AN INVESTIGATION OF THE pH METHOD FOR DETERMINING THE DURABILITY OF GLASS

BY

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Approved:

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Head of Department

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Dean of Engineering

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Chairman, Graduate Committee

Acknowledgements

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I ABSTRACT

An investigation was made of the pH method for determining the durability of soda-lime glass. An experimental method was devised for converting pH measurements to grams of dissolved Na_2O. Durability tests were made on three soda-lime glasses by three methods of testing, and a significant difference was found between the results of each method. The methods of testing were discussed on the basis of this investigation.

II INTRODUCTION

"Whatever[1] may be our beliefs to the contrary, glass is not a completely insoluble substance. When we see it in windows or bottles for example, its apparent permanence gives rise to the casual belief that it is insoluble. The simple experiment of powdering a small portion of such glass, wetting the powder and testing it with an indicator such as phenolphthalein, demonstrates at once the presence of dissolved alkali."

The extent to which any glass may be attacked, or partially dissolved by water or other agents, depends entirely upon its composition. Because practically all commercial glasses contain both soda and silica in varying proportions, they are soluble in both acids and bases, to a certain extent.

According to Morey[2], the resistance which glass offers to the corroding action of water, atmospheric agencies, and of aqueous solutions of acids, bases, and salts is a property of great practical significance and is denoted by the term "chemical durability." The manufacturers and users of glass articles are today becoming more and more concerned with this property of this resistance. The flat glass manufacturer is becoming more concerned with resistance to water and atmospheric agencies; whereas, the container glass manufacturer is primarily concerned with the resistance of his glass to the attack by whatever products are to be stored in the containers.

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1. S. R. Scholes, Modern Glass Practice. Industrial Publications, Inc., Chicago, 1946, 236.

2. G. W. Morey, The Properties of Glass. Rheinhold Publishing Corporation, New York, 1938, 103.

Through the years numerous tests have been devised to measure the chemical durability of glass. Unfortunately, however, the tests have been so numerous, and the methods have varied so widely that the results cannot be compared with any degree of accuracy. During the last few years glass manufacturers, technicians, etc., realizing this deplorable condition, began clamoring for the adoption of a standard method for measuring the chemical durability of glass. Consequently, numerous committees were appointed and a great deal of study was given to the correlation of laboratory test methods with experience under actual working conditions.

The result of this cooperative research has demonstrated the utility of the method first proposed by O. G. Burch[3], which is known as the American Ceramic Society Tentative Method. Although this method is generally accepted as a standard, it is still not without faults, and there are many reasons for doubting its effectiveness and practicability.

Following the acceptance of this method by the Glass Division of the American Ceramic Society, a pH method of testing the chemical durability of glass was proposed by R. F. Doran and S. R. Scholes[4] that attracted the writer's attention. Although no results were obtained on actual glasses to promote the use of this method, it was the writer's opinion that the method was fundamentally sound, and warranted further investigation.

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3. O. G. Burch, "The Development of a Reliable Method for the Determination of the Solubility of Soda-Lime Glasses", Bulletin American Ceramic Society, 13, 200-04, (1934).

4. R. F. Doran and S. R. Scholes, "Durability of Glass - Estimating Dissolved Alkali by pH Determination", Journal American Ceramic Society, 23, 91-2, (1940).

The object of this thesis was to investigate the pH method, recommended by Doran and Scholes, to determine its value and the possible correlation with the American Ceramic Society Tentative Method.

III REVIEW OF LITERATURE

So important is the chemical durability of glass that Zschimmer[5] included such resistance to corroding agencies in his definition of glass. While such a definition seems too restrictive, it does illustrate the importance of durability. Many glasses possessing desirable mechanical properties are often rejected because of their inability to withstand corrosion. The methods of testing glass for this property thus become of fundamental importance.

Before considering the testing methods that have been employed and those that are in use today, it is important that the nature of the decomposition of glass by water and atmospheric agencies be considered.

According to Scholes[6], it is incorrect to speak of the solubility of a glass as we would discuss the solubility of a salt. The action is one of diffusion and disintegration and not one of true solution. The attack of water upon glass is highly complex, and cannot be accurately set forth.

When moisture is in contact with glass, it is first adsorbed and then absorbed. In the soda-lime system sodium silicate is leached from the glass. This undergoes hydrolysis resulting in the liberation of sodium hydroxide and colloidal silicic acid. The sodium hydroxide liberated by the hydrolysis becomes a film on the surface of the glass. Carbon dioxide in the atmosphere then reacts with this film to form sodium carbonate as a white

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5. Zschimmer, E., in Doetter, C., "Handbuch der Mineralchemie", Vol. 1, 855, T. Steinkopff, Dresden u. Leipzig, 1912.

6. S. R. Scholes, Modern Glass Practice. Industrial Publications, Inc., Chicago, 1946, 236-37.

deposit that dulls the surface of the glass. Under similar conditions, but with the use of alkalies, these reactions may be duplicated to a more pronounced degree.

Scholes[7] maintains that because of the insolubility of lime or lime silicate, and the relative insolubility of silica, these materials exert a protective action which causes the attack to proceed much more slowly as time goes on.

Due to the fact that about 90% of the glass products manufactured today predominate in soda, lime, and silica, the alkali that is leached from the glass by water or atmospheric agencies is usually considered to be all soda. It is upon this theory that many of the durability tests are based, and results are reported as the weight or per cent of Na_2O or NaOH leached from the glass by the attacking agent.

Burch[8] states that the methods in general use for determining the chemical durability of glass may be grouped in four classes:

(1) determination of the alkali extracted by an aqueous solution from a definite surface area of the finished glass article.

(2) determination of the total material dissolved from a definite surface area of the finished article by solutions of water, acids, and bases.

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7. S. R. Scholes, Modern Glass Practice. Industrial Publications, Inc., Chicago, 1946, 237.

8. C. G. Burch, "Methods for Determining the Chemical Durability of Soda-Lime Glasses", Bulletin American Ceramic Society, 15, 175, (1936).

(3) a measure of the alkali extracted from definite weights of crushed glass of specified grain size, by water or dilute acids.

(4) determination of the total material extracted from a definite amount of crushed glass of specified grain size, by water, acids, and bases.

History of Testing Methods

O. G. Burch[9] has summarized a few of the more important methods in the chronological order in which they have been brought forth.

"One of the earliest powder methods was that of Peddle[10] whereby 5g. of powdered glass, which would pass through a 160-mesh screen, were treated with distilled water for a period of one hour at 80°C. The solution was filtered and the undissolved material was determined by drying, the filtrate being titrated for alkali leached out. There are several factors about this test which make accurate conclusions difficult. Specifying grain size as finer than 160-mesh allows too great a variability in the surface area exposed to get reproducable results. The time of one hour is too short. Weighing the glass after extraction is inaccurate because of the different degrees of hydration which different glasses may undergo.

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9. O. G. Burch, "Methods for Determining the Chemical Durability of Soda-Lime Glasses", Bulletin American Ceramic Society, 15, 175-76, 1936.

10. J. C. Peddle, "Development of Various Types of Glass: I, Interaction of Silica with the Oxides of Sodium and Potassium," Journal Society Glass Technology, 4, 14 (1920).

In 1922, Turner[11] published a review and criticism of the different types of durability tests then in use. Regarding loss in weight, alkali dissolved, etc., he stated that (1) loss-in-weight methods are inaccurate owing to hydration of the glass; (2) the alkali extracted by water is inaccurate owing to the difference of free and total alkali dissolved; and (3) determination of the extracted material is the best method, but the time element is too great.

Concerning the form of the glass tested, he made the following statements: (1) it is nearly impossible to secure glass vessels of the same size and shape; the action of the vapor given off by the contained liquid also varies from that of the liquid for different shapes of containers; (2) autoclave tests cannot be accepted as criteria of durability because some glasses exceptionally durable to hot water are inferior in the autoclave tests and vice versa; (3) samples of plates for immersion are difficult to prepare and a surface chilled by metal differs from an air chilled surface; and (4) in powdered glass the surface differences due to cords, etc., are eliminated; the length of time necessary to get sufficient attack even on good glasses is greatly reduced over plane surface methods.

Dimbleby and Turner[12] used a powder method on grains of glass, lying between 20- and 30- mesh screens, carefully washed with alcohol to a constant weight.

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11. W. E. S. Turner, "Critical Examination of Methods Commonly Used in Determining Durability of Glass", Journal Society Glass Technology, 6, 30-45 (1922).

12. V. Dimbleby and W.E.S. Turner, "Relationship Between Chemical Composition and Resistance of Glass to the Action of Chemical Reagents: Part I, "Journal Society Glass Technology, 10, 304-58 (1926).

They subjected 10g. samples of the glass to treatment at the boiling temperature for one-hour periods with water, acid, and alkali, measuring the loss in weight each instance and titrating the alkali leached from the glass by water. They claimed the advantages for their method to be (a) a larger exposed surface over the use of glass disks, and (b) a more average condition of the glass.

Fischer and Tepohl[13] used a sample of 1cc. of glass of grain size 0.15 to 0.30mm.; this was washed with water to free from dust, treated with 50 cc. of H_2O for a period of 3 hours at 80°C., and 25 cc. of the filtrate was titrated with N/100 acid. The durability was expressed as volume of acid required.

