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TITRATION AND CONDUCTIVITY MEASUREMENTS OF AQUEOUS EXTRACTS FROM BOTTLES

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ABSTRACT

In a study of the titration of aqueous extracts from glass containers, it was shown that certain precautions must be observed if reliable results are to be obtained. "Direct" and "back" titrations were made potentiometrically and with a series of indicators to demonstrate the effect of the presence of CO_2 and of "flakes."

When the alkalinities of the aqueous extracts from bottles, as determined by direct titration, were plotted against their specific conductivities, a linear relation was obtained for 9 out of 13 different bottles. The "back titers" of the filtered extracts, when plotted against the conductivities, gave a similar straight line for the same 9 bottles. The relation between the "back titers" and the conductivities of unfiltered extracts was variable. The results indicate that the determination of only one property of the extracts, such as alkalinity or conductivity, may lead to erroneous conclusions.

CONTENTS

I. INTRODUCTION

Many liquids upon storage in glass containers have been known, at times, to undergo unexpected and undesirable changes in appearance, odor, composition, and alkalinity. Beverages have developed "flakes" high in silica content, which are objectionable from the standpoint of appearance of the product. Neutral saline solutions prepared for intravenous injection have also developed these flakes and have even become toxic because of changes in alkalinity. Serums have undergone alkalinity shifts with accompanying changes in composition, color, and potency; and culture media have shown changes in pH sufficient to render them useless. Since the source of most of these objectionable features has been traced to the quality of glass from which the containers were made, reliable methods for determining the chemical durability of glass are needed.

The selection of a method depends upon the circumstances involved. In the case of popular beverages the effect of flakes on their appearance is the important factor. For pharmaceutical preparations the absence of toxic effects is the prime consideration. Freedom from change of pH may be the vital factor in preserving culture media. In seeking suitable means for evaluating the relative suitability of glass containers for storing liquids, much attention has been given to determining the quantity of alkali extracted from the inner surfaces by distilled water. The question arises whether this determination offers a satisfactory criterion for durability comparison, but because of the extensive use which has been made of this method an investigation was undertaken of some of the factors affecting it.

At first glance this evaluation would seem to be a simple question of an alkali titration or of a conductivity measurement, with few precautions necessary for obtaining reproducible and comparable results. Such is far from being the case. Since there is no suitable method for measuring the area of the inner surface of the containers, it is obvious that bottles of equal capacity and similar shapes are the only ones that can be readily compared. Furthermore, it cannot be too strongly emphasized that this test is not one of true solubility [1].[1] The test involves a decomposition of the glass and a subsequent solution of some of the decomposition products, followed in some cases by mechanical removal of insoluble materials (flakes) from the attacked area. This type of reaction is highly susceptible to slight differences in experimental conditions, such as temperature [1, 2, 9] and pH [2]. However, assuming that these factors are adequately controlled, certain other precautions for titrating the alkali extracts are necessary. Since these precautions, in much of the work reported, have been overlooked or disregarded, the present work was undertaken in an attempt to clarify the situation and to show what is necessary to obtain comparable results.

II. TITRATIONS OF AQUEOUS EXTRACTS FROM GLASS BOTTLES

1. EXPERIMENTAL PROCEDURE

New commercial bottles were rinsed three times and filled to their rated capacity with distilled water, covered with Pyrex covers, heated at 100° C in a covered boiler for 24 hours, and cooled to room temperature. The alkali extracted from the inner surface was then determined by titration. The standard, approximately 0.02 *N*, sodium hydroxide and sulfuric acid solutions were prepared by the usual procedures for minimizing the quantity of carbon dioxide present. The sodium hydroxide was standardized potentiometrically against potassium acid phthalate (NBS Standard Sample No. 84) and the sulfuric acid standardized against this sodium hydroxide.

All the titration data obtained with organic indicators were compared with the values obtained potentiometrically, using the saturated

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[1] Figures in brackets indicate the literature references at the end of this paper.

calomel half-cell and glass electrode as reference and indicator electrodes, respectively. The emf measurements were made with a Leeds and Northrup portable potentiometer electrometer. The glass electrode was prepared by blowing a small bulb of Corning 015 glass [3] on the end of a soft glass tube and filling the bulb with mercury [4] for the electric connection. Although metal-filled glass electrodes are not considered as reliable for precise work as the solution-filled types, they were satisfactory for the present investigation.

