AN INVESTIGATION OF FREE ALKALI DETERMINATIONS IN SOAP*

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THE determination of free alkali in soap has received widespread attention for many years and is still the subject of considerable discussion. No method has been generally agreed upon as free from objection as well as convenient; in fact, such a method, it is usually conceded, has not as yet been proposed. A review of the literature brings to light many suggestions for the determination of so-called free caustic and total free alkali. The term, free caustic alkali, is defined in the usual way: namely, free NaOH; whereas total free alkali includes free caustic alkali and additional alkaline substances other than soap, principally sodium carbonate and sodium silicate. The same definitions are applied in this paper.

In methods commonly used in determining these quantities, clear chemical distinction between NaOH and other alkalies has not always been made. For several reasons, including a more exact kettle room control and better reproducibility among laboratories, it is desirable to distinguish unmistakably between these two types of alkali. In this paper, a method is proposed for determining free caustic alkali in soap which has certain inherent advantages over methods previously employed. It is not a method for which startling claims can be made, but from the standpoint of precision, accuracy, and convenience, it represents, we believe, an improvement.

In many standard books of reference, free caustic alkali is cited as being determined by solution of the soap in absolute alcohol, filtering, and titrating the filtrate with .1N acid, using phenolphthalein indicator. The alkalies other than NaOH are insoluble in absolute alcohol and remain as a residue which can then be dissolved in water and titrated, using methyl orange. A disadvantage in using this method lies in the slight solubility of soap in absolute alcohol even at the boiling point. A one-gram sample of soap in 100 cc. of absolute alcohol requires only .03 cc. of .1N acid for each .01% of free Na_2O; hence, the experimental error is large. Furthermore, although sodium carbonate is only slightly soluble in absolute alcohol (.0006 g./100 cc. at 73°C.), its solubility is sufficient to account for high results in free caustic alkali to the extent of .02% Na_2O. In addition, the solubility of Na_2CO_3 increases appreciably with increase in water content through moisture in the soap sample or through the aqueous titrating acid. Some procedures call for titrating hot because of the higher solubility of soap at elevated temperature, but a titration hot is neither as reproducible nor as convenient as a titration at room temperature. The temperature coefficient of the end-point, we found to be large enough to account for variations in results unless special precautions were taken to titrate each time at exactly the same temperature.

The same objections can be raised against an alternative method: for example, the standard A. O. C. S. method, employing 95% alcohol in place of absolute alcohol. In this case, the solubility of soap at boiling temperatures is considerably higher, offering some advantage, but the solubility of sodium carbonate is also higher. The value determined in this laboratory is .0037 grams Na_2CO_3 per 100 cc. 95% alcohol (formula No. 30) at 71°C. This corresponds on the basis of a 12-gram sample of soap in 150 cc. of solvent to .017% NaOH or .013% Na_2O free caustic alkali.

We found that the rate of solution of carbonate is slow enough so that only the amount actually dissolved is titrated. It must be borne in mind, therefore, that in results on commercial soaps using the 95% alcohol method as we have outlined below, approximately .013% Na_2O of free caustic alkali is due to the titration of Na_2CO_3, this being the extent of the solubility of carbonate in 150 cc. of alcohol. In the A. O. C. S. Method, the titratable carbonate may be as high as .02 to .1% Na_2O, depending on the weight of sample taken. Calculation shows that 12 g. soap need contain only .05% Na_2CO_3 to saturate 150 cc. of alcohol when the titration is carried out hot; more than this amount is always found in soaps prepared by the usual commercial methods.

Proposed Modifications

Divine[1] suggested that in the determination of total free alkali, an excess of alcoholic stearic acid be refluxed with the soap solution, and then the solution titrated with standard caustic. To obtain free caustic alkali, he suggested adding first $BaCl_2$ to precipitate all carbonate, and then titrating with a standardized alcoholic solution of stearic acid. This method is suitable for the determination of total free alkali; in the determination of free caustic alkali, it is subject to the same disadvantages as the Barium Chloride Method mentioned in a later paragraph.

Davidsohn[2] suggested a modification of the 95% alcohol method in which anhydrous Na_2SO_4 is used to absorb the water of high-moisture soaps, which, it is claimed, if not removed accounts for an appreciable titration of Na_2CO_3 with the NaOH. Knigge,[3] commenting on this suggestion, recommended the substitution of absolute alcohol to decrease solubility of carbonates. He also excluded CO_2 to prevent conversion of free alkali to Na_2CO_3 and filtered off the Na_2SO_4 (using a neutral filter paper) to avoid a recurring end-point at the surface of the sodium sulphate and alcohol. Although carbonate is titrated to an appreciable extent, using 95% alcohol, the lower solubility of carbonate in absolute alcohol is not sufficient to offset the disadvantage of lower solubility of soap. The percentage effect of carbonate solubility in free alkali titration we found to be approximately the same in either alcohol because of the necessity of using different weight samples for sake of convenience in titration. Knigge's suggestion to use absolute alcohol has, therefore, little or no advantage. The suggestion to filter the Na_2SO_4 avoids, as

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[1] R. Divine: *J. A. C. S.*, 22, 693 (1900).

[2] J. Davidsohn: *Chem. Umschau*, 33, 273 (1926); **34**, 260 (1927); *Rayon and Melliand Text. Monthly*, **16**, 55 (1935).

[3] G. Knigge: *Seifensieder Ztg.*, **61**, 772 (1934); *Chem. Umschau*, **39**, 173 (1932).

he mentions, recurrence of the end-point, but this advantage is offset: first, by some conversion of alkali into carbonate in the process of filtering in which the solution comes in contact with the air; secondly, by some adsorption of alkali on the filter paper; and thirdly, by the inconvenience involved in a filtration. By actual experience, we found that the effect of CO_2 in the normal concentration found in the atmosphere is not appreciable in the length of time necessary for titration, although in all operations the general precaution to avoid exposure to CO_2 should always be observed.

