5 and 6, respectively.

The data of Table VI and Fig. 5 indicate that the recovery of free acid is essentially independent of the thorium(IV) content of the solution; the data of Table VII and Fig. 6 indicate that very little bias exists in the recovery of nitric acid.

An additional study was made of a solution that contained $Th(NO_3)_4$, $UO_2(NO_3)_2$, and HNO_3. In this study the concentrations of free acid and of

TABLE V

Precision of the Results of the Determination of Free Acid in a Solution of Sulfuric Acid, Uranyl Ion, and Copper(II) Ion

Composition of test solution:

H_2SO_4 concentration, 0.05 N

UO_2^{+2} concentration (as U(VI)), 5 mg/ml

Cu(II) concentration, 1 mg/ml

Volume of test aliquot, 0.50 ml

Titrant, 1.0115 N NaOH

Aliquot No.	Titer Value, inches of chart travel	Deviation x 10^2	(Deviation)^2 x 10^4
1	1.20	2	4
2	1.20	2	4
3	1.18	0	0
4	1.15	3	9
5	1.25	7	49
6	1.15	3	9
7	1.10	8	64
	8.23	25	130
Average	1.18	3	

Standard Error = 0.0168

S.E. at 95% confidence level, % = 3.51

thorium were held constant, and the uranyl ion content was varied in order to determine its effect, if any, on the recovery of free acid. The results of the investigation are summarized in Table VIII and Fig. 7. No appreciable effect was observed.

TABLE VI

Effect of Variation in the Amount of Thorium(IV) on the Recovery of a Fixed Amount of Nitric Acid

Test solution:

0.250 ml of 1.0890 N HNO_3

Indicated weight of thorium(IV) (added as $Th(NO_3)_4$)

9.75 ml of water

Titrant, 1.000 N NaOH

Thorium Content, g	Titer Value	
	inches of chart travel	meq of NaOH*,**
------	8.40	0.272
0.0056	8.21	0.266
0.0056	8.49	0.275
0.0552	7.95	0.257
0.0552	7.85	0.254
0.5522	8.00	0.259
0.5522	8.25	0.267
5.5220	8.52	0.276
5.5220	8.50	0.277

* Same as the milliequivalents of HNO_3.

** Theoretical value = 0.272.

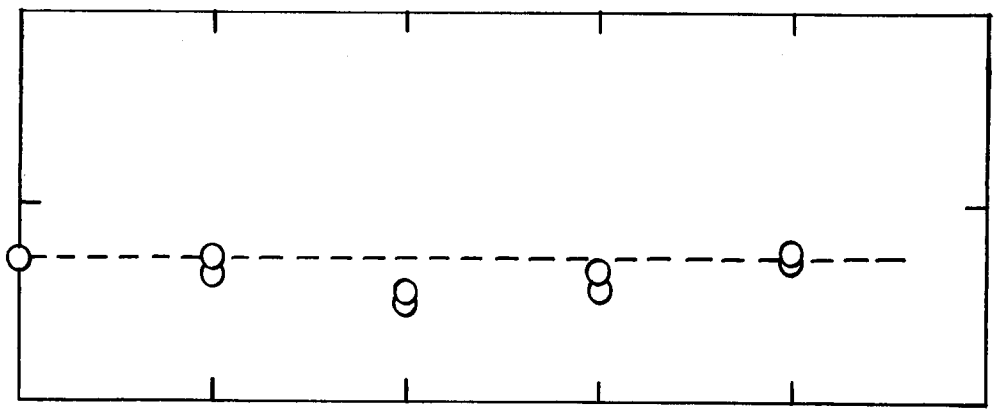


Fig. 5 Plot of the Data of Table VI

TABLE VII

Results of the Recovery of Various Amounts of Nitric Acid from the Same-Sized Volumes of a Solution of Thorium Nitrate

Test solution,

0.5522 g of Th(IV) (added as $Th(NO_3)_4$)

Indicated volume of HNO_3

Total volume, 10 ml (made up with H_2O)