Enss[14] used grains of glass 0.5 to 1.00 mm. in diameter and subjected an 18-g. sample of glass to treatment with 100cc. of water for seven hours at 100°C. The liquid was filtered off, evaporated to dryness, and the residue was analyzed. He found that treatment for seven hours at 95°C. gave 35% less attack that seven hours at 100°C. and that a 3 1/2-hour treatment at 100°C. gave 20% less attack than seven hours at the same temperature. He also claimed that the degree of annealing of the glass had no effects on results obtained by a powder method but did affect results obtained on a finished bottle.

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13. E. Fischer and W. Tepohl, "Determination of the Soluble Alkali in Ground Glass", Glastech. Ber., 4 (4) 137-42 (1926); Ceram. Abs., 6 (7) 269 (1927).

14. J. Enss, "Relationship of the Relative Water Stability of Glasses to Chemical Composition", Glastech Ber., 5 (10) 449-76 (1928); Ceram. Abs., 7 (10) 749 (1928).

At a joint meeting of the German and English Glass Societies in 1928 a compromise method[15], calling for the use of 10g. of crushed glass of 0.3-to 0.49-mm. size and treatment for five hours with water at 100°C. with subsequent determination of the dissolved material, was proposed.

Fischer and Tepohl[16] tried this method, evaporating 75 cc. of the filtrate to dryness to obtain the extracted material, and found results consistent with those they obtained in their earlier method.

Botvinken and Tanchilevitch[17] used samples of glass of definite grain size and treated them with solutions of 0.01N to 10.0N alkalis and acids at definite temperatures for specified periods of time. They found that (H^+) had very little affect on the degree of attack but that (OH^-) materially affected the amount of corrosion.

Moller and Zschimmer[18] used a surface method for determining alkali dissolved. They had the glass formed as rods, 1 mm. in diameter and 125 mm. in length, and suspended these in water for three hours at 98°C., having

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15. "Proposed Standards for Measuring the Durability of Glass", Journ. Soc. Glass Tech., 12, 87 (1928).

16. E. Fischer and W. Tepohl, "Solubility of Glasses in Water", Glastech. Ber., 6 (9) 532-39 (1928); Ceram. Abs., 8 (1) 641 (1929).

17. O. Botvinken and A. Tanchilevitch, "Dependence of Alkaline and Acid Condition of Glass on Hydrogen-Ion Concentrations", Z. anorg. allgem. Chem., 168, 356-60 (1928); Ceram. Abs., 8 (9) 647 (1929).

18. W. Moller and E. Zschimmer, "Hot Alkaline Solubility of the Fire-Polished Sodium-Lime-Silica Glasses as Function of the Chemical Composition", Sprechsaal, 62 (7) 115-16 (1929); Ceram. Abs., 8 (9) 535 (1929).

sufficient rods that 1 cc. of water was present for each square centimeter of glass surface exposed. The alkali dissolved was then titrated with N/100 HCl. This method would probably give consistent results but the necessity of drawing the glass into rods makes it somewhat laborious.

Schnud[19] studied the durability of glass in water as a function of time and temperature by a conductivity method. The glass was made in the form of cylindrical containers of definite shape and volume. The containers were then filled with water of previously determined conductivity and maintained at constant temperature for definite periods of time, the conductivity being measured at desired intervals.

In 1930 Rexer[20] made a criticism of durability methods then in use and expressed a preference for powder methods. Concerning surface methods in general he stated that (1) with an increasing ratio of volume to surface area, good glasses suffer less attack, poor glasses a greater attack; (2) lehr gases influence the quantity and nature of material extracted; and (3) the manner of blowing of containers has an influence on the surface durability.

Flint and Lyle[21] offered a test in 1933, whereby bottles were filled with distilled water and maintained in an autoclave for six hours under a

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19. C. Schnud, "Effect of Time and Temperature on Solubility of Bottle Glass in Water", Sprechsaal, 63, 759 (1930); Ceram. Abs., 10 (1) 25 (1931)

20. E. Rexer, "Critical Investigation of Methods for the Determination of Glass Durability", Keram. Rundschau, 38, 387 (1930); Ceram. Abs., 10 (7) 481 (1931).

21. F. C. Flint and A. K. Lyle, "Test for Chemical Resistance of Glass Containers", Bull, Amer. Ceram. Soc., 12 (10) 296-99 (1933).

pressure of 35 lb. per sq. in., at the end of which period the alkali leached from the surface was determined by titration with a standard acid solution."

It may be seen from the above history that the methods of testing varied so widely that results could not be compared with any degree of accuracy. The American Ceramic Society Tentative Method, first proposed by Burch[22], was the result of wide cooperative research, and is generally considered to be the standard method for measuring the resistance of glass to water or dilute acids. This test may be summarized briefly as follows:

The glass is crushed in a hardened steel mortar having a pestle of 1 3/4 inch diameter. The product is screened to pass 40-mesh and to be retained on 50-mesh screen. Iron particles are removed by a magnet. The particles are washed in alcohol to remove fines and dried at 110°C. A 10-gram sample is weighed into a 200 cc. Erlenmeyer flask and exactly 50 cc. of N/50 H_2SO_4 is added. The flask is closed with a one-hole rubber stopper, set in a thermostat, and heated four hours at 90°C. The flask is then cooled, using a stream of water, and the solution is titrated with N/50 NaOH with phenol red, brom-phenol blue, or other suitable indicator. The results are calculated in per cent Na_2CO_3, or per cent Na_2O dissolved. The use of acid instead of water as the digesting medium eliminates the variable effect of caustic hydrolysis on the decomposition of the glass.

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22. O. G. Burch, "The Development of a Reliable Method for the Determination of the Solubility of Soda-Lime Glasses", Bull, Amer. Ceram. Soc., 13 200-04 (1934).

Shortly after the above method had been accepted as a standard, Doran and Scholes[23] criticised that regardless of the indicator chosen or the care taken to eliminate the presence of CO_2, the end point of the titration is difficult to find accurately because of the high dilution of the reagents. They then advocated a method for estimating the dissolved alkali by pH determinations. This method may be summarized as follows.

The glass sample is prepared and digested exactly as in the American Ceramic Society Tentative Method, and pH measurements are made of the digesting medium before and after digestion. The pH values are converted into the hydrogen-ion concentration . The change in pH and consequently the lowering of the hydrogen-ion concentration represents the entrance of alkali into the solution. This change in concentration is then converted in grams of Na2O leached from the glass sample.

This pH method has several advantages over the American Ceramic Society Tentative Method. One advantage is speed. Readings on the pH meter may be taken much more rapidly than titrations can be made. Another advantage is the elimination of the NaOH solution which is difficult to keep free from CO_2. A third advantage is that the test is not destructive. That is, the tested solution may be replaced in the flasks and further tests may be made at longer intervals of time.

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23. R. F. Doran and S. R. Scholes, "Durability of Glass-Estimating Dissolved Alkali by pH Determination", Journ. Amer. Ceram. Soc., 23, 91 (1940).

IV EXPERIMENTAL PROCEDURE AND DATA

Part I

An Investigation of the Theory of Determining the Durability of Glass by pH Measurements.

1. Introduction

As mentioned in the Review of Literature, Doran and Scholes[24] advocated a pH method for determining the durability of glass. The theory behind their method was that the change in pH of the digesting medium represented the lowering of the hydrogen-ion concentration owing to the entrance of alkali into the solution. The conversion of this value to an amount of Na_2O extracted from the glass was then explained as follows:

The pH values were first converted into the concentration values which they represented, and their respective differences showed the change in acidity or entrance of alkali. This difference was expressed as the grams of H^+ change per liter.

Because the volumes of blanks and digestion solutions were maintained at 50 cc. or 1/20 liter, and the equivalent weight of Na_2O is 31, the conversion factor for the weight of Na_2O from the concentration of the hydrogen ion becomes 31/20 or 1.55.

The accuracy of this method was claimed to be of the order of 0.01 in pH, corresponding to 0.0001 gms. in the usual determination.

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24. R. F. Doran and S. R. Scholes, "Durability of Glass - Estimating Dissolved Alkali by pH Determination", Journ. Amer. Ceram. Soc., 23, 91-2 (1940).

This method seemed fundamentally sound up to the point of converting the grams of H^+ per liter to grams of Na_2O. Here, however, the writer questioned the method. The simple expedient of multiplying the grams of H^+ change per liter by the constant 1.55 necessitates a straight line relationship between pH and grams of Na_2O added to the digesting medium (N/50 H_2SO_4).

From a number of titration curves examined[25] it was found that none showed such a relationship. In all cases it was found that a sharp rise occurred in the curves when the end points of the titrations were reached.

It was believed that for the highly dilute acid used there might be a straight line relation for a limited section of this curve. Some mention may have been given to this fact in the original paper of Doran and Scholes; however, this was not available to the author at the time of this writing.

It was therefore the writer's object to obtain experimentally an Na_2O - H_2SO_4 titration curve to determine if such a relation did exist in the lower section of the curve.

2. Procedure

Because of the impossibility of titrating with Na_2O, it was decided to use NaOH which could be converted to its equivalent of Na_2O. Before preparing the solutions for titration it was first necessary to set up titrating apparatus that would keep the NaOH solution free from CO_2. The apparatus was set up as shown in Fig. 1.