The titration of an alcoholic soap solution hot is usually resorted to in order to make possible the titration of a larger sample of soap; but the increased carbonate solubility at high temperatures plus a temperature effect of the end-point, added to the general inconvenience, lends certain advantage to a procedure which calls for titration at room temperature. Schütte[4] added three grams of potassium benzoate to the alcohol solution (200 cc.) to prevent gelling; the titration could then be carried out at room temperature. He observed, however, that added NaOH could not be back-titrated.

Knigge[5] suggested the use of one gram of soap dissolved in 75 cc. of absolute alcohol, the solution at this concentration remaining liquid on cooling. The small sample of soap used makes the experimental error and the effect of carbonate solubility disproportionately large.

Poethke[6] recently investigated the use of various solvent mixtures for soap in free caustic alkali titration and recommended as a result of his work the use of a mixture of propyl alcohol (80 parts by volume) and ethylene glycol. This solvent has the advantage of dissolving soap rapidly and the property that its soap solutions do not gel at room temperature. The solubility of carbonate is appreciable, however, and is partially titrated in the analysis of a commercial soap, the amount depending on the moisture content of the soap sample. The results for free caustic alkali obtained by this method we found to be lower than the results by the alcohol methods. The explanation for these low results is apparent in the conclusion of our work on another solvent mixture mentioned below.

The investigation of free alkali determinations in this laboratory began as a survey of all methods already proposed. The 95% Alcohol, Absolute Alcohol, and Barium Chloride Methods received most attention since they showed promise of being useful in routine examination of soaps. Criticism of the first two methods has already been given. It was found that the Barium Chloride Method applied to soap chips gave reproducible results independent of carbonate content. The results were lower than those of the first two methods, but this is to be expected since it is known that Na_2CO_3 is partially titrated in alcohol solvents, whereas all carbonates are precipitated in the $BaCl_2$ procedure. The titration of a carbonate-free soap[7] indicated that the difference between the 95% Alcohol and Barium Chloride Methods is attributable to carbonate. In addition, the solubility of Na_2CO_3 in 95% alcohol was found to correspond to the difference in results by the two methods. The results are given in Table I.

TABLE I

Soap	% Na_2O Free Caustic Alkali 95% Alcohol Method	 $BaCl_2$ Method	 Difference
Carbonate-free	.027	.024	.003
+ Excess Na_2CO_3	.040	.029	.011
Commercial Chips	.046	.036	.010

Solubility of Na_2CO_3 in alcohol-soap solution from above difference: .0045 g./100 cc.
Solubility of Na_2CO_3 as determined in 95% alcohol: .0037 g./100 cc.[8]

[8] The solubility of Na_2CO_3 in non-aqueous media was determined by adding an excess of the carbonate to a known volume of solvent, boiling the solvent for 15 minutes or more, filtering rapidly through a sintered glass funnel, adding water to the filtrate, and titrating with .1N HCl. The value obtained in this way was checked by another determination in which a known weight of carbonate was added to a known volume of solvent and the residue on filtration dissolved in water and titrated. The two values checked each other.

The figures indicate that within a reasonable experimental error (limited by sharpness of end-point; .0025% Na_2O in 12-gram soap sample = 2 drops of .1N acid) the Barium Chloride Method coincides with the 95% Alcohol Method for a carbonate-free soap. In the titration of a commercial soap containing no fillers, the difference in results is equal, approximately, to the solubility of Na_2CO_3 in alcohol at the titrating temperature. The higher solubility obtained from the difference of the two methods is possibly caused by the presence of soap in the alcohol, or by an absorption effect which increases the observed difference.

There are, however, certain inherent disadvantages in the use of the Barium Chloride Method. Poethke[6a] claimed that the Barium Chloride Method gave low results because of adsorption and that added NaOH could not be entirely back-titrated. We found that the low results given by this method, as compared with the 95% Alcohol Method, are explained by the partial titration in 95% alcohol of Na_2CO_3 present in all commercial soaps and that, if *carbonate-free NaOH* were added, all could be back-titrated. Adsorption, we found, is a relatively small effect. The method does not, however, give a sharp end-point, especially as a color change is obscured by flocs of barium soap suspended in the solvent.

Another method was sought which would eliminate many of the disadvantages of procedure already discussed and increase the reproducibility and accuracy of the determination. The uncertain end-point of the Alcohol and Barium Chloride Methods, with the inconvenience of titrating hot, leaves much to be desired. An attempt to improve the end-point by using other indicators disclosed none that were better than phenolphthalein. A potentiometric end-point using the glass electrode both for the Alcohol and Barium Chloride Methods was not successful. The use of various solvents in place of alcohol was investigated. Cellosolve, butyl alcohol, and n-propyl alcohol were not satisfactory. Solvent mixtures led to better results. In particular, it was found that by using a mixture of benzene-alcohol or carbon tetrachloride-alcohol, the phenolphthalein end-point was sharper and the soap solution did not gel at room temperature. After some preliminary work, benzene-alcohol appeared the better of the two mixtures, and a method for determining free caustic alkali was worked out, using this solvent mixture. It was found that soap dissolved very rapidly, more rapidly

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[4] O. Schütte: *Seifensieder Ztg.*, **57**, 49 (1930).

[5] G. Knigge: *Am. Perfumer*, **29**, 403 (1934).

[6] W. Poethke: (a) *Chem. Umschau*, **39**, 121 (1932); (b) *Chem. Umschau*, **42**, 180, 197 (1935).