2. FILTERED SOLUTIONS

(a) EFFECT OF CARBON DIOXIDE

Since glass is a fused mixture of strong, basic oxides, such as Na_2O and CaO, and weak acidic oxides, such as SiO_2 and B_2O_3, any attack on the glass by water will result in an alkaline solution. Such solutions when exposed to the atmosphere react readily with carbon dioxide, and, as a result, all unprotected bottle extracts absorb from small to appreciable amounts of carbon dioxide. The results of a direct titration made potentiometrically on a filtered bottle extract are shown in figure 1 (*A*) and table 1. The double end point is characteristic of solutions containing carbon dioxide.

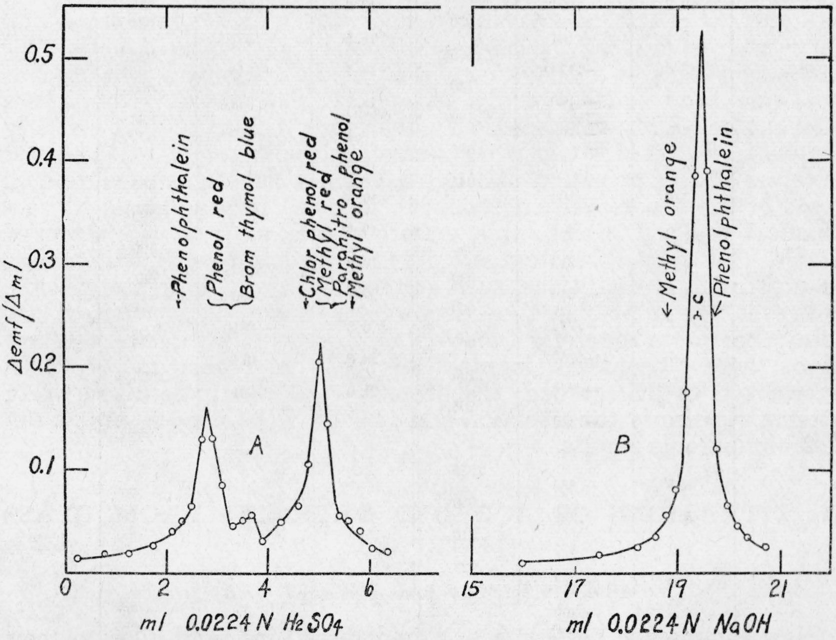

FIGURE 1.—*Comparison of potentiometric titrations with titrations made to the end point of seven organic indicators.*

A, Direct titrations. *B*, Back titrations after removal of CO_2 by the addition of 25.0 ml of 0.0224 *N* H_2SO_4, and exhaustion under reduced pressure. (Bracket indicated by *C* shows the titration spread for all the indicators from paranitrophenol to phenol red.)

TABLE 1.—*Typical potentiometric titrations (direct and back) of 100-ml filtered water extract from American Ceramic Society bottle glass No. 1, for comparison with titrations made on aliquots, using dye indicators.*

[25.0 ml of 0.0224 *N* H_2SO_4 was added to the extract prior to the back titration]

Direct titer			Back titer		
0.0224 *N* H_2SO_4	emf	Δemf/Δml	0.0224 *N* NaOH	emf	Δemf/Δml
ml	*Volts*		*ml*	*Volts*	
0.0	−0.045		0.0	−0.439	
		0.014			0.002
.5	−.052		5.0	−.430	
		.018			.001
1.0	−.061		10.0	−.418	
		.018			.004
1.5	−.070		15.0	−.397	
		.026			.008
2.0	−.083		17.0	−.380	
		.040			.017
2.2	−.091		18.0	−.363	
		.050			.024
2.4	−.101		18.5	−.351	
		.065			.035
2.6	−.114		18.7	−.344	
		.130			.055
2.8	−.140		18.9	−.333	
		.130			.080
3.0	−.166		19.1	−.317	
		.085			.175
3.2	−.183		19.3	−.282	
		.045			.385
3.4	−.192		19.5	−.205	
		.050			.390
3.6	−.202		19.7	−.127	
		.055			.120
3.8	−.213		19.9	−.103	
		.030			.065
4.0	−.219		20.1	−.090	
		.050			.045
4.5	−.244		20.3	−.081	
		.065			.035
4.7	−.257		20.5	−.074	
		.105			.026
4.9	−.278		21.0	−.061	
		.205			
5.1	−.319				
		.145			
5.3	−.348				
		.055			
5.5	−.359				
		.050			
5.7	−.369				
		.040			
5.9	−.377				
		.023			
6.2	−.384				
		.020			
6.5	−.390				

Upon removal of this carbon dioxide by the addition of 25.0 ml of the standard sulfuric acid (a quantity known to be in excess of the alkali in the extract), heating, boiling under reduced pressure, and then titrating the excess acid, a marked change appears in the characteristics of the potentiometric titration curve. The results are shown in figure 1 (*B*) and in table 1. A comparison of the curves in figure 1 for the direct and back titrations emphasizes certain facts. The direct titration, *A*, shows the glass extract to be partially buffered, with relatively small voltage changes accompanying each addition of the titrating solution near the end points, while the back titration, *B*, in which the extract is unbuffered, shows much larger voltage changes per unit of addition. From these facts it is evident that the choice of an indicator which will give the correct answer by the direct titration is more limited than for the back titration.