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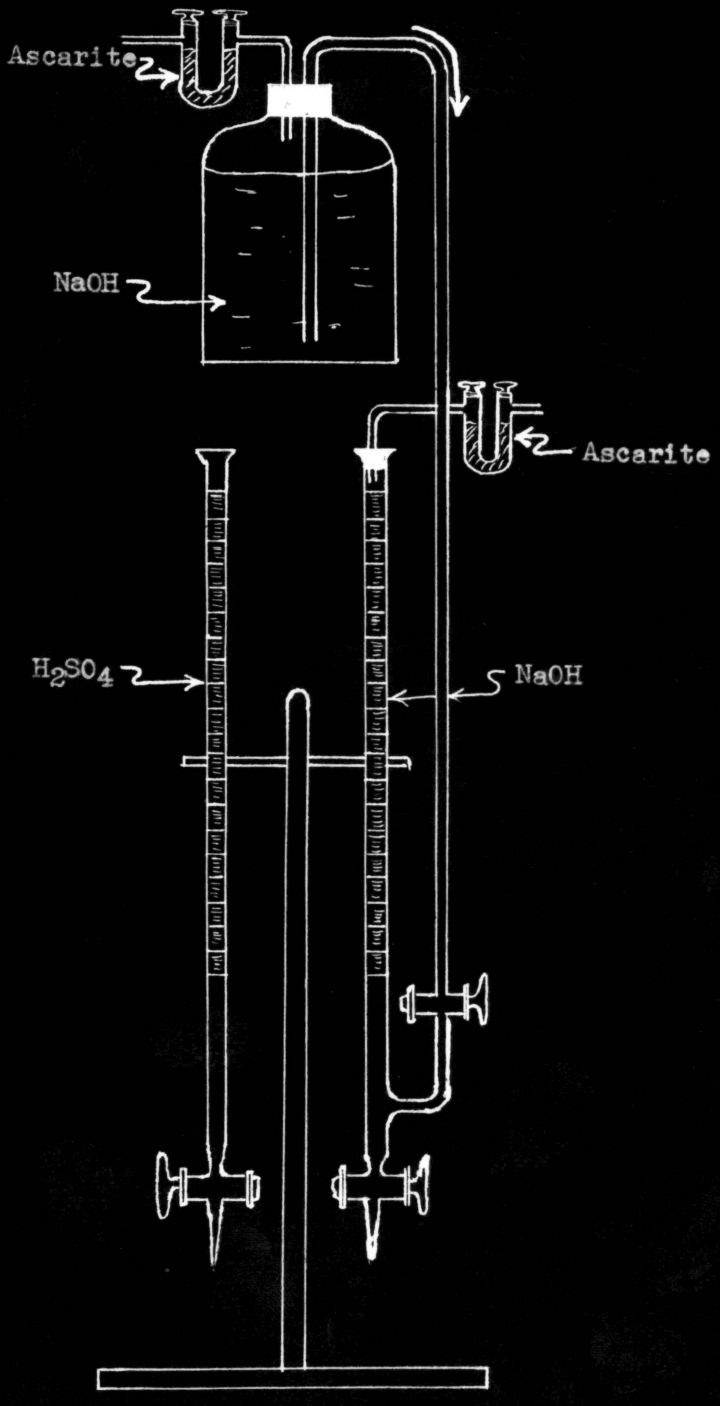
25. J. Hildebrand, Journ. Amer. Chem. Soc., 35, 847 (1913).

Fig. 1

Diagram of Apparatus Used in the Titration Method



Preparation of Solutions

1. Potassium Acid Phthalate: To prepare N/50 $HKC_8H_4O_4$ exactly 2.0422g of powdered $HKC_8H_4O_4$ was weighed into a 500 cc. pyrex flask and distilled water was added to make exactly 500 cc.

2. Sodium Hydroxide: To prepare N/50 NaOH 100 g. of NaOH was dissolved in 100 cc. of distilled water and transferred to a 150 cc. pyrex test tube. The test tube was stoppered lightly with a stopper covered with tin foil and allowed to stand in a vertical position until the supernatant liquid was clear. Exactly 1.3 ml. of the clear solution was carefully withdrawn in a measuring pipette, and delivered into the glass bottle, shown in Fig. 1. An excess of BaCl was then added to remove any CO_2 that was present.

3. Sulfuric Acid: The N/50 H_2SO_4 was prepared by diluting exactly 0.56 cc. of H_2SO_4 (sp. gr. 1.84, assay 95%) with 1000 cc. of distilled water.

The NaOH was standardized against the N/50 $HKC_8H_4O_4$ by means of a Fisher Electrometric Titrimeter. The H_2SO_4 was in turn standardized against the NaOH by treating 50 cc. of the acid with 5 drops of a 0.1% solution of phenol red. The alkali was added until the solution turned pink, and then titrated with the acid until the indicator just turned yellow. It would have been desirable to adjust the solutions so that they were exactly equivalent; however, this is very difficult, and in this experiment they were made as nearly equivalent as was possible, without consuming too much time and their exact normalities were recorded.

Obtaining Titration Curves

The Beckman pH Meter (Fig. 2) was used for determining all pH measurements. This was first adjusted and standardized against a buffer solution. The pH of the acid was then found.

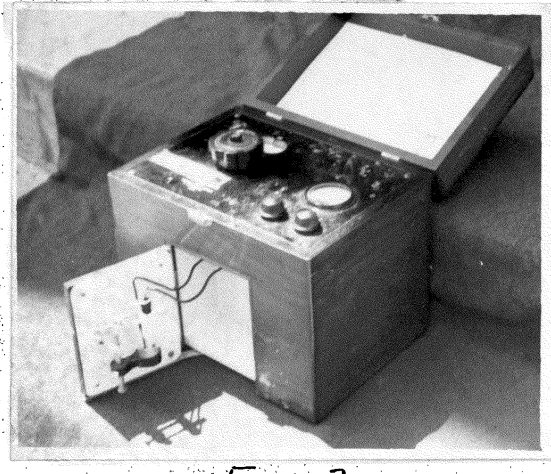


Fig. 2

Exactly 50 cc. of the acid was withdrawn from the burette (Fig. 1) into a 100 cc. pyrex beaker. Exactly 2.5 cc. of the alkali was then withdrawn from the other burette into the acid. This solution was stirred for about 3 seconds and the pH was determined as rapidly as possible. The electrodes of the pH meter were cleaned thoroughly and the procedure was repeated, with increasing additions of the NaOH.

Knowing the normality of the alkali the cc. of NaOH were converted to grams of Na_2O as follows.

$$cc(NaOH) \times N(NaOH) \times M.E.(NaOH) = gms.\ (NaOH)$$

$$gms.(NaOH) \times \frac{Mol.\ Wt.\ Na_2O}{2 \times Mol.\ Wt.\ NaOH} = gms.\ Na_2O$$

The results from this procedure were recorded in Table I, and from these results Graphs I and II were plotted.

Several days later the normalities of both solutions were found to be different from what they were originally. Using these solutions another titration curve was obtained. Owing to the change in concentration of the acid, its pH had also changed, thus giving the curve a slightly different intercept. It was noticed that the curves were approximately parallel in the lower portion but not so in the upper regions. This suggested that for the lower section there might be a family of curves.

Titration curves were then obtained, in the manner previously described, for an acid whose pH was slightly lower, and an acid whose pH was slightly higher than the original acid. The titrations were only carried to a point up to which the curves were believed to be parallel.

The curves were then compared graphically.

3. Data

Table No. I

Run No. 1: Determination of Titration Curve

Solutions: N/0.0197 H_2SO_4 pH = 1.87
N/0.0205 NaOH pH = 11.85

cc. H_2SO_4	cc. NaOH	pH	gms. NaOH	gms. Na_2O
50	0	1.87	0.00000	0.00000
50	2.5	1.88	0.00205	0.00159
50	5	1.91	0.00410	0.00318
50	7.5	1.93	0.00615	0.00477
50	10	1.96	0.00820	0.00636
50	12.5	2.00	0.01025	0.00794
50	15	2.04	0.01230	0.00953
50	20	2.14	0.01640	0.01271
50	25	2.28	0.02050	0.01589
50	30	2.40	0.02460	0.01907
50	35	2.61	0.02870	0.02224
50	40	2.88	0.03280	0.02542
50	45	3.44	0.03690	0.02860
50	46	3.67	0.03772	0.02923
50	47	4.09	0.03854	0.02987
50	48	6.88	0.03936	0.03050
50	49	8.82	0.04018	0.03114
50	50	9.90	0.04100	0.03178
50	55	10.90	0.04510	0.03495
50	60	11.12	0.04920	0.03813

Data

Table No. II

Run No. 2: Determination of Titration Curve*

Solutions: N/0.0255 H_2SO_4 pH = 1.80
N/0.0228 NaOH pH = 11.92

cc. H_2SO_4	cc. NaOH	pH	gms. NaOH	gms. Na_2O
50	0	1.80	0.00000	0.00000
50	2.5	1.81	0.00228	0.00177
50	5	1.82	0.00456	0.00353
50	7.5	1.84	0.00684	0.00530
50	10	1.87	0.00912	0.00707
50	12.5	1.91	0.01140	0.00884
50	15	1.96	0.01368	0.01060
50	17.5	2.02	0.01596	0.01237
50	20	2.08	0.01825	0.01415
50	22.5	2.14	0.02052	0.01590
50	25	2.20	0.02280	0.01768

* For lower portion of curve only.