[7] The carbonate-free soap was prepared from sodium ethylate and a mixture of fatty acids. Metallic sodium was added to absolute alcohol and allowed to react, out of contact with air. The fatty acids were prepared by adding HCl to a water solution of soap, washing the fatty acid layer several times with water, dissolving in alcohol, and adding the alcohol solution of sodium ethylate in slight excess with phenolphthalein as indicator.

than in alcohol, and that if the proportions of 100 parts of benzene, 75 parts of alcohol, and 2½ parts of water by volume were used, 12.4 g. of soap dissolved in 175 cc. of this mixture did not gel at room temperature. By actual determination, it was found that Na_2CO_3 is less soluble in this mixture at 25°C. than in 95% alcohol at 71°C., the value being .0003 g./100 cc. compared with .0037 g./100 cc. With the addition of water, this solubility increases and the end-point becomes less sharp; for example, with the addition of 1% water, the solubility is .0007 g./100 cc. The non-polar nature of benzene accounts for the low solubility of a polar substance like Na_2CO_3 in a mixture of benzene-alcohol-water; hence, when water is added, it is plausible that the solubility of Na_2CO_3 would increase. The solubility of carbonate affects the free caustic alkali titrated to the extent of about .0013% Na_2O, when the proportions of soap to solvent are those given above and the soap is essentially anhydrous. This value is much smaller than a corresponding effect in 95% or absolute alcohol. The experimental values are given in Table II.

TABLE II

Effect of Na_2CO_3 on Titration of Free Caustic Alkali in Benzene-Alcohol Solvent
12.4 g. of soap, 175 cc. of solvent

Solution	cc. .1N HCl Used for Titration			% Free Caustic Alkali as Na_2O		
	A	B		A	B	
Soap, Carbonate-free	.20	.25		.005	.006	
Soap, Carbonate-free, + Excess Na_2CO_3	.23	.30		.006	.0075	
Difference	.03	.05		.001	.0015	
	A	B	C	A	B	C
Soap Chips	1.52	1.52	0.61	.038	.038	.015
Soap Chips, + Excess Na_2CO_3	1.53	1.55	0.63	.038	.039	.016
Difference	.01	.03	.02	.000	.001	.001

The results indicate in the case of soap chips, which always contain a small natural percentage of Na_2CO_3, that there is no effect, within the experimental error, on the addition of an excess of carbonate. The results also show that an excess of Na_2CO_3 does not titrate more than its normal solubility. Its rate of solution in benzene-alcohol at room temperature is so low that when added in excess and titrated, the pink shade of the phenolphthalein does not reappear unless the solution is boiled to hasten the dissolving of the salt. In the alcohol methods, the recurring end-point caused, as we now know, by carbonates is a source of difficulty which is not encountered in the benzene-alcohol method. The addition of Na_2CO_3 to anhydrous carbonate-free soap causes an increase in titration barely within the experimental error. Were the moisture content of the soap higher, the effect of addition of Na_2CO_3 would have been correspondingly higher (about .001% Na_2O per cc. H_2O addition).

In Table III results are given which show that standard NaOH solution when added to the benzene-alcohol solvent is entirely accounted for when added either to the solvent itself or in the presence of soap. The standard NaOH must be carbonate-free; otherwise, low results are obtained, due to precipitation of carbonates in the solvent. The temperature, it will be noted, has no effect.

TABLE III

Back Titration of Added NaOH

Solution	Temperature of Titration	cc. .1N NaOH Added	cc. .1N HCl Used
Soap Chips	25° C.	1.00	1.00
Soap Chips, Carbonate-free	25° C.	.50 1.00	.50 1.00
	61° C.	1.37	1.35
No solute	30° C. 63° C.	1.37 1.37	1.38 1.39

A study was also made of the effect of water addition to this solvent and amount of indicator on the end-point. The effect of water is shown in Figure 1, in which total water added is plotted with cc. .1N HCl or % free caustic alkali as Na_2O. As water is added, the free caustic alkali increases. Curve A represents a commercial soap chip with initial moisture of 4.5%. A certain amount of water was introduced into this solvent by the moisture of the sample as well as by the titrating solution in neutralizing free caustic alkali. These amounts are indicated on the horizontal axis. When all the alkali had been neutralized, water was added in known amounts and the titration continued. The results show that for each 1 cc. addition of water, the free alkali increases approximately .001% as Na_2O or .0013% as NaOH. This increase on addition of water is due largely to increased solubility of sodium carbonate. Curve B for a carbonate-free soap shows a negligible water correction. In the case of a commercial soap, therefore, an amount of free alkali depending on the initial moisture content and the amount of water added through titration must be subtracted.

For a soap containing 10% moisture and requiring about 1 cc. of standard acid for free caustic al-