(b) CHOICE OF INDICATOR

The end points for seven indicators used in direct and back titrations on 100-ml aliquot portions of a composite bottle extract are given in table 2, which also gives the results of potentiometric titrations on the same solution. It is apparent from this table that among the seven indicators only three—namely paranitrophenol, methyl red, and methyl orange—give end points in direct titration which approach that obtained by potentiometric back titration. Methyl red, which has been used for this titration [5], goes through a series of color appearances and fade-outs, making it difficult to use. However, if one waits for the fade-outs and continues to titrate until a permanent red persists, consistent results can be obtained, although they are still below the value obtained by the back titration. For the back titration all the indicators, with the exception of phenolphthalein and methyl orange, give end points within 0.15 ml of the same value and which are very close to the end point obtained potentiometrically.[2]

TABLE 2.—*Titration values obtained with the organic indicators in "direct" and "back" titrations for comparison with the values obtained potentiometrically*

Indicator	pH range	0.0224 *N* acid		Color	
		Direct titer	Back[a] titer	Base	Acid
		ml	*ml*		
Phenolphthalein	8.3 to 10.0	2.30	5.30	Pink	Colorless.
Phenol red	6.8 to 8.2	3.30	5.50	Red	Straw yellow.
Bromthymol blue	6.0 to 7.6	3.30	5.55	Blue	Do.
Paranitrophenol	5.0 to 7.0	5.20	5.62	Yellow green	Colorless.
Chlorphenol red	4.8 to 6.4	4.85	5.63	Purple	Straw yellow.
Methyl red	4.4 to 6.0	5.2	5.60	Straw yellow	Red.
Methyl orange	2.9 to 4.0	5.7	6.2	Orange yellow	Do.
Potentiometric		[b] 2.8 5.0	5.5		

[a]Values in this column were obtained by subtracting from 25.0 the number of milliliters of 0.0224 *N* NaOH required for full color change for indicators for the back titration.
[b]Double end point (see fig. 1).

The value obtained potentiometrically for the direct titration is approximately 0.5 ml lower than the value obtained by back titration. This difference may be due to interference of carbon dioxide and insoluble materials in the alkaline solution.

3. EFFECT OF SUSPENDED MATTER

Many bottles yield considerable suspended material (flakes) when digested with distilled water. A sample of these flakes taken from bottles made of American Ceramic Society bottle glass No. 1 [5] had the following composition: [3]

	Percent
SiO_2	54.5
R_2O_3	8.9
CaO	8.4
MgO	28.3

In order to determine what effect they might have upon the direct and back titrations, flakes from 18 bottles which had been digested for 24 hours at 100° C were transferred onto a Jena glass filtering

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[2] The reagents were standardized potentiometrically. If the standardizations had been made with each indicator independently, it is possible that the results might have agreed even more closely.
[3] Analysis was made by F. W. Glaze.

crucible, washed once, and then suspended in 500 ml of distilled water. Fifty-milliliter aliquot portions of this suspension were titrated potentiometrically. For the direct titration the value indicated was less than 0.10 ml of 0.0224 N acid; hence it can be reasonably concluded that the presence of these flakes will not cause any appreciable error or lack of reproducibility in the direct titration.

Two series of tests were made on the conditions affecting the back titration, one to ascertain whether or not the time of digestion was a factor and the other to determine what effect, if any, the quantity of excess acid added might have upon the results. Fifty-milliliter aliquot portions were digested in Pyrex beakers on the steam bath for 15 minutes, 30 minutes, and 3 hours with 25.0 ml of 0.0207 N H_2SO_4. The results obtained are plotted in figure 2 and show that alkali continues to be extracted from these flakes for a long time. Other aliquot portions were digested on the steam bath 30 minutes with 10, 25, and 50 ml of 0.0207 N H_2SO_4 and then titrated. The alkali extracted was equivalent to 1.4, 1.8, and 1.7 ml of 0.02 N acid, respectively. Although these latter results are not consistent, in the light of the uncertainties of the heating schedule and of obtaining aliquot portions of the flakes, it appears that the amount of excess acid is not nearly so important a factor as the time of digestion.