Data

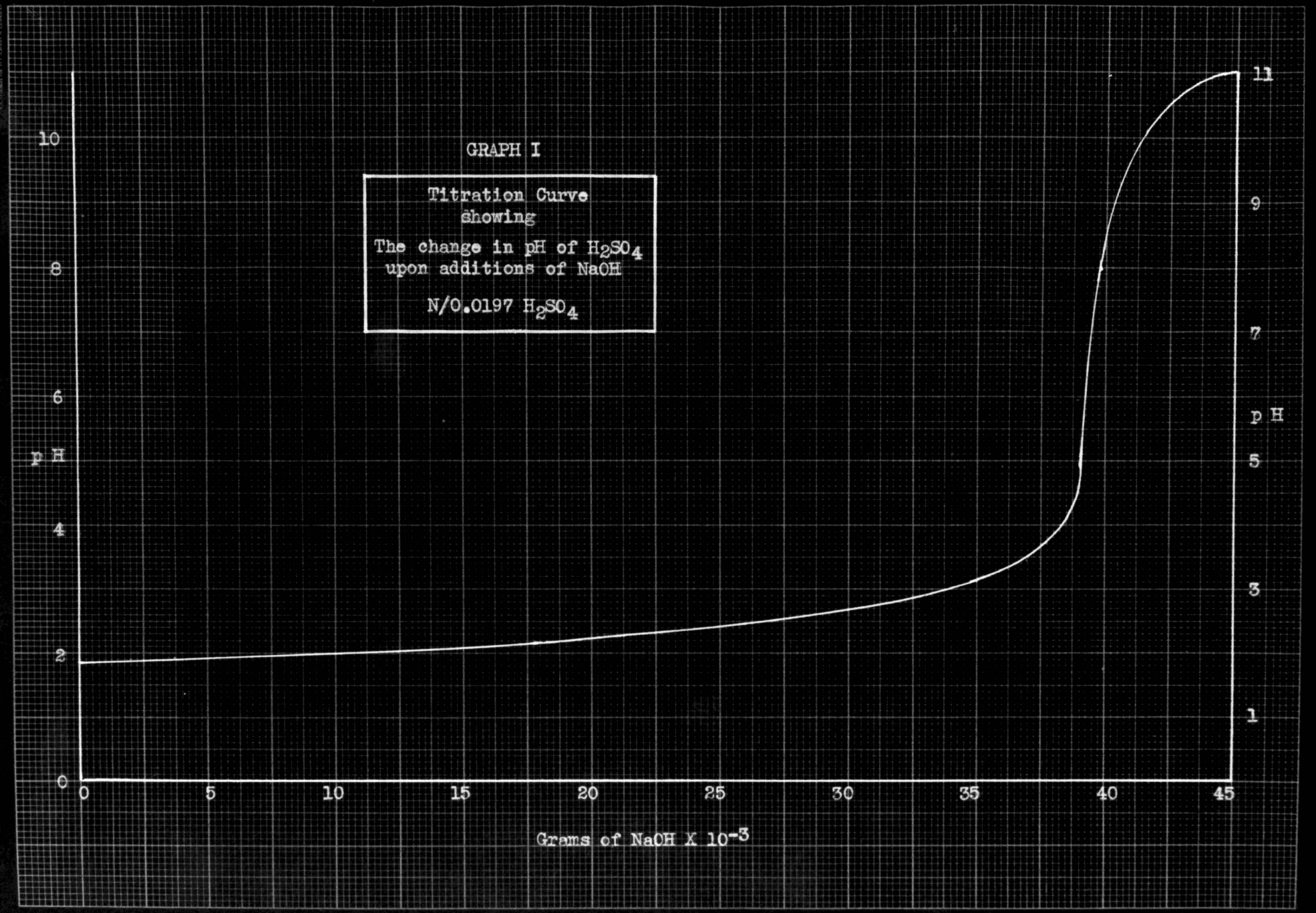
Table No. III

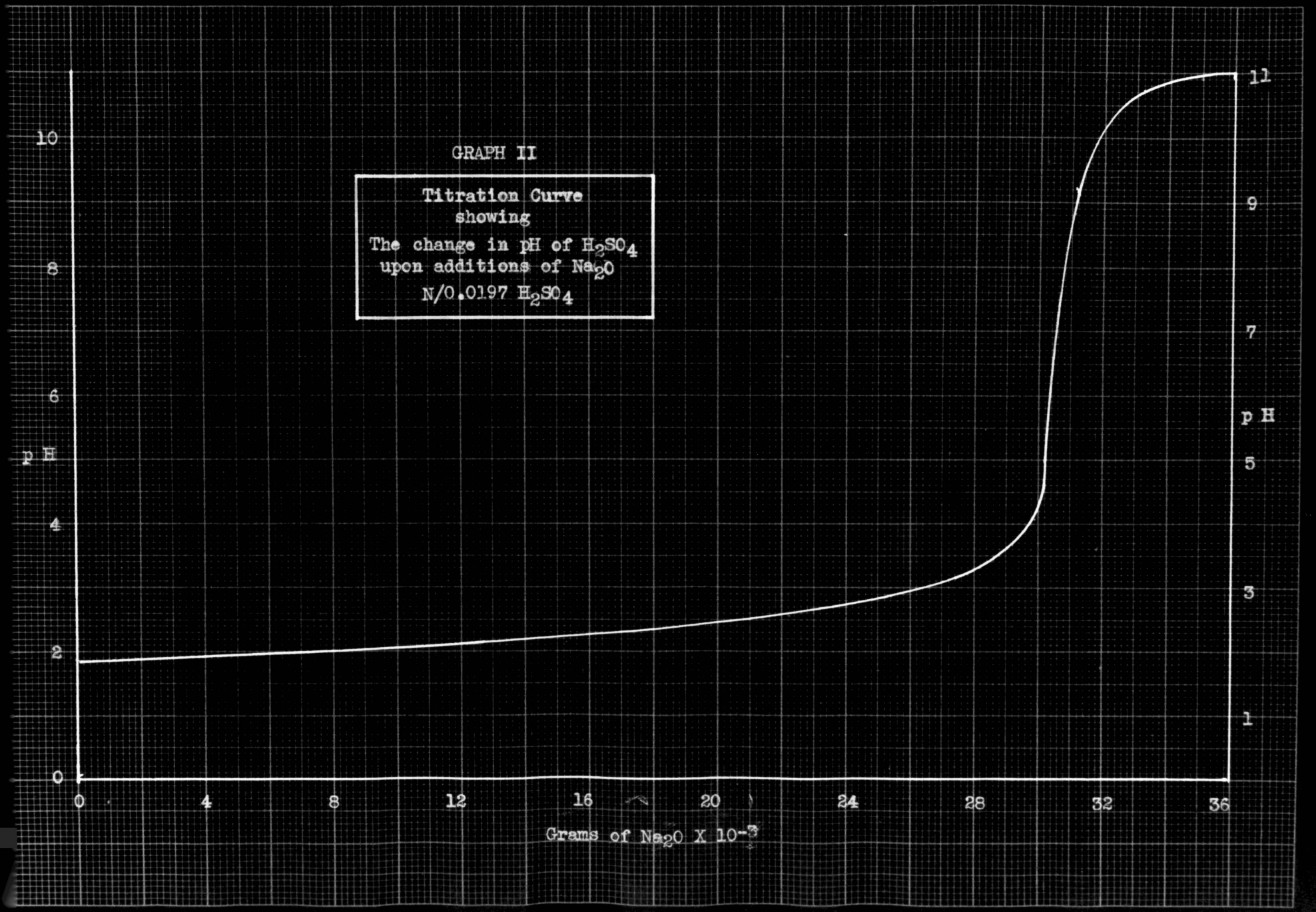
Run No. 3: Determination of Titration Curve*