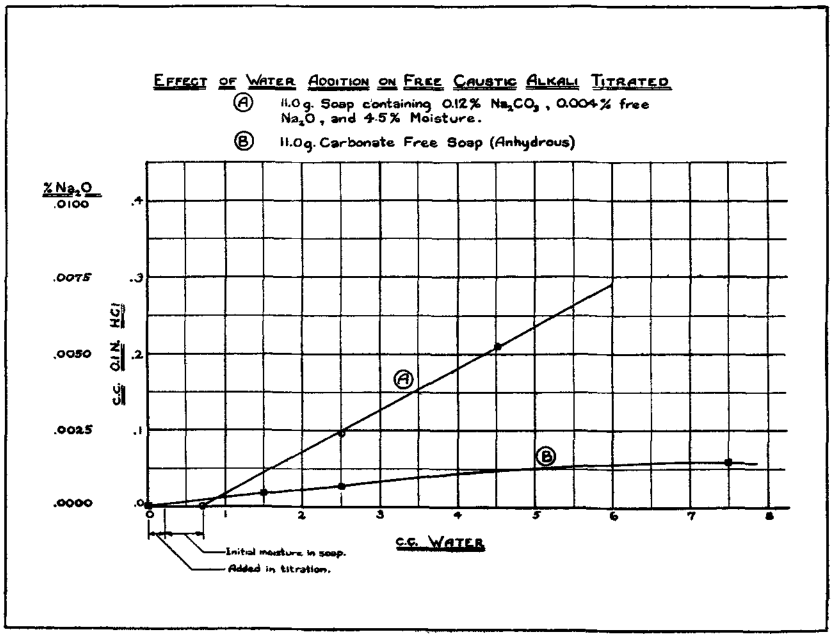

FIGURE 1

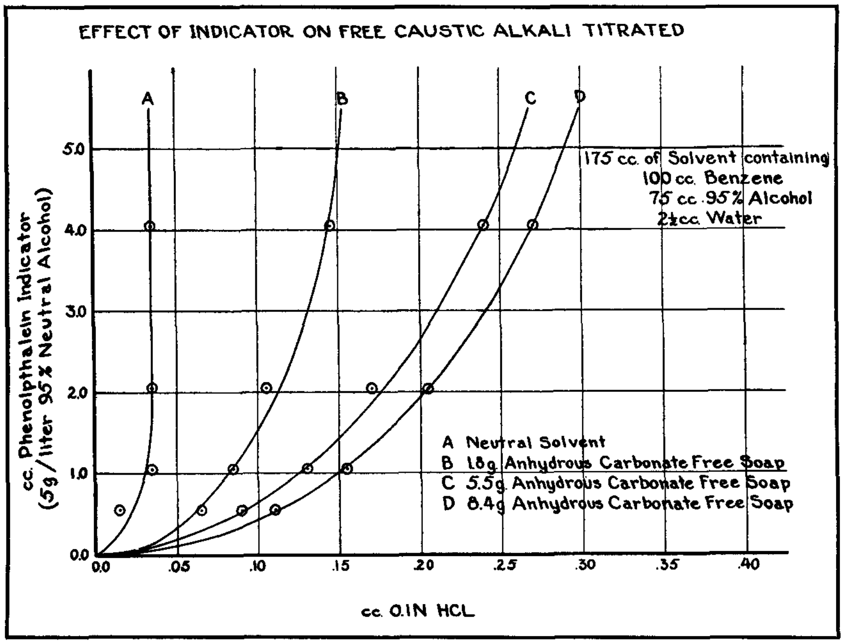

FIGURE 2

kali neutralization, this correction amounts to about .0022% free caustic alkali as Na_2O. For greater precision in the titration of commercial soaps, it would be advisable to use a non-aqueous titrating acid and to dry samples of soap with high moisture content to a moisture of 10% or less in a carbon dioxide-free atmosphere. For practical purposes, it is only necessary that the correction be made of .001% Na_2O per cc. water added, when the volume of solvent and weight of sample are the same as indicated in Figure 1.

The effect of phenolphthalein on the apparent end-point is shown in Figure 2. Phenolphthalein acts as an alkaline addition; furthermore, the greater the concentration of soap, the larger is the apparent alkalinity due to the addition of indicator. Since one cc. of indicator was used in the procedure finally proposed for determining free caustic alkali, the effect of soap concentration on the apparent alkalinity of the solution containing this amount of indicator was plotted and is shown in Figure 3. The apparent effect of one cc. of indicator in a solution of 12 g. of soap in 175 cc. of solvent is an increase of alkalinity by approximately .0045% Na_2O or .0058% NaOH. The curves shown in Figure 2 make it obvious that to obtain reproducible results, phenolphthalein indicator should be measured into the solution in definite amount and a uniform concentration of soap should be adhered to. Should either concentration or amount of indicator solution be varied, the proper corrections can be applied by referring to the data given in the curves of Figures 2 and 3. Although these corrections have been given specifically for the benzene-alcohol method, similar corrections in alcohol solvents would differ numerically but would be of the same order of magnitude.

The measurement of the temperature coefficient of the end-point demonstrated that this effect can be considerable. In the case of a carbonate-free soap, the coefficient was useful in correlating data for free caustic alkali obtained by different methods, since it could be shown that difference in results of the sample by different methods could be traced to difference in carbonate solubility or temperature of titration. The temperature coefficient was measured by titrating the free caustic alkali of a soap at a known temperature; then repeating the titration on another solution of the same sample at a higher temperature. For a commercial soap chip, this coefficient was determined as .00055% Na_2O or .00071% NaOH increase per degree rise. For a carbonate-free soap, the coefficient was less: namely, .00032% Na_2O or .00041% NaOH per degree rise. It is apparent that reproducibility of titration is better, the more constant the temperature. Titration at room temperature should, therefore, make possible better reproducibility than a titration at elevated temperature.

Procedure for Proposed Benzene-Alcohol Method for Free Caustic Alkali

Reagents Required

.1N H_2SO_4 or HCl

.1N NaOH (carbonate-free). For preparation, see Kolthoff and Furman, *Volumetric Analysis*, 1929, Volume II, page 76.

Phenolphthalein Indicator — 5 g./liter neutral alcohol.

Solvent—100 parts by volume Benzene C.P.
75 parts by volume Alcohol 95%
2½ parts by volume Water