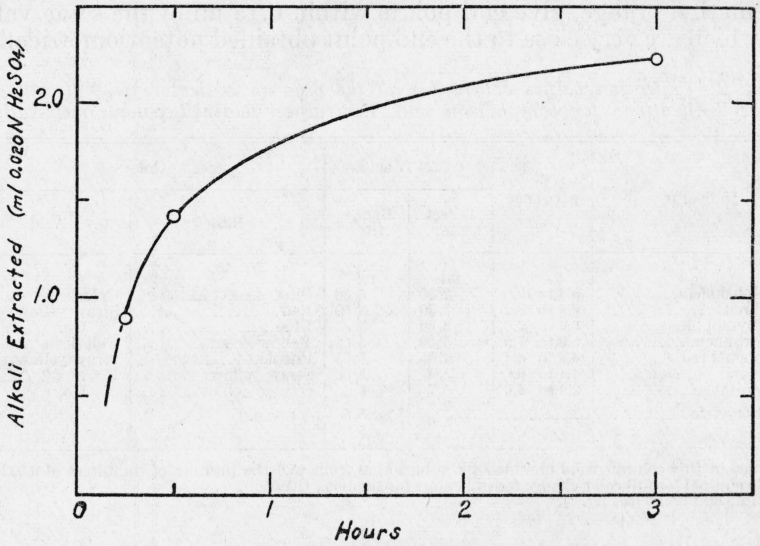

FIGURE 2.—*Effect of the time of digestion on the amount of alkali extracted from "flakes."*

To obtain reproducible results with the back titration on bottle extracts containing flakes, it would be necessary either to establish a carefully controlled digestion procedure or else to filter the flakes before digestion with the excess acid. Since the former could not give a satisfactory answer, even though it were a reproducible one, and because of the indefinite amount of alkali extracted from the flakes, it is necessary to remove the flakes before digestion and evaluate them independently.

III. CONDUCTIVITY MEASUREMENTS OF AQUEOUS EXTRACTS FROM BOTTLES

1. INTRODUCTION

Having established some of the uncertainties in determining the alkalinity of bottle extracts by titration, the next step was to determine the merits of these alkalinity titrations as criteria of the relative durability of glass containers. Conductivity measurements of aqueous extracts have been suggested as a simple and accurate means of determining the chemical durability of glass containers, and this method was investigated [6, 7]. The conductance of the solution will vary approximately as its concentration. A deviation from a strictly linear relation will result from variations in the composition of the extract, since each kind of ion has its own specific conductance. As these water extracts are alkaline, they absorb CO_2 rapidly and must be protected.

2 EXPERIMENTAL PROCEDURE

The bottles were filled to their rated capacity with hot boiled distilled water and placed in the covered boiler at 100° C. At the end of a 24-hr. boiling period the bottles were removed one at a time from the boiler and tightly stoppered with cork stoppers, containing CO_2 guard tubes of Pyrex glass, so constructed that any moisture that might come in contact with the Ascarite in the tube could not drip back into the bottle. The specific conductivities of the extract were determined at 25° C. A pipette-type conductivity cell was used (fig. 3). The constant of this cell was 0.14173 mho (reciprocal ohm) cm. The resistance measurements were made using an a-c bridge similar to that described by Jones and Josephs [8]. All the conductivity determinations were corrected for the conductivity of the distilled water (1.043×10^{-6} mhos/cm).

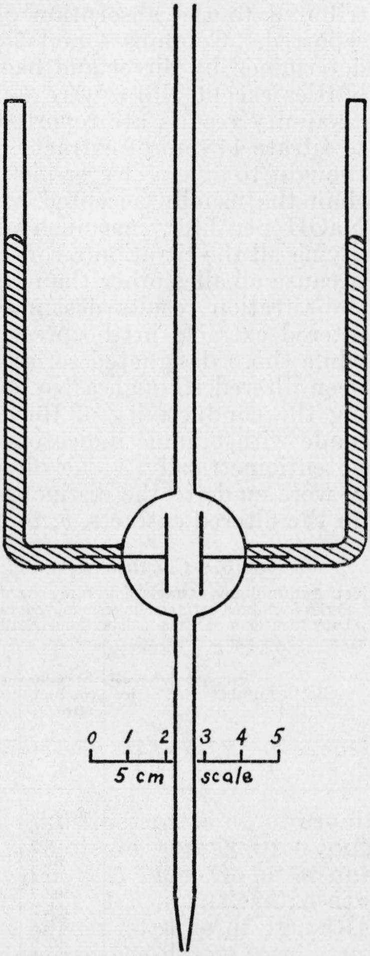

FIGURE 3.—*Pipette-type conductivity cell.*

Following the conductivity determinations, the extracts were titrated directly to the methyl red or the paranitrophenol end point. Then enough standard acid to make its total volume 25.0 ml was added, and the solutions were back-titrated potentiometrically.