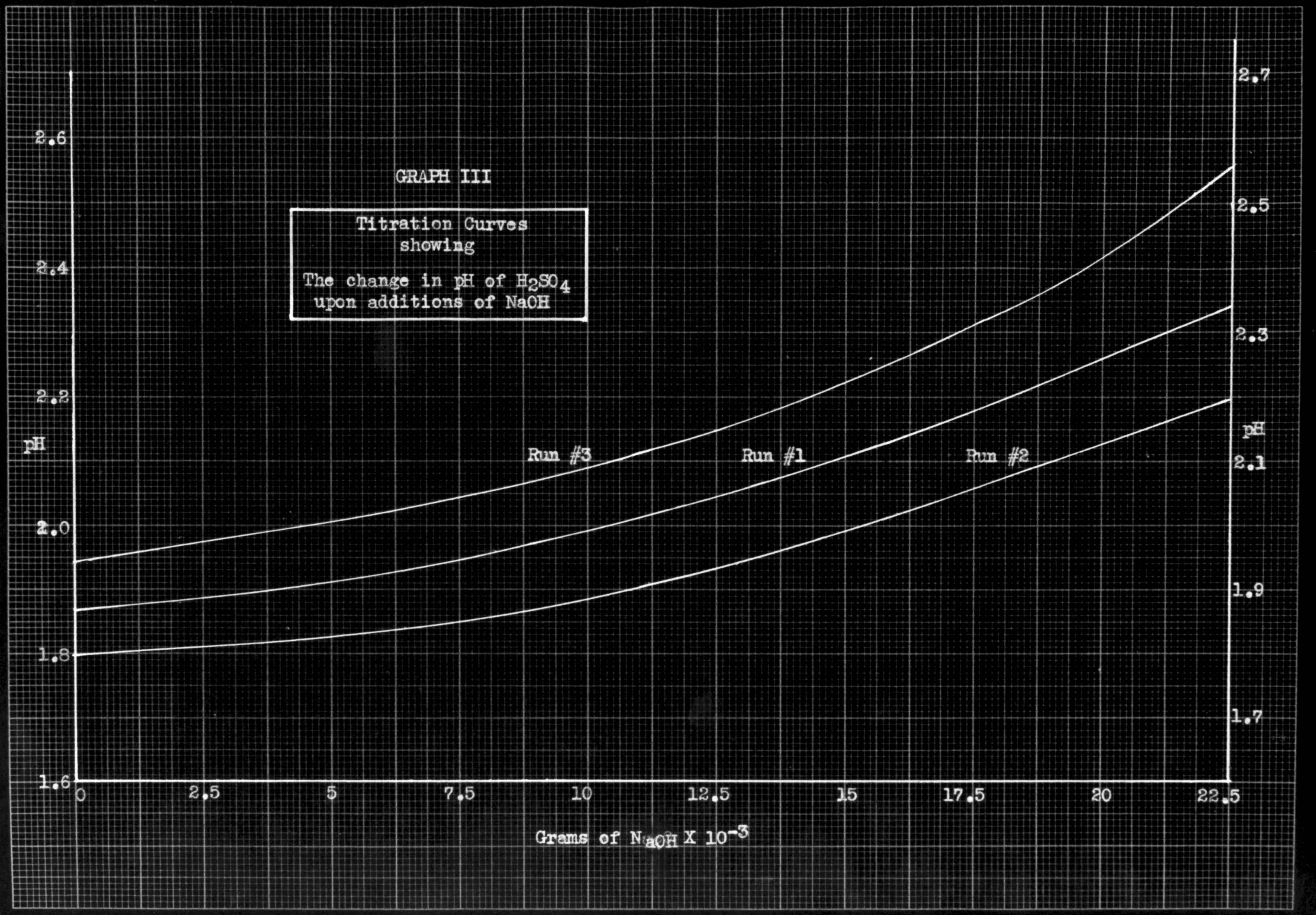
Solutions: N/0.0152 H_2SO_4 pH = 1.94
N/0.0228 NaOH pH = 11.92

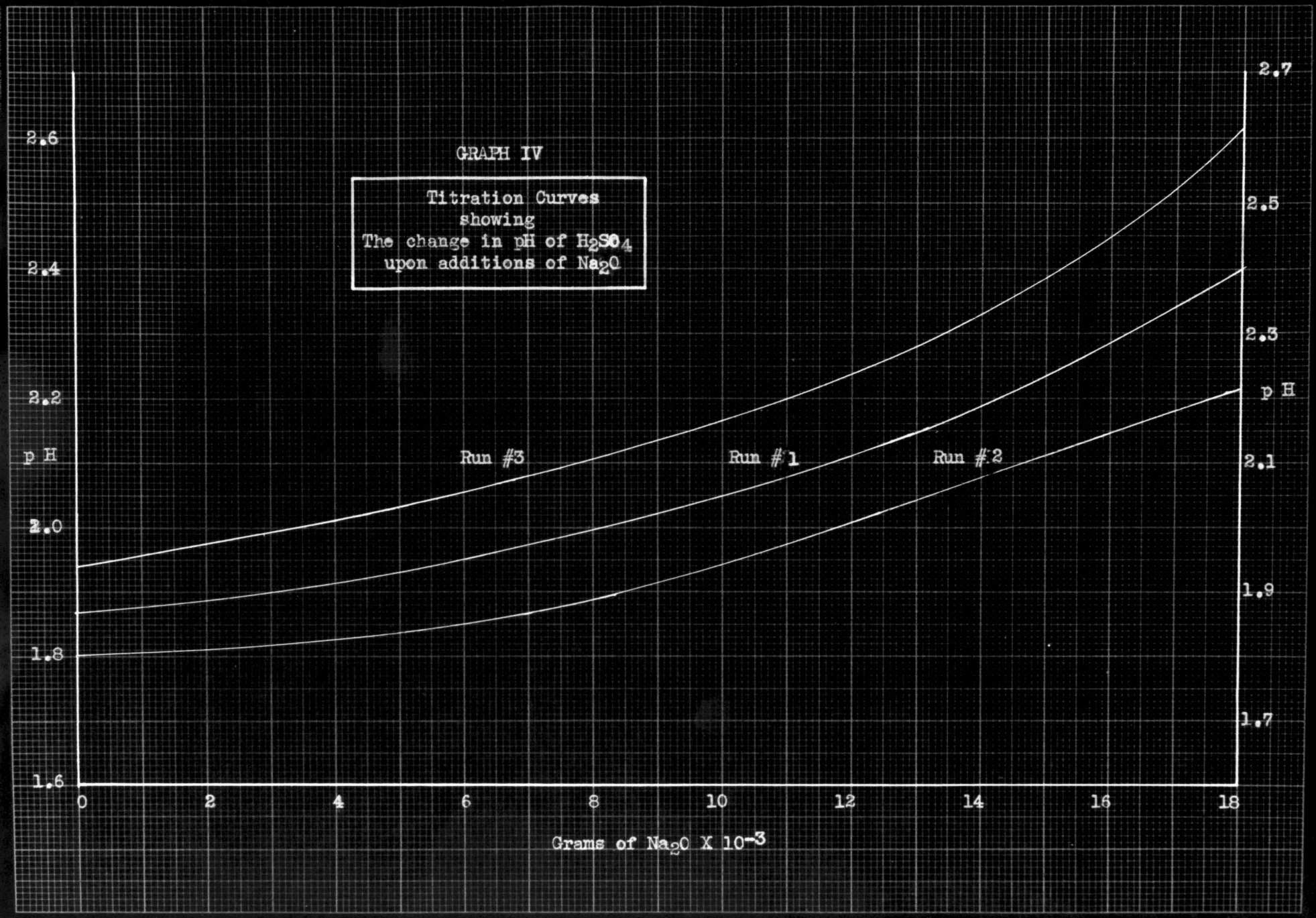
cc. H_2SO_4	cc. NaOH	pH	gms. NaOH	gms. Na_2O
50	0	1.94	0.00000	0.00000
50	2.5	1.97	0.00228	0.00177
50	5	2.00	0.00456	0.00353
50	7.5	2.04	0.00684	0.00530
50	10	2.08	0.00912	0.00707
50	12.5	2.13	0.01140	0.00884
50	15	2.18	0.01368	0.01060
50	17.5	2.25	0.01596	0.01237
50	20	2.34	0.01825	0.01415
50	22.5	2.45	0.02052	0.01590
50	25	2.58	0.02280	0.01768

* For lower portion of curve only.


GRAPH I
Titration Curve
showing
The change in pH of H_2SO_4
upon additions of NaOH
N/0.0197 H_2SO_4
pH
0
2
4
6
8
10
11
9
7
5
3
1
0
5
10
15
20
25
30
35
40
45
Grams of NaOH X 10^{-3}


GRAPH II
Titration Curve
showing
The change in pH of H_2SO_4
upon additions of Na_2O
N/0.0197 H_2SO_4
pH
10
8
6
4
2
0
11
9
7
5
3
1
pH
0
4
8
12
16
20
24
28
32
36
Grams of Na_2O X 10^{-3}


GRAPH III
Titration Curves
showing
The change in pH of H_2SO_4
upon additions of NaOH
Run #3
Run #1
Run #2
pH
2.6
2.4
2.2
2.0
1.8
1.6
2.7
2.5
2.3
2.1
1.9
1.7
0
2.5
5
7.5
10
12.5
15
17.5
20
22.5
Grams of NaOH X 10^{-3}


GRAPH IV
Titration Curves
showing
The change in pH of H_2SO_4
upon additions of Na_2O
Run #3
Run #1
Run #2
pH
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
0
2
4
6
8
10
12
14
16
18
Grams of Na_2O X 10^{-3}

4. Discussion

From the titration curves obtained it may be seen that there is not a straight line relationship between pH and grams of Na_2O added to H_2SO_4. In the lower regions of the curves, however, the relationship does not deviate a great deal from a straight line. It was also noted that acids approximately N/50 having different initial pH's gave curves very nearly parallel. It is the writer's opinion that for any acid whose normality does not vary too far from N/50, its titration curve could be considered to be parallel to those shown in Graph IV for the range shown.

It was originally intended to convert the pH's obtained experimentally to gms. of Na_2O by the Doran method, and compare these values with the actual gms. of Na_2O used. This comparison was decided against, as the Doran method was based upon the fact that the volume of the solution remained constant, whereas, experimentally it was different for each pH determination.

It was the writer's opinion that durability determinations from pH readings could be made more accurately by use of the titration curves obtained, than by the calculations advocated by Doran. It was then decided that actual tests would be made on glass samples to determine, if possible, which method would give more accurate results.