Sufficient 10% NaOH in alcohol is added to the above solvent

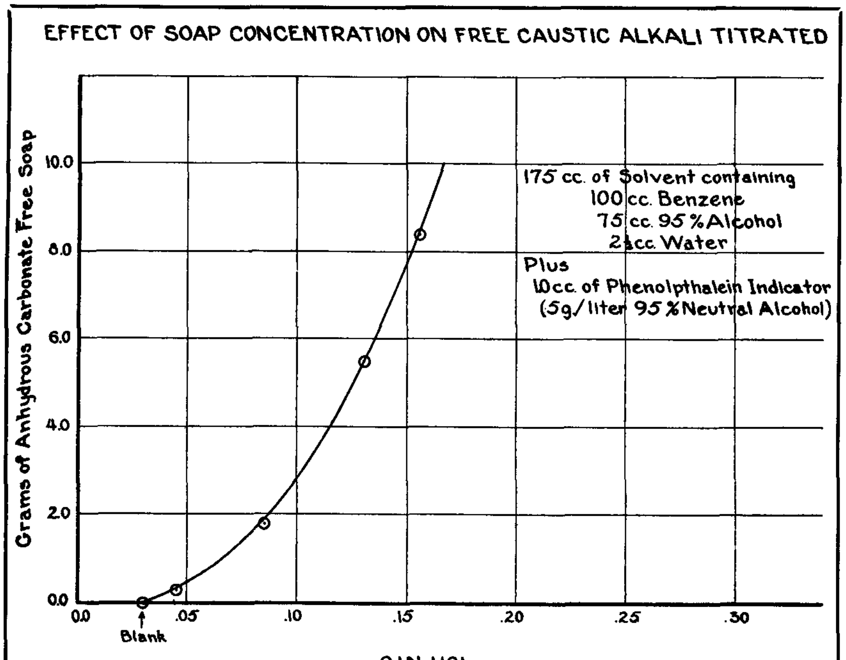

FIGURE 3

mixture until alkaline, using ½ cc. of phenolphthalein indicator for each 2 liters of solvent. Sufficient NaOH in alcohol is added to insure that upon boiling for five minutes or longer (out of contact with air containing CO_2) it retains a slight pink shade. It was found that traces of acidic constituents are in this way neutralized, and the solvent is unchanged upon further boiling with alkali.

Procedure

12.4 grams of soap are weighed out and added to 175 cc. of solvent contained in a 250 cc. extraction flask. A reflux tube about 65 cm. in length with ground glass end (see Figure 4) is joined to the flask and the solvent refluxed until all the soap has dissolved[9]. Upon complete solution of the soap, the flask is immediately immersed in a cold water bath held at approximately 25° C. The reflux tube is not removed during cooling. In this way, a minimum of CO_2 comes in contact with the soap solution and that which does enter through natural contraction of the air volume is not significant. Cooling requires about 8 minutes. The reflux tube is then removed from the flask, exactly one cc. of phenolphthalein indicator pipetted into the flask and the solution titrated[10] with .1N acid to complete disappearance of the pink color, swirling the solution after each addition of acid. Titration, it was found, is best carried out using white reflecting walls on five sides of the flask illuminated by a 75-Watt clear blue Mazda bulb. The use of white light and white background increases the analyst's color sensitivity to a pink to colorless end-point. The end-point is sufficiently sharp to produce disappearance of pink with one or two drops of standard .1N acid. A blank should be run with each series of soaps, following exactly the usual procedure to make allowance for the slight alkalinity of the solvent mixture prepared as outlined above.

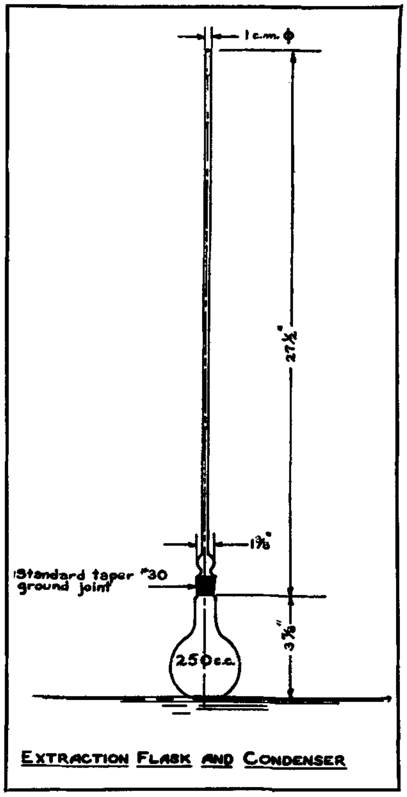

FIGURE 4

Titration (after removing the reflux tube) should be carried out quickly in a place removed from any source of concentrated carbon dioxide, such as, dry ice or a carbon dioxide gas stream. If this precaution is not observed, the caustic alkali is partly converted to carbonate and low results are obtained. The effect of short exposure of the solution to normal air is without great effect. We found that if the solvent containing soap is poured from one flask to another, the free caustic alkali of a soap containing .048% Na_2O free caustic alkali decreased about .001% Na_2O per transfer.

Finished Soaps Containing Fillers

If a soap contains inert fillers, such as are added for purposes of coloring or abrasion, with no alkali present other than sodium carbonate and free sodium hydroxide, the sample is dissolved as outlined above.

The filler suspended in solution obscures the end-point, and must be removed by either filtration or centrifuging. Filtering, we found, is not advisable because of undue exposure of the solution to the atmosphere and because of appreciable adsorption of free alkali on the filtering media. Centrifuging is possible because of the liquid properties of the solution on cooling, representing another advantage of the benzene-alcohol solvent. Experiment showed that filtering produces low results for free alkali, whereas centrifuging has no effect.

The reflux tube is disconnected from the flask after solution of the soap, the flask is stoppered and centrifuged while the solution is still hot (about 5 or 10 minutes at 1500 R. P. M. in "International" Laboratory Centrifuge). The flask and its contents are then cooled to 25° C. and the clear solution decanted into a similar flask. Unless an unusually large volume of filler is found as a residue, it is not necessary to wash the residue. Titration is carried out as usual.

The results for free caustic alkali obtained in this way are independent of the carbonate content of the soap, but some sodium silicate, if present, is titrated, the amount depending on the ratio of Na_2O to SiO_2 in the silicate and the amount of water present. For example, the addition of an excess of sodium silicate (ratio $\frac{SiO_2}{Na_2O} = 3.25$) to a soap solution increased the free caustic alkali results by .01% Na_2O and accounted for a continually recurring end-point. It appears improbable that a satisfactory modification can be made for the analysis of free caustic alkali in a soap containing sodium silicate, particularly if the ratio of SiO_2 to Na_2O is[11] varied.