3. DATA AND DISCUSSION

Typical results are given in table 3, in which column 3 gives the specific conductivities of the various extracts. The effect of absorbed CO_2 on the conductivity of the aqueous extracts cannot be emphasized too strongly. Even with protected extracts, the second determination has always been lower than the first by 1 to 2 percent of the originally determined conductivity. Since this difference was attributed to the absorption of CO_2, only the first determination is reported. Columns 4 and 5 give the alkalinities of the extracts as determined by direct and back titration, respectively. Since all the bottles except No. 6 were 4-fl-oz bottles (118-ml capacity), all the alkalinity results are reported as milliliters of 0.02 N acid required to titrate 118 ml of extract. Reporting the alkalinity in this unit is thought to give a clearer picture of the alkali extracted from a bottle than the usually accepted practice of reporting it as milligrams of NaOH per liter, inasmuch as the latter procedure involves multiplying all the titration errors by a factor of approximately 9 and also because alkalies other than NaOH are present and are titrated. All the titration results designated series *a* were obtained on the unfiltered extracts in the presence of flakes, if any had been formed, while those designated series *b* were obtained on extracts which had been filtered through a No. 40 Whatman filter paper after determining the conductivity of the extract. All the direct titrations were made with organic indicators and all the back titrations were made potentiometrically. The direct titrations of the unfiltered extracts, *a*, were made to the distinct permanent red of methyl red, and those on the filtered extracts, *b*, to the paranitrophenol end point.

TABLE 3.—*Conductivities and alkalinities of some aqueous bottle-extracts*

[Series *a:* unfiltered extracts, flakes are present, if any were formed; direct titration to methyl red end point. Series *b:* filtered extracts, flakes removed; direct titration to paranitrophenol end point. In all cases the back titrations were made potentiometrically]

Bottle number	Series	Specific conductance, L	0.02 N acid required per 118 ml extract		ΔL	Visible flakes	Type of glass
			Direct titer	Back titer			
1	2	3	4	5	6	7	8
		$mhos\times10^{6}$	*ml*	*ml*	%		
1	*a*	95.6	5.37	6.27	7.7	Yes	Flint.
	b	88.2	4.97	5.23			
2	*a*	64.9	3.56	3.92	3.7	No	Blue.
	b	62.4	3.35	3.69			
3	*a*	102.7	5.09	4.94	3.3	do	Flint.
	b	106.2	5.18	5.04			
4	*a*	208.8	13.07	15.25	3.5	Yes	Do.
	b	201.6	12.44	12.83			
5	*a*	139.1	8.56	10.93	4.3	do	Do.
	b	133.1	7.99	8.61			
6	*a*	111.6	6.67	8.30	15.6	do	Do.
	b	94.2	5.55	6.41			
7	*a*	230.9	14.90	19.69	1.8	do	Do.
	b	226.8	14.54	14.72			
8	*a*	194.5	12.06	15.58	0.4	do	Do.
	b	193.8	12.42	12.85			
9	*a*	243.5	15.22	17.12	1.2	do	Green.
	b	246.4	15.44	15.77			
10	*a*	172.3	8.36	8.19	5.4	No	Amber.
	b	163.0	7.56	7.63			
11	*a*	284.3	18.43	20.19		Yes	Green.
12	*a*	164.4	9.18	8.95	4.5	No	Amber.
	b	172.1	9.14	9.47			
13	*a*	92.2		5.09	max 1.8	do	Flint.
	a	91.3		5.09			
	a	91.1		5.15			
	a	92.8	5.00	5.27			

It can be seen from figure 4 (data in columns 3 and 4 of table 3), that, with the exception of bottle extracts 3, 10, 12, and possibly 13, the conductivities are proportional to the alkalinities by direct titration. It should be noted that bottles 10 and 12 are amber bottles, and qualitative tests on their aqueous extracts showed the presence of sulfates, which would contribute to the conductivity but not to the alkalinity of the extracts. Both indicators appear to be equally good provided the titration to the methyl-red end point is continued to a permanent red. As this latter color is easily recognized, methyl red is to be preferred to paranitrophenol, since it is very hard to determine when the faint yellow color of the latter fades into a colorless solution.