Titrant, 1.000 N NaOH

Normality of HNO_3	Test Portion of HNO_3 Solution, ml	Milliequivalents of HNO_3 Experimental	Calculated	Difference
0.01089	10.000	0.1190	0.1089	+0.0101
0.1089	2.000	0.2442	0.2178	+0.0264
1.0890	0.250	0.2592	0.2722	-0.0130
10.8900	0.050	0.5346	0.5445	-0.0099

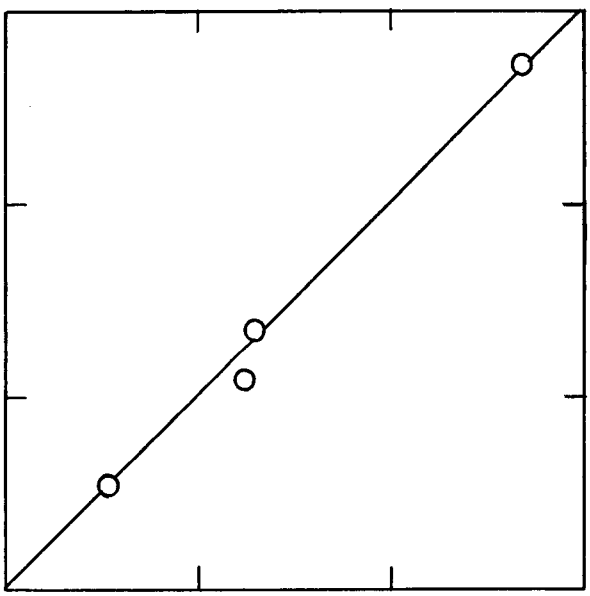


Fig. 6 Plot of the Data of Table VII.

TABLE VIII

Effect of Variation of Uranyl Ion Content on Recovery of a Known Amount of Nitric Acid in the Presence of a Known Amount of Thorium(IV)

Test solution,

0.5522 g of Th(IV) (added as $Th(NO_3)_4$)

0.250 ml of 1.0890 N HNO_3

9.75 ml of water

Indicated amount of U(VI) (added as $UO_2(NO_3)_2$)

Titrant, 1.000 N NaOH

Amount of Uranium(VI), g	Titer Value, inches of chart travel	Milliequivalents of NaOH*,**
0.0093	8.42	0.273
0.0187	8.41	0.272
0.0934	8.46	0.274
0.1869	8.55	0.277
0.1869	8.25	0.267

* Same as meq of HNO_3.

** Theoretical Value = 0.272 meq.

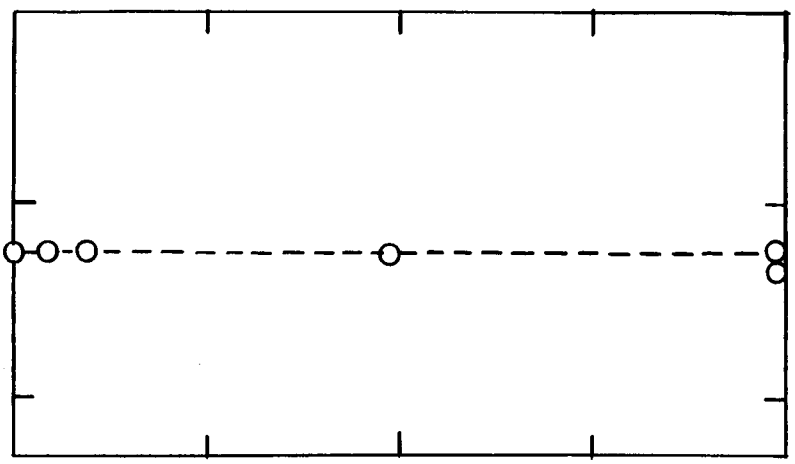


Fig. 7 Plot of the Data of Table VIII.