Titration of Soap Deficient in Caustic Alkali

If upon adding one cc. of indicator, the solution is not colored pink, it is necessary to titrate, using .1N NaOH, free of carbonate. A slight excess is added, and this is back-titrated with standard acid to the usual end-point.

Calculations

The results for free caustic alkali are calculated as follows:

$$\frac{\text{cc. .1N acid} - \text{cc. Blank}}{40} = \%\ Na_2O$$

or

$$\frac{\text{cc. .1N acid} - \text{cc. Blank}}{31} = \%\ NaOH$$

In the case of a soap deficient in free NaOH, the calculation is modified as follows:

$$\frac{\text{cc. .1N NaOH} - \text{cc. .1N acid} + \text{cc. Blank}}{40} =$$

%Na_2O free caustic alkali deficiency

or

$$\frac{\text{cc. .1N NaOH} - \text{cc. .1N acid} + \text{cc. Blank}}{31} =$$

% Na OH free caustic alkali deficiency

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[9] Cork stoppers were not found satisfactory because of an acidic reaction with soap.

[10] The use of a microburette graduated in .01 cc. makes it possible to reduce the size of soap sample and volume of solvent.

[11] For a discussion of the titration of free alkalies in the presence of silicates, see A. Edeler, *Ind. Eng. Chem.*, 17, 196 (1925).

Determination of Total Free Alkali

Several methods are suitable for determination of total free alkali as distinguished from free caustic alkali. The sodium carbonate of soap can be conveniently determined by CO_2 absorption or using Divine's[1] method. These methods we found preferable to those in which the alcohol insoluble portion is filtered and separately titrated.

We tried the use of benzene-alcohol solvent in the determination of carbonates in soap and found that a satisfactory method was possible. After the determination of free caustic alkali, an excess of standard acid was added to the soap solution, a reflux condenser connected, and the solution refluxed for sixty minutes to decompose the carbonates. At the end of this time, the solution was cooled and titrated with carbonate-free NaOH to the first appearance of pink. The total free alkali is calculated as follows:

$$\frac{\text{cc. .1N Acid} - \text{cc. .1N NaOH}}{40} + \% \ Na_2O \text{ free caustic alkali} = \% \ Na_2O \text{ Total Free Alkali}$$

Comparison of Results for Free Caustic Alkali by Different Methods

The free caustic alkali of several samples of soap chips was determined by each of the various methods previously discussed. The procedure used for the benzene-alcohol method has been described in detail. The procedures used for the other methods are as follows:

1. 95% *Alcohol Method*:

12.4 grams of soap are added to 150 cc. of neutral 95% alcohol (Formula No. 30 was used) contained in a flask already described in the benzene-alcohol procedure. The solvent is refluxed until the soap has dissolved. The solution is then titrated hot to complete disappearance of the pink color, using 1 cc. of phenolphthalein indicator. This is essentially the Standard A. O. C. S. Method with the exception that since no fillers were present, the filtration before titration was omitted.

2. *Absolute Alcohol Method*:

The same procedure as above is used with the substitution of absolute ethyl alcohol for 95% alcohol. Because of limited solubility, only 3 g. of soap can be dissolved conveniently. The titration of the solution is carried out hot, with .1N acid, using a microburette.

3. *Barium Chloride Method*:

Solution of the soap in 95% alcohol is the same as for the 95% Alcohol Method. To the hot soap solution are added dropwise 2½ cc. of 6% $BaCl_2$ solution. The reflux tube is replaced, and the solution boiled for 5 minutes to insure complete reaction of the $BaCl_2$. Titration is carried out on hot solution, using phenolphthalein.

A comparison of the results given by the 4 methods on 12 samples of soap chips, disclosed that the Benzene-Alcohol Method gave lowest results, the Barium Chloride Method higher results by .012% Na_2O, and the 95% or A. O. C. S. and Absolute Alcohol Methods higher than the benzene-alcohol results by .022% Na_2O. The reason for the difference between the $BaCl_2$ and 95% Alcohol Methods has already been discussed as being due to an appreciable solubility and titration of sodium carbonate in the alcohol. Notwithstanding the difference between 95% alcohol and absolute alcohol in their ability to dissolve sodium carbonate and soap, it was found that the free caustic alkali results by the two methods were practically the same. A knowledge of the respective solubilities of sodium carbonate in the two solvents made the reason quite evident. In the previously described method, it was stated that because of limited solubility, the weight of soap sample in the Absolute Alcohol Method was only 3 grams, or one-fourth the weight of the sample taken in the case of the 95% Alcohol Method. The solubility of carbonate in absolute alcohol is, however, one-fifth to one-sixth that in 95% alcohol, the net result being that the percentage effect of titratable carbonate is appreciably higher in the absolute alcohol than the solubility of carbonate would indicate.

The reason for the low result by the Benzene-Alcohol Method presents another problem. The amount of carbonate titrated using this method, for chips with 12% moisture, is equal to .003% Na_2O. Subtracting this, the results are still lower by this amount. We must, however, take into account the fact that titration was carried out at room temperature and that the temperature coefficient of the end-point is such that the solution titrates more alkaline the higher the temperature. We can, with a knowledge of the exact change in alkalinity per degree, calculate from the result at 25° C. the free caustic alkali at 71° C., which is the titrating temperature of the Alcohol and Barium Chloride Methods. This temperature coefficient or change in free caustic alkali with change in temperature was determined by titrating soap solutions at 25° C. and at temperatures near the boiling point of the solvent. The value obtained for a carbonate-free soap was .00032% Na_2O per degree. This value multiplied by 46, the difference between 71° and 25°, gives a product, .015, which is equal to the difference in % Na_2O free caustic alkali obtained by titration at 25° C. and titration of the same solution hot, neglecting carbonate solubilities. Hence, to compare the results of the Benzene-Alcohol Method with the results of other methods under identical conditions, the value .015% Na_2O should be added to the benzene-alcohol results to make allowance for difference in titrating temperature. Making this correction and those corresponding to sodium carbonate solubilities brings the results of all four methods into substantial agreement with one another. The results are shown in Table IV.