Part II

A Comparison of Methods for Measuring the Durability of Soda-Lime Glass

1. Introduction

The primary object of this thesis was to investigate the pH method for measuring the durability of glass as compared to the American Ceramic Society Tentative Method. The investigation thus far has led the writer to believe that the pH method could be improved upon by using a different method for converting pH changes into grams of Na_2O.

It was therefore the object of this part of the investigation to make a comparison of the three methods by means of actual tests, namely:

(1) The A.C.S. Tentative Method

(2) The Doran Method - converting pH changes into gms. of Na_2O by calculations

(3) The Experimental Method - converting pH changes into gms. of Na_2O by titration curves.

To make a true comparison of the methods it was decided to apply a statistical analysis to the results to determine if there was a significant difference between or within the three methods.

2. Procedure

Durability tests were made upon three soda-lime glasses:

Glass A - Container glass (Whiskey bottle)

Glass B - Flat glass (Window pane)

Glass C - Container glass (Fruit jar)

The glass samples were prepared separately in the following manner:

Crushing: The glass was broken by a hammer into pieces approximately one inch in size. The broken glass was divided into batches of about 150 gms. 20-30 gms. was placed in a hardened steel mortar having a pestle of 1 3/4 inch diameter. The pestle was inserted and struck sharply with a hammer 3 or 4 times. The sample was emptied into a nest of 20, 40, and 50-mesh sieves. This procedure was continued until all of a 150 g. batch was on the screens. The screens were placed on a mechanical vibrator and vibrated for several minutes. The glass remaining on the 20 and 40 mesh sieves was removed, recrushed and sieved as before. This was repeated until none of the original 150 g. batch was retained on either the 20 or 40-mesh sieve.

Sieving: The glass retained on the 50-mesh screen was vibrated for 15 minutes, removed and shaked by hand over a sheet of paper. This process was repeated until few, if any, particles passed through the 50-mesh sieve in five seconds. The usual portion remaining on the 50-mesh sieve did not weigh over 20 g. If it weighed more than this it was divided into 10 g. portions and resieved for five minutes.

This whole procedure of crushing and sieving was repeated until approximately 70 g. of each type glass was obtained.

Cleaning and Washing: Each glass sample was spread on a piece of clean paper and a magnet was passed through it to remove any tramp iron. The sample was transferred to copper mesh baskets equipped with a handle of copper wire. The mesh was a trifle finer than 50, and a small enough amount of the sample was placed in each basket to allow the particles of glass to

move freely and not pack together during washing. The samples were washed by agitating the baskets by hand for about 1 minute, first in a beaker of distilled water, and then in each of two beakers of neutral alcohol.

Drying and Storing: The washed samples were dried by placing the samples in a drier at 110°C. for one hour. After drying the samples were removed from the baskets and allowed to cool in a desiccator containing activated alumina, where they were kept until ready for the digestion operation.

Digestion: Six 200 cc. Erlenmeyer flasks were digested with approximately N/50 H_2SO_4 for four hours at 90°C. after which the acid was poured out and the flasks allowed to dry. The exact normality and pH of the H_2SO_4, prepared in Part I, was determined and exactly 50 cc. was added to each flask. From the previously prepared glass to be tested 10,0000 g. samples were placed into five of the flasks (the sixth flask was used as a blank), and the flasks were stoppered with one-hole (3/16") rubber stoppers. All six flasks were placed in an oven (Fig. 4) whose temperature was controlled at 90° ± 2°C. and heated for exactly four hours.

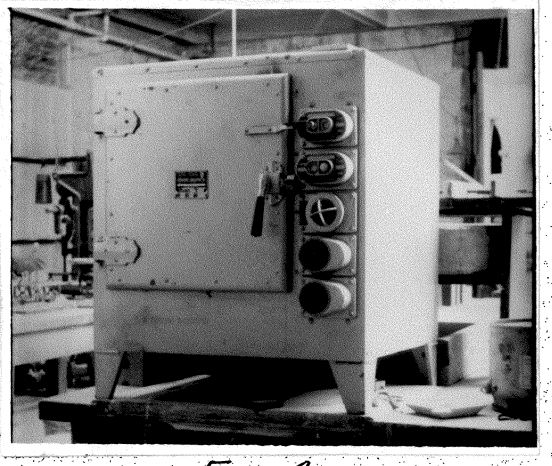


Fig. 4

Testing: At the end of four hours the flasks were removed from the oven and cooled quickly under water. Each flask was carefully rotated to take into solution any drops around the edges. Approximately 3 ml. were poured from the flasks into the small beaker of the Beckman pH meter and pH readings were taken for the solutions in each flask. The 3 ml. of solution was then returned to its respective flask.

To each of the five flasks containing glass samples five drops of the phenol red indicator was added. The solutions in each flask were then titrated with NaOH, whose exact normality was known, until about 1 cc. was added in excess (after the solution turned pink). The titration apparatus shown in Fig. 1 was used. The solution was then immediately titrated with H_2SO_4, whose exact normality was known, until one drop caused the color to change from pink to yellow. The exact amount of NaOH and H_2SO_4 used was recorded.

The blank solution was then measured to determine its exact volume. Its difference in volume from the original 50 cc. was considered to be lost due to evaporation in the oven. This new volume was considered to be representative of the other solutions and was used in determining the total amount of acid used.

Results of these tests were then calculated into grams of Na_2O leached from the glass by the three methods previously named. Results were recorded in Tables IV, V, VI, and VII. A distribution plot was made to give a clear overall picture of the results, and a statistical analysis was applied to obtain further information.

Table IV
Data

Durability Determinations

Glass A - A.C.S. Titration Method

Flask No.	Total cc. H_2SO_4	Total cc. NaOH	Required cc. H_2SO_4	Excess cc. H_2SO_4	Equivalent cc. NaOH	gms. NaOH	gms. Na_2O
1	49.2	34.7	35.2	14.0	13.8	0.01148	0.00890
2	50.2	33.0	33.5	16.7	16.5	0.01353	0.01049
3	49.9	33.2	33.7	16.2	16.0	0.01312	0.01017
4	49.7	32.7	33.2	16.5	16.3	0.01337	0.01036
5*	-	-	-	-	-	-	-
					Average	0.01288	0.00998

N/0.0197 H_2SO_4

N/0.0205 NaOH

Glass A - pH Method

			Doran Calculation		Experimental Calculation	
Flask No.	pH Before Digestion	pH After Digestion	gms. NaOH	gms. Na_2O	gms. NaOH	gms. Na_2O
1	1.87	1.95	0.00454	0.00352	0.00765	0.00593
2	1.87	1.97	0.00556	0.00431	0.00884	0.00685
3	1.87	1.95	0.00454	0.00352	0.00765	0.00593
4	1.87	1.96	0.00506	0.00392	0.00826	0.00640
5*	1.87	-	-	-	-	-
Blank	1.87	1.87				
		Average	0.00493	0.00382	0.00810	0.00628

* Sample destroyed.

Data

Table V

Durability Determinations

Glass B - A.C.S. Titration Method

Flask No.	Total cc. H_2SO_4	Total cc. NaOH	Required cc. H_2SO_4	Excess cc. H_2SO_4	Equivalent cc. NaOH	gms. NaOH	gms. Na_2O
1	48.9	42.3	44.2	4.7	4.5	0.00425	0.00329
2	49.0	42.6	44.5	4.5	4.3	0.00406	0.00315
3	49.1	42.8	44.7	4.4	4.2	0.00396	0.00307
4	48.9	42.5	44.4	4.5	4.3	0.00406	0.00315
5	48.3	42.0	43.9	4.4	4.2	0.00396	0.00307
					Average	0.00406	0.00314

N/0.0220 H_2SO_4

N/0.0236 NaOH

Glass B - pH Method

			Doran Calculation		Experimental Calculation	
Flask No.	pH Before Digestion	pH After Digestion	gms. NaOH	gms. Na_2O	gms. NaOH	gms. Na_2O
1	1.80	1.88	0.00760	0.00589	0.01181	0.00915
2	1.80	1.87	0.00698	0.00541	0.01129	0.00875
3	1.80	1.87	0.00698	0.00541	0.01129	0.00875
4	1.80	1.85	0.00570	0.00442	0.01023	0.00793
5	1.80	1.84	0.00505	0.00391	0.00957	0.00742
Blank	1.80	1.77				
		Average	0.00646	0.00501	0.01084	0.00840

Data

Table VI

Durability Determinations

Glass C - A.C.S. Titration Method

Flask No.	Total cc. H_2SO_4	Total cc. NaOH	Required cc. H_2SO_4	Excess cc. H_2SO_4	Equivalent cc. NaOH	gms. NaOH	gms. Na_2O
1	49.0	31.2	32.6	16.4	15.7	0.01432	0.01110
2	49.2	31.4	32.8	17.8	17.0	0.01551	0.01202
3	48.8	31.6	33.1	15.7	15.0	0.01368	0.01060
4	49.4	31.3	32.7	16.7	16.0	0.01458	0.01130
5	49.4	32.8	34.3	15.1	14.4	0.01314	0.01018
					Average	0.01425	0.01104