5. ACKNOWLEDGEMENT

The authors are indebted to Dr. M. T. Kelley for his invaluable advice, to Mr. Harold C. Jones of the Analytical Instrumentation Group for the motorizing of the Greiner microburet, and to Mrs. Helen P. Raaen for her editing of this report.

6. APPENDICES

6.1 Appendix I: Specifications for the Apparatus

The apparatus is shown in Photographs 1 and 2.

1. Stirring Motor. A. S. LaPine and Co., No. 38286, type S. P., speed 1600 rpm on one shaft with a 5-to-1 reduction on the slow-speed shaft, 110-v, a-c, type 73644. The slow-speed shaft is used. The stirring motor should have a cooling coil of 1/8 in. copper tubing wound around it. Water is allowed to drip through the copper tubing in order to prevent excessive temperature rise in the motor during operation.

2. Glass Stirrer. A flat piece of glass, 1/2 in. wide, twisted into a spiral approximately 1 1/2 to 2 in. long, is attached to a 1/4-in. dia glass rod for use as a stirrer.

3. Thermistor. A suitable thermistor for use in measuring temperature rise is the Western Electric Co.'s type 14 B. This is no longer available from the Western Electric Co. but can be purchased from the Victory Engineering Corp., Springfield Road, Union, N. J., as their type 32-A-1. This thermistor has the following characteristics:

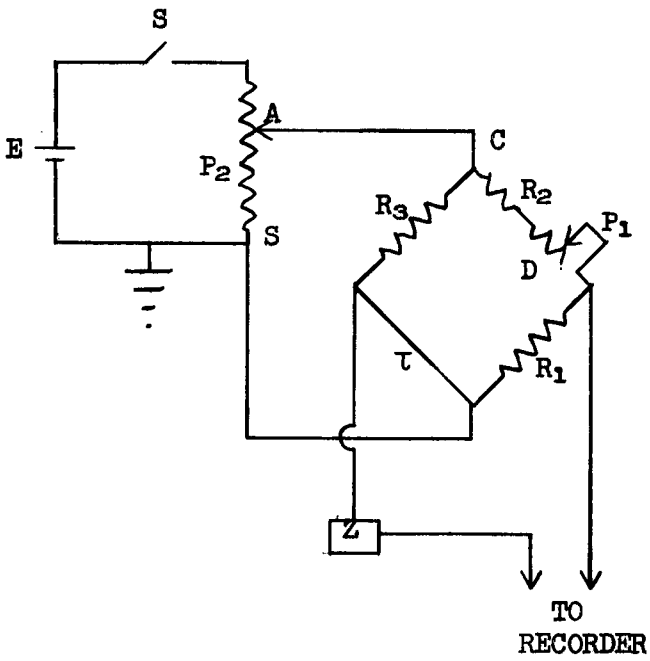
sensitivity in the range of 25°C temperature, 0.04 ohm/ohm/°C

approximate resistance at 25°C, 2,000 ohms

thermal time lag, < 1 second

A thermistor is defined as a resistance element, made of a semiconducting material, that exhibits a high negative temperature coefficient of resistivity.

For the measurement of temperature, the thermistor is incorporated as a branch in a d-c bridge circuit as shown:



Thermistor bridge circuit

E. 1.5-volt source
P_1. 1000-ohm potentiometer
P_2. 50-ohm potentiometer
τ Thermistor
R_1, R_3. 2000-ohm resistors
R_2. 1500-ohm resistor
S. Single-pole single-throw switch
Z. Zero adjuster (4)