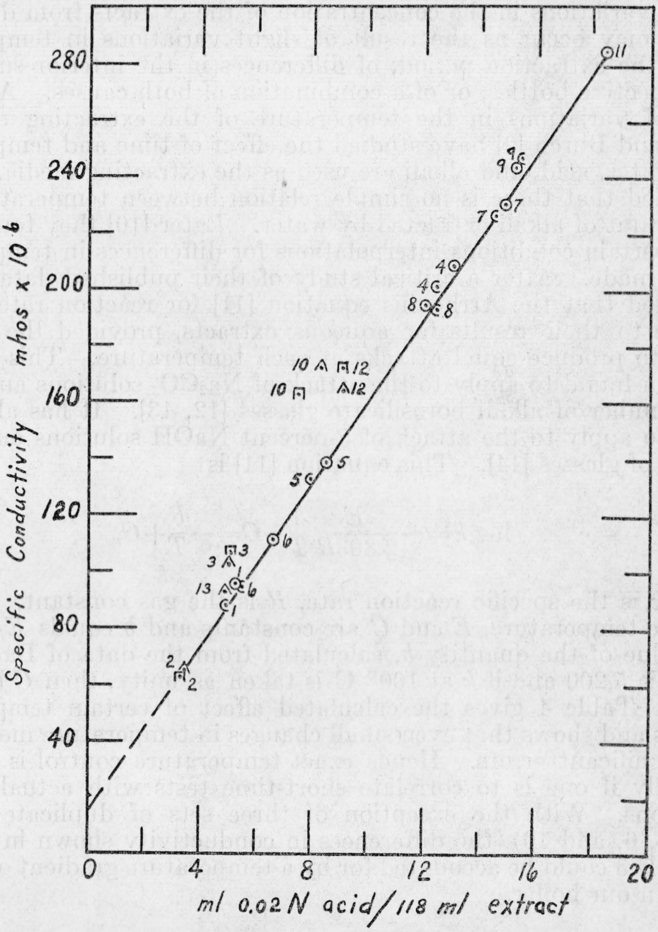

FIGURE 4.—*Conductivity versus alkalinity ("direct" titrations).*

1. Unfiltered extracts. Titrations to methyl red: ○, extract contained flakes; ∧, no visible flakes in extract.
2. Filtered extracts. Titrations to paranitrophenol: (, original solution contained flakes; ⊓, no visible flakes in original extract.

Column 6 of table 3 shows the percentage differences in the specific conductances of duplicate bottles (*a* and *b*). Although some large differences between duplicate bottles are indicated by both conductivity measurements and direct titrations, the conductivity always bears approximately the same ratio to the alkalinity. Therefore, these differences must represent real differences between the extracts and not errors in the determinations.

Such variations in the concentration of the extracts from duplicate bottles may occur as the result of slight variations in temperature during the extraction period, of differences in the interior surface of the respective bottles, or of a combination of both causes. As to the effect of variations in the temperature of the extracting medium, Bacon and Burch [9] have studied the effect of time and temperature when water, acid, and alkali are used as the extracting media. They concluded that there is no simple relation between temperature and the amount of alkali extracted by water. Later [10] they found that under certain conditions interpolations for differences in temperature can be made. After a critical study of their published data, it was concluded that the Arrhenius equation [11] for reaction rates is applicable to their results for aqueous extracts, provided the time is varied to produce equal attacks at each temperature. This relation has been found to apply to the attack of Na_2CO_3 solutions and water on a number of alkali borosilicate glasses [12, 13]. It has also been found to apply to the attack of 5-percent NaOH solutions on a wide variety of glasses [14]. This equation [11] is

$$\log k = -\frac{E}{2.303R}\,\frac{1}{T} + C = -\frac{b}{T} + C,$$

where k is the specific reaction rate, R is the gas constant, T is the absolute temperature, E and C are constants and b equals $E/2.303R$. The value of the quantity b, calculated from the data of Bacon and Burch, is 5,200 and if k at 100° C is taken as unity, then C becomes 13.937. Table 4 gives the calculated effect of certain temperature changes and shows that even small changes in temperature may introduce significant errors. Hence exact temperature control is needed, especially if one is to correlate short-time tests with actual service conditions. With the exception of three sets of duplicate bottles (Nos. 1, 6, and 10), the differences in conductivity shown in column 6 of table 3 could be accounted for by a temperature gradient of 0.5° C or less in our boiler.