N/0.0218 H_2SO_4

N/0.0228 NaOH

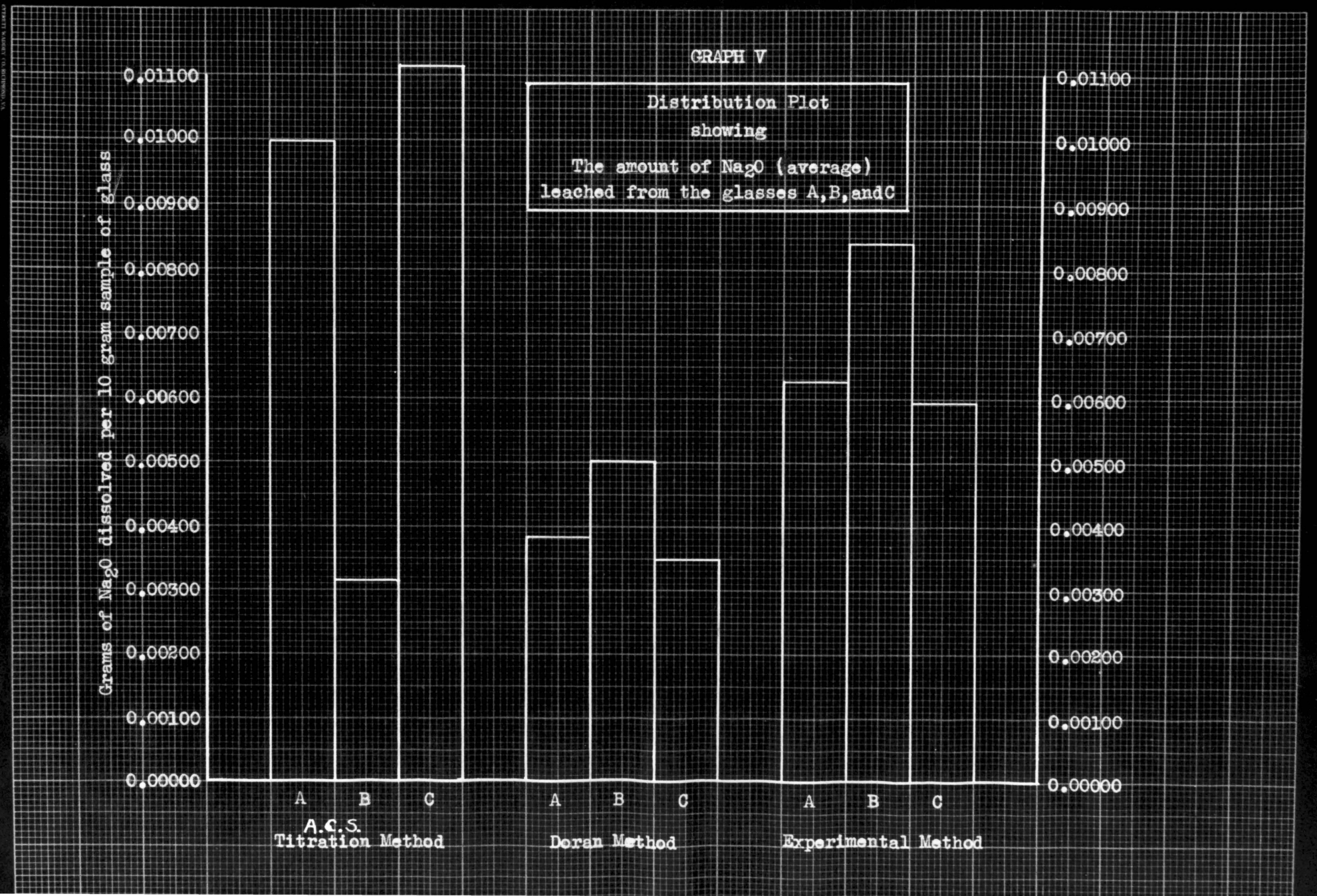
Glass C - pH Method

			Doran Calculation		Experimental Calculation	
Flask No.	pH Before Digestion	pH After Digestion	gms. NaOH	gms. Na_2O	gms. NaOH	gms. Na_2O
1	1.88	2.00	0.00697	0.00540	0.01052	0.00815
2	1.88	1.94	0.00403	0.00312	0.00710	0.00550
3	1.88	1.94	0.00403	0.00312	0.00710	0.00550
4	1.88	1.93	0.00348	0.00270	0.00639	0.00495
5	1.88	1.94	0.00403	0.00312	0.00710	0.00550
Blank	1.88	1.87	-	-	-	-
		Average	0.00451	0.00349	0.00764	0.00592

Table VII

Chemical Durability of Glasses Tested Expressed as gms. Na_2O (Average)

Glass A			Glass B			Glass C		
A.C.S. Method	Doran Method	Experimental Method	A.C.S. Method	Doran Method	Experimental Method	A.C.S. Method	Doran Method	Experimental Method
0.00890	0.00352	0.00593	0.00329	0.00589	0.00915	0.01110	0.00540	0.00815
0.01049	0.00431	0.00685	0.00315	0.00541	0.00875	0.01202	0.00312	0.00550
0.01017	0.00352	0.00593	0.00307	0.00541	0.00875	0.01060	0.00312	0.00550
0.01036	0.00392	0.00640	0.00315	0.00442	0.00793	0.01130	0.00270	0.00495
-	-	-	0.00307	0.00391	0.00742	0.01018	0.00312	0.00550
0.00998	0.00382	0.00628	0.00314	0.00501	0.00840	0.01104	0.00349	0.00592


GRAPH V
Distribution Plot
showing
The amount of Na_2O (average)
leached from the glasses A, B, and C
Grams of Na_2O dissolved per 10 gram sample of glass
0.01100
0.01000
0.00900
0.00800
0.00700
0.00600
0.00500
0.00400
0.00300
0.00200
0.00100
0.00000
A B C
A.C.S.
Titration Method
A B C
Doran Method
A B C
Experimental Method

4. Sample Calculations

1. Determination of gms. Na_2O by the A.C.S. Method.

Glass A - Flask 1

Total cc. H_2SO_4 Used = 49.2 N/0.0197
Total cc. NaOH Used = 34.7 N/0.0205

$x \cdot 0.0197 \cdot 0.049 = 34.7 \cdot 0.0205 \cdot 0.040$

$x = 35.2$ = cc. H_2SO_4 required

$35.2 - 34.7 = 14.0$ = Excess cc H_2SO_4 Used

$x \cdot 0.0205 \cdot 0.040 = 14.0 \cdot 0.0197 \cdot 0.049$

$x = 13.8$ = Equivalent cc. NaOH

$13.8 \cdot 0.0205 \cdot 0.040 = 0.01148$ = gms. NaOH

$0.01148 \cdot \frac{62}{80} = 0.00890$ = gms Na_2O

2. Determination of gms. Na_2O by Doran Method.

Glass A - Flask 1

Initial pH = 1.87 (pH of Blank after heating)

Final pH = 1.95

pH = Minus log C_H = 1.87 $C_H = 0.01350$ gm. H^+/liter

pH = Minus log C_H = 1.95 $C_H = \underline{0.01122}$ gm. H^+/liter

0.00228 gm. H^+/liter change

$0.00228 \cdot 1.55 = 0.00353$

5. Statistical Analysis of Data

Durability of Glasses Tested (gms. $Na_2O \times 10^5$)

	Glass A			Glass B			Glass C		
	A.C.S. Method	Doran Method	Exp. Method	A.C.S. Method	Doran Method	Exp. Method	A.C.S. Method	Doran Method	Exp. Method
	890	352	593	329	589	915	1110	540	815
	1049	431	685	315	541	875	1202	312	550
	1017	352	593	307	541	875	1060	312	550
	1036	392	640	315	442	793	1130	270	495
	998*	382*	628*	307	391	742	1018	312	550
Sum	4990	1909	3139	1573	2504	4200	5520	1746	2960
Average	998	382	628	314	501	840	1104	349	592

Grand Sum	28,541
Grand Avg.	634

Source of Variation	Degrees of Freedom	
Between Glasses	2	
Between Methods	2	
Glasses x Methods	4	
Within A.C.S. Method	12	
Glass A		(4)
Glass B		(4)
Glass C		(4)
Within Doran Method	12	
Glass A		(4)
Glass B		(4)
Glass C		(4)
Within Exp. Method	12	
Glass A		(4)
Glass B		(4)
Glass C		(4)
Total	44	

* An average was used to facilitate calculations.

To Find the Sum of Squares for Sources of Variation:

Correction Term = $C = \frac{(28,541)^2}{45} = 18,101,971$

Total Sum of Squares = $\Sigma\left[(890)^2 + (1049)^2 + \cdots + (550)^2\right] - C = 3,514,398$

Between Glasses S.S. =

$$\frac{\Sigma\left[(4990 + 1909 + 3139)^2 + (1573 + 2504 + 4200)^2 + (5520 + 1746 + 2960)^2\right]}{15} - C = 154,112$$

Between Methods S.S. =

$$\frac{\Sigma\left[(4990 + 1573 + 5520)^2 + (1909 + 2504 + 1746)^2 + (3139 + 4200 + 2960)^2\right]}{15} - C = 1,231,46$$

Sub Table

Glass / Method	A	B	C	Total
A.C.S.	4990	1573	5520	12,083
Doran	1909	2504	1746	6,159
Exp.	3139	4200	2960	10,299
Total	10038	8277	10226	28,541

Sub Total S.S. = $\frac{\Sigma\left[(4990)^2 + (1909)^2 + \cdots + (2960)^2\right]}{5} - C = 3,310,542$

Between Glasses S.S.	154,112
Between Methods S.S.	1,231,467
Glasses . Methods S.S.	1,924,963 (By Subtraction)
Sub Total S.S.	3,310,542

Within A.C.S. Method S.S.