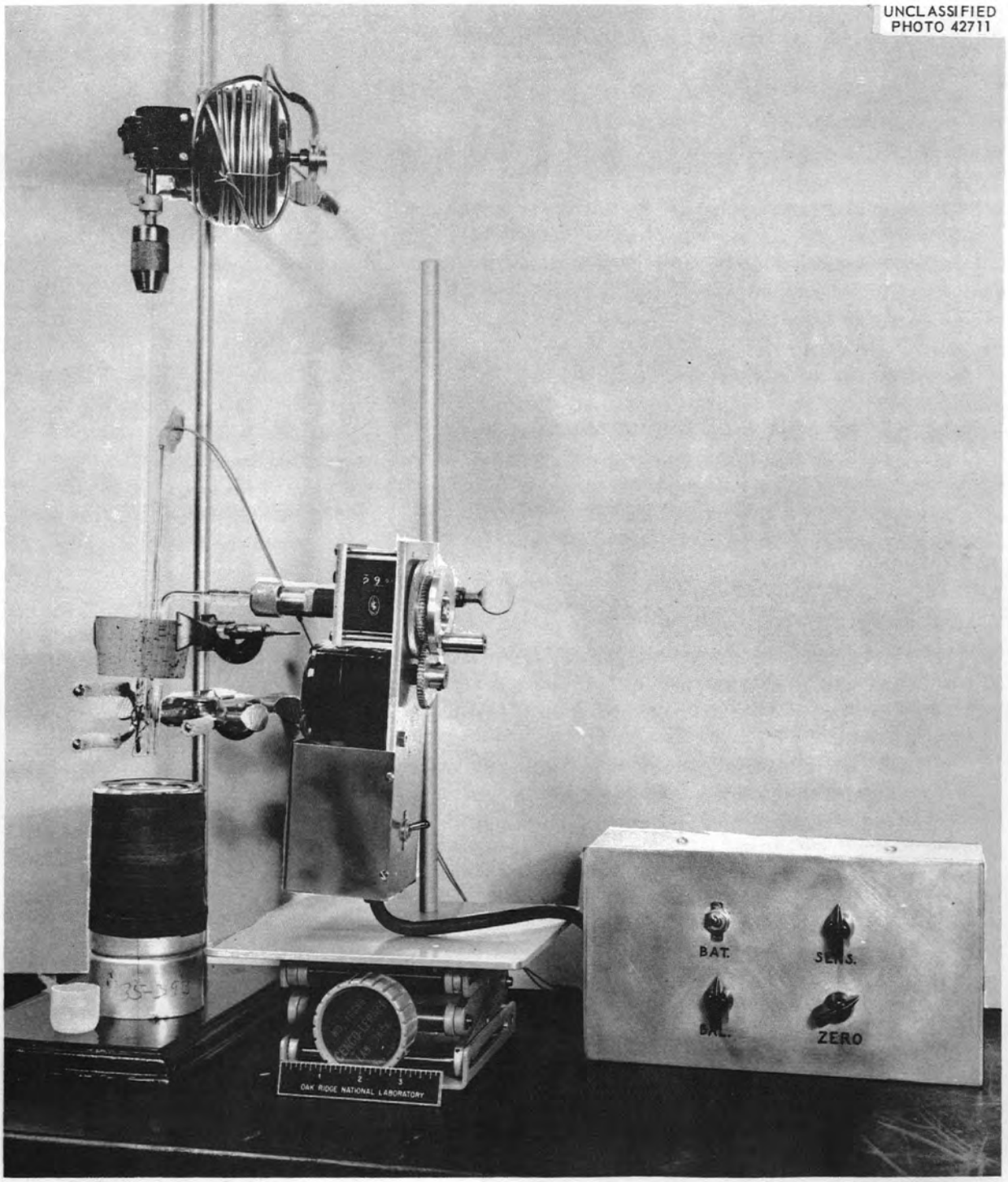
4. Recorder. A Brown Electronik recorder is used to measure the potential across the bridge. The recorder is listed as Model No. Y153x17(VA)-X-30A3C2G, range 1: span 0 to 1, 0 to 50 mv; range: suppress -50 to 50 mv; made by the Minneapolis-Honeywell Regulator Co., Brown Instruments Division, Philadelphia, Pa.