TABLE 4.—*Calculated effect of temperature by Arrhenius equation on the rate of attack and the concentration of the resulting aqueous extract.*

[The rate of attack at 100° C is taken as unity]

Extraction temperature	Calculated "relative" rate of attack	Resultant decrease in concentration
° C		*Percent*
100.0	1.000	0.0
99.9	.992	.8
99.5	.958	4.2
99.4	.950	5.0
99.0	.917	8.3
98.0	.841	15.9
25.0	.0003	99.97

The series *b* results plotted in figure 5 (data in columns 3 and 5 of table 3) show that, with the exception of bottle extracts 3, 10, and 12, the conductivities of the various extracts are directly proportional to their respective alkalinities as determined by the back titration of the filtered extracts (flakes removed). Since all the conductivity determinations were corrected for the specific conductivity of the boiled distilled water, the line through the points in figures 4 and 5 should pass through zero if the specific conductivities of the extracts are directly proportional to their alkalinities. The fact that the line does pass through zero for back titrations (fig. 5) but not for direct (fig. 4) indicates that the difference between the direct and back titrations is real and that the back titrations are the more accurate.

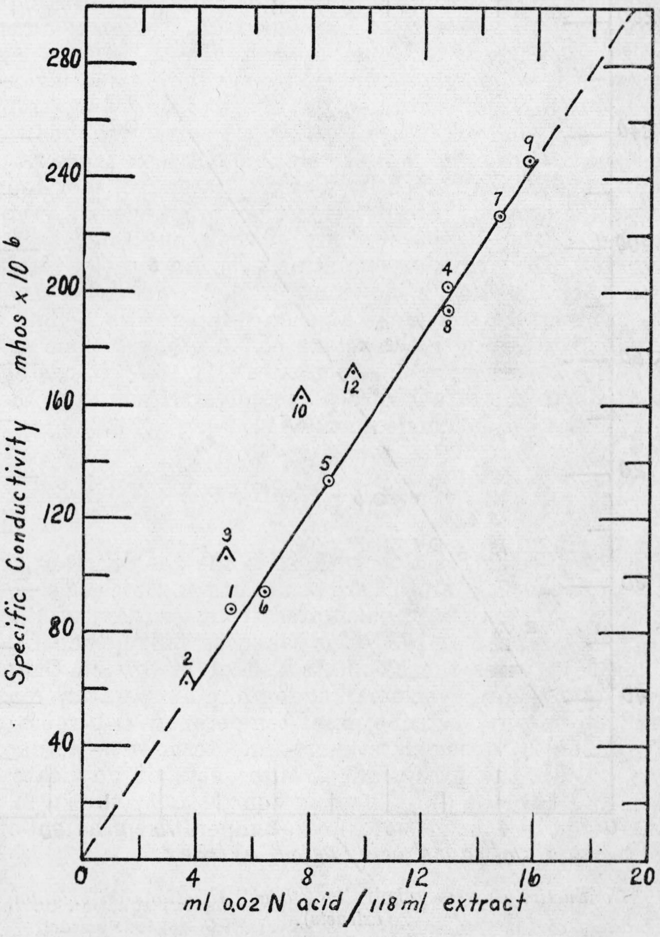

FIGURE 5.—*Conductivity versus alkalinity ("back" titrations on filtered extracts).*

○, original extract contained flakes; ∧, no visible flakes in original extract.

The series *a* results in columns 3 and 5 of table 3 and in figure 6 show that no simple relation exists between the conductivities of the extracts and their respective back titrations in the presence of flakes.

As has been stated earlier in this paper, these titrations will include all of the bases originally in solution plus parts of the alkali initially in the flakes. The amount of the latter depends on the time of digestion on the steam bath, and the conductivity measures only the material originally in solution. It is evident from figures 4, 5, and 6 that the amount of flakes produced by the attacking medium bears no simple relation to the alkalinity and conductivity of the resulting extract. Therefore, the flakes must be evaluated independently as a factor in the durability of glass containers.

