Determination of Bicarbonate in Soap Products

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Introduction

In summarizing the analytical results obtained in the analysis of built soaps, particularly sprayed soap products, it is frequently found that there is little or no alkali available to combine with the silica that is present. In extreme cases there may be insufficient alkali available to form a normal carbonate. Under such circumstances it is reasonable to assume that bicarbonates may be present in the sample.

Principle of Method

The amount of bicarbonate present in a sprayed soap can be ascertained by determining the amount of carbon dioxide present in the alcohol-insoluble material before and after ignition. The success of this method is due to the fact that on heating, bicarbonates decompose into normal carbonate, water and carbon dioxide in accordance with the equation:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

A widely used method of determining bicarbonate in mixtures of carbonate and bicarbonate is to add sufficient sodium hydroxide to react with the bicarbonate and then to back titrate with 0.1 normal hydrochloric acid after precipitation of the sodium carbonate with barium chloride. This method can not be employed in the analysis of soap builders because of the almost invariable presence of SiO_2 in the alcohol insoluble from soaps and the reaction of this SiO_2 with the sodium hydroxide. Nor can the differential titration method employing phenolphthalein and methyl orange as indicators be used on account of interference by the various other alkali salts present in the builder. However, if only carbonate and bicarbonate are present as builders the differential titration will give good results. This is the basis of the method described by Prager and Schaeffer (1).

It should be noted at this point that if bicarbonate is found to be present in a sample any moisture value obtained by distillation must be corrected by subtracting the amount of water liberated by decomposition of the salt.

Experimental

Effect of Heat on Mixtures of Na_2CO_3, $NaHCO_3$ and Various Soap Builders

Various authorities differ as to the temperature required for the quantitative conversion of $NaHCO_3$ to Na_2CO_3. According to Lunge (2) bicarbonate is quantitatively converted into carbonate by heating to 270°-300°C.

Hillebrand and Lundell (3) heat at 260°C. to 265°C. for 30 minutes taking care not to exceed a temperature of 270° lest sodium carbonate be decomposed.

As the procedure under discussion depends upon the complete conversion of sodium bicarbonate to sodium carbonate by heating, a number of experiments were run with the object of determining whether any untoward reactions would occur when the bicarbonate was heated in the presence of any or all of the various chemical compounds used as builders in sprayed soap products.

A quantity of Baker's C.P. analyzed sodium bicarbonate was dried over $CaCl_2$ for a period of 48 hours. One gram portions of this material were heated on a sand bath in platinum crucibles for a period of one hour at various temperatures ranging from 100 to 300°C. It was found that the loss in weight was nearest to theory at 260° ± 10°C.

A quantity of Baker's C.P. analyzed sodium carbonate was dried overnight at 105°C. The dried material assayed 99.97% sodium carbonate. A quantity of C.P. tetrasodium pyrophosphate was similarly dried at 105°C. A 1:1 mixture of the two was ignited at 260°C. for one hour and the % CO_2 left in the mixture was determined using the standard train method. The carbon dioxide content of the mixture before ignition was also determined. Similar experiments were run on the various mixtures tabulated in Table I. In each case the mixtures were heated for one hour at 260°C. Heating was done on a sand bath.

TABLE I

Effect of Heat on Mixtures of Na_2CO_3, $NaHCO_3$ and Various Soap Builders

Mixture*	Ratio	CO_2 before ignition at 260°C.		CO_2 after ignition at 260°C.	
		Theory	Found	Theory	Found
		Gram	*Gram*	*Gram*	*Gram*
Na_2CO_3—$NaHCO_3$	1:1	0.1876	0.1874	0.1354	0.1356
Na_2CO_3—$Na_4P_2O_7$	1:1	0.0830	0.0835	0.0830	0.0838
Na_2CO_3—$NaHCO_3$—$Na_4P_2O_7$	1:1:1	0.1876	0.1857	0.1354	0.1363
Na_2CO_3—$NaHCO_3$—$Na_2SiO_3 \cdot 9H_2O$	1:1:1	0.1876	0.1870	0.1354	0.1366
Na_2CO_3—$NaHCO_3$—$Na_2SiO_3 \cdot 9H_2O$—$Na_4P_2O_7$	1:1:1:1	0.1876	0.1871	0.1354	0.1400
$NaHCO_3$—$Na_4P_2O_7$	1:1	0.1046	0.1050	0.0524	0.0549
$NaHCO_3$—$Na_4P_2O_7$—$Na_2SiO_3 \cdot 9H_2O$	1:1:1	0.1046	0.1048	0.0524	0.0597
$Na_4P_2O_7$—$Na_2SiO_3 \cdot 9H_2O$	1:1	Nil	Nil	Nil	Nil

* Equal weights of all components in each mixture, namely 0.2000 gram.