5. Buret. A syringe buret, equipped with either a 1-ml or 0.5-ml syringe is used to supply the titrant. A similar buret may be obtained from the Micro-Metric Instrument Co., Cleveland, Ohio, under their catalog No. SB-1. In the present set-up, the buret is coupled to the drive unit

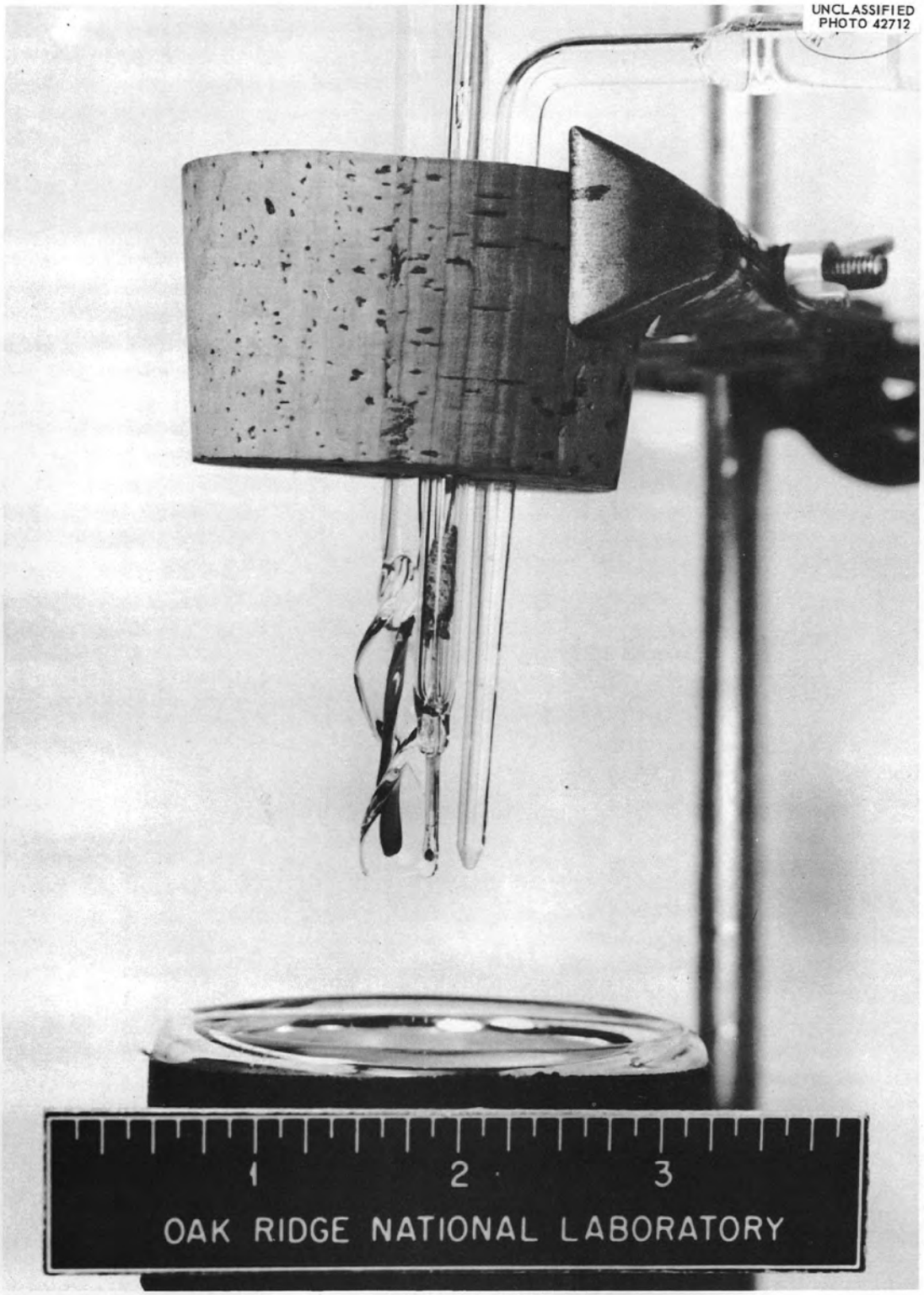
of an ORNL model Q-945 automatic titrator that is set to drive at a constant rate. Thus a flow of titrant is provided that is constant with time. It is planned to change from this buret arrangement to a Greiner buret that is driven at a constant rate by a Bodine, constant-speed motor through a coupling gear. This arrangement has been built but not yet tested.