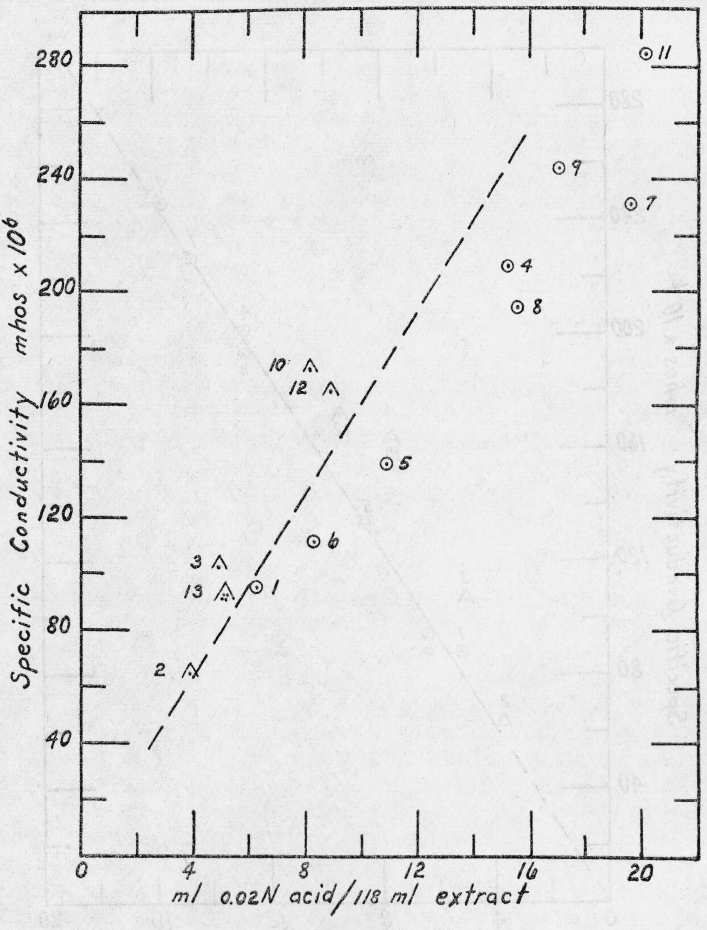

FIGURE 6.—*Conductivity versus alkalinity ("back" titrations on original unfilterd extracts).*

○, extract contained flakes; ∧, no visible flakes in extract.

From the foregoing considerations it is evident that, in any study of the chemical durability of glass containers, other factors besides the alkalinity and conductivity of the extracts must be considered. One such factor which logically presents itself is the determination of the SiO_2 in the extracts.[4] Silica is the principal constituent of most glasses, and it has been demonstrated that with sodium silicate solutions of the same Na_2O concentration, the conductivity of the solutions increases as the SiO_2 concentration is decreased [15]. This fact may account for the position in figures 4, 5, and 6 of the points to the left of the line, which represent extracts from the five bottles which did not produce visible flakes in 24 hours at 100° C. The position of these points on the figure shows that the conductivity-alkalinity ratio, and hence probably the $Na_2O:SiO_2$ ratio, is higher in the extracts from the bottles which did not produce flakes than in the extracts from the other bottles. However, as has already been pointed out, in the case of extracts from bottles 10 and 12, the presence of sulfates may account at least in part for this effect. Of course, other factors, such as extremely low MgO, in the composition of these bottles might also affect the conductivity-alkalinity ratio of the extracts, since MgO is thought to be required for the formation of flakes.[5]

IV. SUMMARY

The amount of flakes produced in glass bottles as a result of attack by water bears no direct relation to the alkalinity or conductivity of the resulting extract. Therefore, the flakes must be evaluated independently as a factor in the durability of glass containers. For evaluating the liquid portion of the extracts, alkalinity or conductivity measurements may be used. If the alkalinity is measured, certain precautions must be observed in order to obtain reproducible results. For the direct titration of these aqueous extracts the choice of indicator is important because of the probability of contamination by CO_2. A more reliable procedure is to make a back titration after elimination of CO_2 by adding an excess of acid and heating and boiling under reduced pressure, in which case the choice of indicator is not so critical. In the latter case the flakes, which are often plentiful in aqueous bottle extracts, must be removed prior to heating in order to prevent their affecting the results.

Both the titration and conductivity methods are capable of giving reproducible results. Although they may not place a given series of bottles in exactly the same order of resistance to attack by distilled water, each gives data which will differentiate between bottles of equal capacities and shapes. Within reasonable limits it can be stated that the greater the titration value or the higher the conductivity of the aqueous extracts from the container, the less satisfactory is the durability of the glass. Since the titration procedure indicates only the alkali extracted from the glass, while the conductivity method is sensitive to all the ions dissolved, the conductivity method probably gives the fairer comparison between containers made from all types of glasses.

However, the question still remains whether the resistance offered by glass to the attack of water is a satisfactory criterion of durability. The enormous difference observed between the attack upon optical glasses by buffer solutions near neutrality and that produced by

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[4] Quick, easy methods have been developed for the colormetric determination of SiO_2. While the application of such methods would require the use of a good spectrophotometer, they would have the advantage that SiO_2 could be conveniently determined in acidic, basic, and neutral extracting media over a wide range of pH [2, 14], provided interfering ions, such as phosphates, were absent. If additional data are required, Na_2O, CaO and MgO, and SO_3 could be determined.

[5] Private communication from W. R. Lester, Maryland Glass Corporation, Baltimore, Md.

water [14] indicates that data obtained for water must not be used too freely in predicting resistance to attack by aqueous solutions.

The authors are indebted to A. N. Finn for his helpful suggestions and cooperation during the progress of this investigation.

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