TABLE IV

% Free Caustic Alkali as Na_2O

(Average analysis of 12 samples of soap chips, moisture 12%)

	Benzene-Alcohol Method	95% Alcohol Method (A.O.C.S.)	Absolute Alcohol Method	Barium Chloride Method
	.024	.046	.046	.036
Correction for Na_2CO_3 solubility......	—.003	—.013	—.009	...
Correction for Titration at 71° C. ...	.015	...	...	...
Corrected Value Free Caustic Alkali.	.036	.033	.037	.036
		Average .036		

It is interesting that the results obtained by the use of any one of the above methods can be translated into the results of the others by making use of the solubilities of sodium carbonate in the solvents and the temperature coefficients of the end-point. It is possible and practical, therefore, to use the Benzene-Alcohol Method, which we found the most convenient and precise of the four methods, and, by adding constant factors having theoretical significance, obtain the results of the Alcohol or Barium Chloride Methods.

Absolute Value of Free Alkali

In the determinations of free caustic alkali given in Table IV, the question naturally arises, "What is the correct or absolute value?" It is true that the corrections for sodium carbonate solubility bring methods into agreement with one another, but the resulting corrected values may or may not correspond to the true absolute value of free caustic alkali. The temperature effect introduces a complication, for the free alkali measured at one temperature is not the same at another temperature. The choice of one temperature over another is purely arbitrary; hence, the present standard for free caustic alkali is, within certain limits, arbitrary. Heretofore, the change in color of phenolphthalein in alcohol at temperatures in the neighborhood of 70° or 25° has been established as the neutral point, the justification being that it is a convenient reference and that the alkali-acid equivalence point must (analogous to aqueous systems) come at least near this reference point. The use of two arbitrary temperatures, however, leads to two sets of results for free caustic alkali, with an appreciable difference between them.

The one obvious manner in which the neutral point could be accurately established would be to prepare a pure neutral soap, titrate this, and find at what alkalinity or acidity the color change of phenolphthalein occurred. The preparation of a pure soap is not a little tedious, but preliminary work in this laboratory has given results that appear promising. A sample of a pure soap was prepared by successive crystallizations, using a technique in which all filtrations and crystallizations were done in an inert atmosphere. This sample was titrated and gave the value of .001% Na_2O or .0013% NaOH free caustic alkali at 25° C., and .0155% Na_2O or .020% NaOH free caustic alkali at 71° C., in the presence of one cc. of phenolphthalein indicator. The value at 71° was obtained by making use of the temperature coefficient of the end-point of a carbonate-free soap. Using this preliminary result, the absolute value for free alkali would be even lower than the results given by the Benzene-Alcohol Method and considerably lower than the results obtained by other methods. Some evidence has been noted, however, that soap hydrolyzes in the presence of the small amount of water in the solvent or, perhaps, solvates in the presence of alcohol to form sodium ethylate which, we know, gives a red coloration with phenolphthalein. This evidence is presented in the temperature coefficient of titration of NaOH. In Table V, figures are given which show that the titration of NaOH, carbonate-free, at any temperature is only slightly different at higher temperatures, as compared with a large difference for soap.

TABLE V

Temperature Coefficient of Titration of NaOH and Soap in Benzene-Alcohol

Solute	Temperature of Titration	cc. .1N HCl	% Na_2O/10° rise (Basis 12.4 g. soap)	
NaOH	28° C.	.08		
	64	.16	.0006	mean .0005
NaOH	31°	1.42		
	62	1.47	.0004	
Soap (carbonate-free)	29°	.14		
	60	.52	.0031	

These results were obtained by titrating identical solutions in each case at two different temperatures. In the fourth column, the temperature effect is given in terms of % Na_2O on a weight of 12.4 g. of soap. The results apparently show that it is not the indicator that is changing with temperature, for the temperature effect at constant OH concentration is small, but the amount of free alkali is increased by increased hydrolysis or solvation of soaps at higher temperatures. If this hypothesis is corroborated by further experiment, the question of absolute free alkali in soap will be established only under specific conditions relating to the kind of solvent, temperature, and indicator. In addition, since hydrolysis and solvation of a soap are a function of the molecular weight of the fatty acids comprising the soap, this factor, too, may be involved.

For a practical working standard, useful in control of soap boiling and in the grading of final products, it is suggested that until further work is done in establishing the absolute amount of free caustic alkali in soap, an arbitrary standard be approved. It is suggested that for the present a carbonate-free soap be defined as neutral, if when dissolved in 95% ethyl alcohol at 70° C. to the extent of 12.4 g. in 150 cc. of solvent containing one cc. of phenolphthalein indicator, the solution will be colorless, but will assume a slight pink shade on the addition of one drop of .1N NaOH. These specific conditions have been chosen since results are then obtained for free caustic alkali in soap not radically different from those which have been reported in past years. A soap neutral according to this definition in 95% alcohol would within practical limits be also neutral in absolute alcohol and in benzene-alcohol. In the use of benzene-alcohol, results obtained by titration carried out at 25° C. can be calculated to 70° C., making use of the quantitative temperature effect of the end-point.

SUMMARY

A method for the determination of free caustic alkali in soap is proposed in which soap dissolved in a solvent composed of 100 parts of benzene, 75 parts of alcohol, and 2½ parts of water by volume is titrated at room temperature with .1N acid, using phenolphthalein. The method has the following advantages:

1. A sharper end-point is observed.

2. Sodium carbonate is only slightly titrated. Its rate of solution at room temperature is less than in other solvents at higher temperature, so that a recurring end-point is not experienced.