6. Dewar Flask. A 250-ml, wide-mouth, Dewar flask that is fitted with a three-hole cork stopper is used to contain the beaker in which the titration is performed. The buret tip, the stirrer, and the thermistor pass through the holes in the stopper and enter the beaker. A cork stopper having a hole cut in the center is used to position the beaker properly inside the Dewar flask.

7. Beakers. Small, polyethylene beakers of from 10- to 20-ml capacity are used to contain the acid-fluoride solution during the titration. If beakers are not available, they can be made by cutting 2-oz, polyethylene bottles to size.



Photograph 1. Apparatus Used for the Determination of Free Acid by Thermometric Titration.



Photograph 2. Close-Up View of the Thermistor, Stirrer, and Buret Tip Used in the Determination of Free Acid by Thermometric Titration.

6.2 Appendix II: Detailed Procedure for the Determination of Free Acid in Hydrofluoric Acid Solutions of Zirconium

1. Calibrate the chart travel of the recorder by marking the chart and then simultaneously driving the buret and the chart until 0.1 in. is recorded on the dial of the buret. Mark the chart at this point. The measured distance on the chart is then equivalent to 0.1 in. x 1 ml/in. or a 0.1-ml volume of titrant as long as a 1-ml syringe is used on the buret. If a 0.5-ml syringe is used the distance is equal to 0.1 in. x 0.5 ml/in. or 0.05 ml of titrant.

2. By means of a micropipet, take a test portion of the sample such that is contains no more than 0.5 meq of acid.

3. Place the test portion in a 10- to 20-ml plastic beaker.

4. Dilute the test portion to a volume of 10 ml with water.

5. Place the beaker in the Dewar flask.

6. Fill the buret with titrant and zero the buret. Rinse the buret tip thoroughly and wipe it dry.

7. Raise the Dewar flask into position under the stopper; make certain that the buret tip, thermistor, and stirrer blade are immersed in the solution and are not touching each other.

8. Start the stirring motor.

9. Start the recorder and chart drive.

10. Close the battery switch on the bridge. The recorder pen should immediately move from the zero mark. Bring the pen back near the zero mark by adjusting the balancing potentiometer on the bridge.

11. Allow sufficient time for the pen to cease drifting sharply up or down scale.

12. Simultaneously mark the chart and turn on the buret drive. The pen should move upscale linearly with the addition of titrant and then level off. Continue the titration until the upper branch of the curve has leveled out so that it becomes a straight line; then stop the titration.

13. Remove the chart paper from the recorder. Draw a straight line along the initial portion of the curve and a second straight line along the second branch of the curve. Extrapolate these lines until they intersect. Measure the vertical distance along the chart from the starting point of the titration to the point of intersection of the two straight lines. Calculate as follows:

Let A = measured distance on chart, in.,

B = calibration factor for converting inches of chart travel to inches of syringe plunger travel, and thus to milliliters of titrant,

C = normality of titrant, and

D = dilution factor.

Then Free Acid in Sample, meq/ml = A x B x C x D.

7. BIBLIOGRAPHY

1. G. L. Booman, M. C. Elliott, R. B. Kimball, F. O. Cartan, and J. E. Rein, "Determination of Free Acid in the Presence of Hydrolyzable Ions," Anal. Chem., 30, 284 (1958).

2. R. E. Connick and W. H. McVey, "The Aqueous Chemistry of Zirconium," UCRL-101 (Mar. 1, 1948).

3. P. Dutoit and E. Grobet, "Sur une Nouvelle Methode de Volumetrie Physico-Chimique Appliquee a Quelques Problemes de Chimie Minerale," J. chim. phys., 19, 324 (1921).