Glass A S.S. $= \Sigma\left[(890)^2 + (1049)^2 + \cdots + (998)^2\right] - \frac{(4990)^2}{5} = 16,070$

Glass B S.S. $= \Sigma\left[(329)^2 + (315)^2 + \cdots + (307)^2\right] - \frac{(1573)^2}{5} = 324$

Glass C S.S. $= \Sigma\left[(1110)^2 + (1202)^2 + \cdots + (1018)^2\right] - \frac{(5520)^2}{5} = 19,648$

$\therefore$ Within A.C.S. Method S.S. = 16070 + 323 + 19648 = 36,042

Within Doran Method S.S.

Glass A S.S. $= \Sigma\left[(352)^2 + (431)^2 + \cdots + (382)^2\right] - \frac{(1909)^2}{5} = 4,301$

Glass B S. S. $= \Sigma\left[(589)^2 + (541)^2 + \cdots + (391)^2\right] - \frac{(2504)^2}{5} = 26,525$

Glass C S.S. $= \Sigma\left[(540)^2 + (312)^2 + \cdots + (312)^2\right] - \frac{(1746)^2}{5} = 46,829$

$\therefore$ Within Doran Method S.S. = 4301 + 26525 + 46829 = 77,655

Within Experimental Method S.S.

Glass A S.S. $= \Sigma\left[(593)^2 + (685)^2 + \cdots + (628)^2\right] - \frac{(3139)^2}{5} = 5,843$

Glass B S.S. $= \Sigma\left[(915)^2 + (875)^2 + \cdots + (742)^2\right] - \frac{(4200)^2}{5} = 19,888$

Glass C S.S. $= \Sigma\left[(815)^2 + (550)^2 + \cdots + (550)^2\right] - \frac{(2960)^2}{5} = 64,430$

$\therefore$ Within Experimental Method S.S. = 5843 + 19888 + 64430 = 90,161

Source of Variation	D/F	Sum of Squares	Mean Squares
Between Glasses	2	154,112	77,056
Between Methods	2	1,231,467	615,734
Glasses x Methods	4	1,924,963	481,241
Within A.C.S. Method	12	36,042	3,004
Glass A	(4)	(16070)	(4018)
Glass B	(4)	(324)	81)
Glass C	(4)	(19648)	(4912)
Within Doran Method	12	77,655	6,471
Glass A	(4)	(4301)	(1075)
Glass B	(4)	(26525)	(6631)
Glass C	(4)	(46829)	(11,707)
Within Exp. Method	12	90,161	7,513
Glass A6	(4)	(5843)	(1461)
Glass B	(4)	(19888)	(4972)
Glass C	(4)	(64430)	(16,108)
	Total 44 (36)	(203,858)	

"F"* Tests for Significance

The smallest mean square of the within variables (Within A.C.S. Method = 3004) was used as the error term in testing the other within variables.

Within Doran Method $F = \frac{6,471}{3,004} = 2.15$

Within Exp. Method $F = \frac{7,513}{3,004} = 2.50$

The allowable "F" in both cases was 2.69. As there was no significant difference within any of the three methods, these variances were "pooled" to form a valid error term as follows:

---

* H. A. Freeman, Industrial Statistics. John Wiley and Sons., Inc., New York, 1942.

"Pooled" Error Term = $\frac{(36042 + 77655 + 90161)}{36} = 5663$

This error term was used in testing the other sources of variation.

Between Glasses: $F = \frac{77056}{5663} = 13.61$

The allowable "F" was 3.26; therefore, there was a significant difference between glasses as was expected.

Between Methods: $F = \frac{615734}{5663} = 108.73$

The allowable "F" was 3.26; therefore, there was a highly significant difference between methods. An orthogonal comparison was then used to determine between which methods there was the greatest difference.

Orthogonal Comparison

	A(A.C.S. Method)			B(Doran Method)			C(Exp. Method)		
	4990	1573	5520	1909	2504	1746	3139	4200	2960
A vs. B	+	+	+	-	-	-	0	0	0
(A+B) vs. C	+	+	+	+	+	+	-2	-2	-2
A vs. C	+	+	+	0	0	0	-	-	-
(A+C) vs. B	+	+	+	-2	-2	-2	+	+	+
B vs. C	0	0	0	+	+	+	-	-	-
(B+C) vs. A	-2	-2	-2	+	+	+	-	-	-

S.S. A vs. B = $\Sigma\left[\frac{(4990 + 1573 + 5520)-(1909 + 2504 + 1746)}{6(5)}\right]^2$ = 1,169,792

S.S. (A+B) vs. C = $\Sigma\left[\frac{(4990 + 1573 + 5520 + 1909 + 2504 - 1746)-2(3139+4200+2960)}{18(5)}\right]^2$ =

61,675

S.S. A vs. C = $\Sigma\left[\frac{(4990 + 1573 + 5520)-(3139 + 4200 + 2960)}{6(5)}\right]^2$ = 106,088

S.S. (A+C) vs. B =

$\Sigma\left[\frac{(4990 + 1573 + 5520 + 3139 + 4200 + 2960) - 2(1909 + 2504 + 1746)}{18(5)}\right]^2$ = 1,125,379

S.S. B vs. C = $\Sigma\left[\frac{(1909 + 2504 + 1746)-(3139 + 4200 + 2960)}{6(5)}\right]^2$ = 571,320

S.S. (B+C) vs. A =

$\Sigma\left[\frac{(1909 = 2504 + 1746 + 3139 + 4200 + 2960)- 2(4990 + 1573 + 5520)}{18(5)}\right]^2$ = 660,147

The " pooled " error term previously found was used to test for significance.

A.C.S. Method vs. Doran Method: $F = \frac{1,169,792}{5663} = 206.6$

A.C.S. Method vs. Exp. Method: $F = \frac{106088}{5663} = 18.7$

Doran Method vs. Exp. Method: $F = \frac{571320}{5663} = 100.9$

The allowable "F" in each case was 4.11; therefore each method differed significantly from the other. The greatest difference occurred between the A.C.S. Method and the Doran Method. The least difference occurred bet-

ween the A.C.S. Method and the Experimental Method.

A further statistical breakdown could be employed to determine which method had the greatest or least variance for each glass tested; however, this information was not considered relevant to this investigation.

V DISCUSSION

From the results obtained in this investigation, there seemed to be very little agreement between the three methods used. It was considered necessary, however, to apply a statistical analysis to these results to determine if this difference between methods was real or merely due to chance. This analysis proved conclusively that a real difference between methods did exist.

The order of durability of the glasses tested was C, A, B for both the Doran and Experimental method. The Doran method, in each case, gave results significantly lower than the Experimental Method. This indicated that the straight line relationship, necessitated by the Doran method, if plotted, would have a greater slope than the actual titration curves. Because the results of both methods were parallel and because the titration curves were determined by actual measurements, it was the writer's opinion that the Experimental method is more accurate in converting pH determinations into grams of dissolved alkali.

The order of durability of the glasses tested by the A.C.S. method was B, A, C. If this method was known to be a true and accurate measure of durability, the pH method would have to be completely disregarded, if this investigation was to be used as a basis. In performing the tests in this investigation, however, the writer noticed several things that led him to believe the A.C.S. method to be rather inaccurate. For one thing it was very difficult to determine the exact end point of the titrations. Another was the fact that a portion of the digesting solution

was evaporated in the oven, thus making it nearly impossible to determine the exact amount of H_2SO_4 that was used. The writer attempted to correct this by determining the final volume of the blank solution, and applying this correction to the other solutions which were heated at the same time. This method of correction could not, however, be considered to be entirely adequate.

These two faults were considered to be highly important, as small inaccuracies in volumes of H_2SO_4 used appreciably affected the calculations for determining grams of Na_2O.

From the statistical analysis it may be seen that the A.C.S. method had the least variation and the Experimental method the greatest. It was found, however, that there was no significant difference between the variations of the methods. This merely means that according to the laws of probability the differences in variations could be accounted for by chance.

Although there was found to be a highly significant difference between each method, it was interesting to note that the least difference occurred between the A.C.S. Method and the Experimental Method. This fact led the writer to believe that the Doran Method gave results significantly lower than they should be.

VI SUMMARY

Because of the wide variation of results obtained in this investigation it is impossible to draw any accurate conclusions. If the American Ceramic Society Tentative Method for measuring the durability of glass is to be considered a true and accurate testing method, and if the results obtained in this investigation are to be considered entirely accurate, the pH method would have to be disregarded as a durability testing method. However, from a working knowledge of the testing methods obtained in this investigation, and the results obtained, the writer has expressed as his own opinion the following conclusions:

1. Due to inherent inaccuracies of methods, no numerical value can be stated to be the exact durability of a glass. Durabilities may be expressed only relatively, with the testing method specified.

2. Relative durabilities of glasses may be determined by pH measurements. This method is simpler in operation and fewer inaccuracies are encountered than in the American Ceramic Society Tentative Method.

3. More accurate conversions of pH changes to grams of dissolved alkali may be obtained by the use of titration curves. The Doran method for making this conversion is a faster method, but results are significantly lower. As measurements are relative, either method of conversion may be used if the method is specified.

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