3. The titration can be carried out at room temperature. Among other advantages, this largely minimizes errors through variation of the titrating temperature, not easy to avoid in a hot titration.

4. Soap fillers, exclusive of sodium silicate, can be conveniently separated from solution by using a simple form of laboratory centrifuge. This is made possible because soap does not gel in the benzene-alcohol solvent. Unlike filtration, centrifuging was found to have no effect on the determined free caustic alkali.

5. Soap dissolves more rapidly than in alcohol solvents.

A comparison was made between the results of the Benzene-Alcohol, Standard A. O. C. S. or 95% Alcohol, Absolute Alcohol, and Barium Chloride Methods. The four methods, although giving results which initially differ, are shown to coincide, if certain corrections are made, making use of the solubilities of Na_2CO_3 in the solvents and the temperature coefficient of the end-

point in the case of Benzene-Alcohol. Sodium carbonate, it was shown, is appreciably titrated in the Alcohol methods to an extent determined by the solubility of sodium carbonate at the titrating temperature. The Barium Chloride Method gave results independent of the carbonate concentration, which checked the corrected results of other methods.

A comparison was made between the four methods, averaging the results on 12 samples of soap chips containing 12% moisture. It was shown that by making appropriate correction for carbonate solubility in each solvent and the temperature effect of the end-point, all methods are in substantial agreement. The following table shows the comparison between results by the proposed Benzene-Alcohol Method and the Standard A. O. C. S. Method.

	% Na O	
	Benzene-Alcohol	Standard A.O.C.S.
	.024	.046
Correction for Na_2CO_3 solubility	—.003	—.013
Correction for Titration at 71° C........	.015	...
Corrected Value Free Caustic Alkali	.036	.033

Hence, if the Benzene-Alcohol Method is used, the results of the Standard A. O. C. S. Method are obtained by adding .012% Na_2O to the % Na_2O calculated from the titration. This additive factor will vary slightly with variations in the moisture of the soap and water added through titration, the quantitative effect of which was given.

A study was made of the effect of indicator, water, temperature, and amount of sample on the titrated free caustic alkali. The addition of water increases the free caustic alkali titrated in a commercial chip about .001% Na_2O per cc., using 12.4 g. of soap and 175 cc. of solvent. An increase of 10° increases the free caustic alkali titrated by .0031% Na_2O in a carbonate-free soap and .0055% Na_2O in a commercial soap.

Preliminary study of the titration of a pure neutral soap indicates that soap undergoes some hydrolysis or solvation in the presence of alcohol and water and that this effect is greater the higher the temperature. The absolute value for free alkali is, according to our present concepts, arbitrary. It is suggested for practical purposes that until the absolute value of free alkali in soap is established experimentally, that a soap be called neutral when 12.4 g. carbonate-free, dissolved in 150 cc. of 95% alcohol at 70° C. containing one cc. of phenolphthalein indicator, is colorless, or assumes a slight pink upon addition of one drop of .1N NaOH.

ELDERBERRY SEED OIL (*Sambucus canadensis* L.): PRELIMINARY COMMUNICATION*

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FOR centuries man has found in the genus Sambucus, of which there are approximately twenty different species, one source or another of satisfying a medicinal, a pharmaceutical or a domestic need. An infusion of the leaves has been an old-fashioned household remedy (Fliedertee) among German families since the Middle Ages. The flowers, although perhaps almost devoid of active medicinal virtue and possessing no real curative properties, besides having been esteemed for their diaphoretic and diuretic properties, in infusion, ointment or poultice have been applied to old sores, blisters and hemorrhoides. The young shoots and leaves of one species not only share the diuretic, and in larger doses, the purgative properties of the inner bark but are also effective, it is said, as a repellant for flies. The American Indians sought the ripe berries for their pigment, later chemists discovered that the juice had possibilities as an indicator, and man from time immemorial seems to have appreciated the fact that a very palatable spicy wine can be made from them.

The fatty oil, however, remains alone of those products of the elder shrub for which man—except in times of national emergency as when Germans and Austrians cast contemplative eyes upon this plant as a war-time source of fat—has not at one time or another found an alimentary or a medicinal use. Although it was hinted some seventy-five years ago[1] that this oil bears a similarity to linseed oil, an observation which was eventually verified experimentally by Zellner[2] with respect to the seed oil of *S. racemosa* L., and by Thoms[3], in so far as that he demonstrated the presence herein of acids representative of three types of unsaturation, yet the possibilities of adapting it to some useful technical ends appear still to be latent.

The literature on the characteristics and the component acids of the fatty oil is not large nor is the treatment of the subject comprehensive. It covers two types of oil somewhat unlike in properties because of differences in their respective origins: fruit flesh and seed. Relevant only to this communication are the reports by Zellner[2] and Thoms[3] on *S. racemosa* L.

In view of the wide-spread distribution in this country of another member of this genus, the habitat of which was so charmingly described by Peter Kalm, the Swedish botanist and traveler, *ca* 1749 ("Travels"), who said of it

> " The American elder, *S. canadensis* Linn., and the wild vines, only appear in places where the ground has been cultivated, as if they were desirous of being the companions of man,"

it is indeed strange that the oil of this species to date has not been investigated.

This communication marks the beginning of an attempt to fill this gap in the literature. It also records data which make possible comparisons with those pertinent to other species from the standpoint of genetic relationships of the plant source and biochemical similarities of the oil. Presented herein are (1) data showing yield of fatty oil with respect to menstruum employed in their recovery, (2) the simpler physical and a few chemical constants of the oils and their fatty acids, and (3) a comparative tabulation of the characteristics of the fatty oils of related species of *Sambucus*.

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