4. G. W. Ewing, Instrumental Methods of Chemical Analysis, pp. 311-313, McGraw-Hill, New York, 1954.

5. M. E. Jones, B. F. Rider, and H. C. Hendrickson, "The Determination of Free Acid in Solutions of Aluminum and Thorium and Uranyl Nitrates," KAPL-1497 (Feb. 1, 1956).

6. J. Jordan and T. G. Alleman, "Thermochemical Titrations (Enthalpy Titrations)," Anal. Chem., 29, 9 (1957).

7. H. W. Linde, L. B. Rogers, and D. N. Hume, "Automatic Thermometric Titrations," Ibid., 25, 404 (1953).

8. O. Menis, D. L. Manning, and G. Goldstein, "Determination of Free Acid in Solutions of Uranyl Sulfate," ORNL-2178 (Nov. 8, 1956).

9. R. H. Müller, "Instrumental Methods of Chemical Analysis," Ind. Eng. Chem., Anal. Ed., 13, 667 (1941).

10. L. P. Pepkowitz, W. W. Sabol, and D. Dutina, "Determination of Free Acid in the Presence of Hydrolyzable Ions," Anal. Chem., 24, 1956 (1952).

11. R. C. Propst, "Conductometric Acidimetry in the Presence of Hydrolyzable Ions," DP-76 (June, 1955).

12. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Selected Values of Chemical Thermodynamic Properties, Circular of the National Bureau of Standards 500, U. S. Government Printing Office, Washington, D. C., 1950.

13. W. A. Roth and K. Scheel, Landolt-Bornstein, Physikalisch-Chemische Tabellen, p. 1547, Table 322, J. Springer, Berlin (1923).

ORNL-2489
Chemistry-General
TID-4500 (13th ed., Rev.)
February 15, 1958

INTERNAL DISTRIBUTION

1. C. E. Center
2. Biology Library
3. Health Physics Library
4-5. Central Research Library
6. Reactor Experimental Engineering Library
7-26. Laboratory Records Department
27. Laboratory Records, ORNL R.C.
28. A. M. Weinberg
29. L. B. Emlet (K-25)
30. J. P. Murray (Y-12)
31. J. A. Swartout
32. E. H. Taylor
33. E. D. Shipley
34. M. L. Nelson
35. M. T. Kelley
36. C. P. Keim
37. J. H. Frye, Jr.
38. W. H. Jordan
39. R. R. Dickison
40. F. L. Culler
41. S. C. Lind
42. A. H. Snell
43. A. Hollaender
44. K. Z. Morgan
45. T. A. Lincoln
46. A. S. Householder
47. R. S. Livingston
48. D. S. Billington
49. C. E. Winters
50. D. W. Cardwell
51. D. Phillips
52. J. A. Lane
53. M. J. Skinner
54. G. E. Boyd
55. C. L. Burros
56. J. H. Cooper
57. L. T. Corbin
58. C. Feldman
59. D. J. Fisher
60. U. Koskela
61. W. R. Laing
62. C. E. Lamb
63. D. E. LaValle
64. G. W. Leddicotte
65. S. A. Reynolds
66. P. F. Thomason
67. T. E. Willmarth
68. G. R. Wilson
69. E. I. Wyatt
70. L. J. Brady
71. H. P. House
72. J. R. Lund
73. E. C. Lynn
74. O. Menis
75. A. S. Meyer, Jr.
76. C. D. Susano
77. C. K. Talbott
78. W. F. Vaughan
79. J. C. White
80. H. P. Raaen
81. J. A. Norris
82. D. L. Manning
83. T. C. Rains
84. A. E. Cameron
85. H. Eyring (consultant)
86. N. H. Furman (consultant)
87. C. E. Larson (consultant)
88. F. J. Miller
89. ORNL - Y-12 Technical Library, Document Reference Section

EXTERNAL DISTRIBUTION

90. Division of Research and Development, AEC, ORO
91-645. Given distribution as shown in TID-4500 (13th ed., Rev., Feb. 15, 1958) under Chemistry-General category (75 copies - OTS)