An examination of the data presented in Table I reveals that for the mixtures investigated no unexpected reactions occur on heating to 260°C. Satisfactory checks between the theoretical and determined values for CO_2 before and after ignition were obtained in all cases.

Solubility of Na_2CO_3 and $NaHCO_3$ in Methyl and Ethyl Alcohol

A search of the literature revealed little information as to the solubility of sodium carbonate and sodium bicarbonate in methyl and ethyl alcohol. The Handbook of Chemistry and Physics (4) states only that sodium carbonate and bicarbonate are slightly soluble in alcohol. The International Critical Tables (5) gives values for the solubility of sodium carbonate in ethyl alcohol over the range of 10 to 60% by weight of ethyl alcohol. Sixty percent by weight ethyl alcohol dissolves 0.4 ± 0.1% sodium carbonate at 30°C. Landolt-Börnstein (6) states that sodium carbonate dissolves in 95.06% ethyl alcohol to the extent of 0.03% at 30°C. According to Griffin (7) 200 mls. of 95% ethyl alcohol dissolves 0.0075 gram of Na_2CO_3. In the case of absolute ethyl alcohol 0.0050 gram dissolved. Presumably these solubilities are at room temperature, roughly 25°C.

Owing to the scarcity and discrepancy of information in the literature as to the actual solubility of sodium carbonate and bicarbonate in methyl and ethyl alcohol, solubility values were experimentally determined. The values obtained have been plotted and are shown in Figs. 1 and 2.

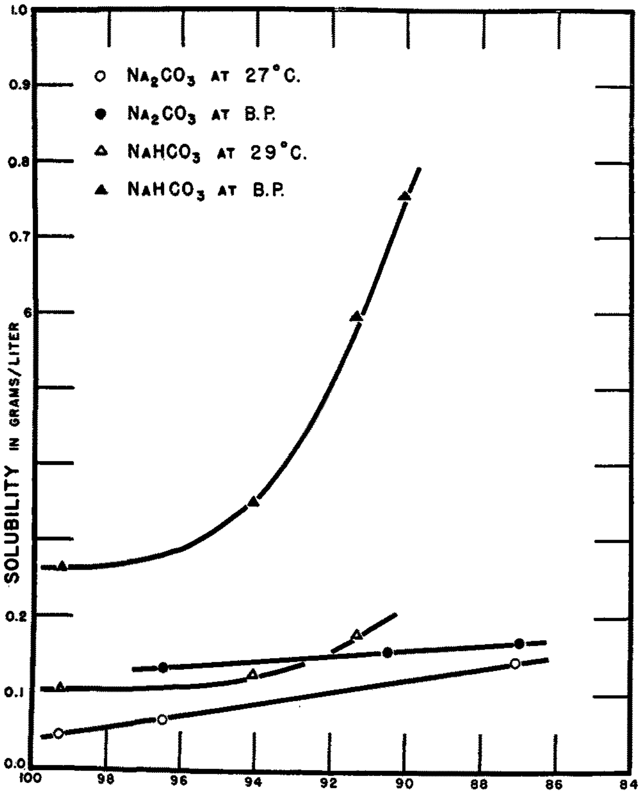

FIG. 1. Solubility curves for Na_2CO_3 and $NaHCO_3$ in various concentrations of ethyl alcohol and water.

An inspection of the curves will show that errors caused by loss of sodium bicarbonate due to solubility will be quite small in comparison with other and larger errors peculiar to the method. These errors are unavoidably introduced by use of large numerical factors in the calculation of analytical results.

Inspection of Fig. 1 indicates that our solubility values for sodium carbonate and sodium bicarbonate in ethyl alcohol are considerably lower than those given by Landolt-Börnstein and more on the order of the magnitude of the results given by Griffin though slightly greater numerically.

Since the solubilities are much greater in methyl alcohol than in ethyl it is preferable to use the latter in the following procedure.

To determine the effect of hot alcohol on bicarbonates several one-gram samples of $NaHCO_3$ were digested for 12 hours in 95% ethyl alcohol. Titration before and after contact with the alcohol showed no change in composition.

Procedure

From preliminary experiments which have been described and from a study of the solubility of sodium bicarbonate in ethyl alcohol the following procedure was evolved.

Weigh sufficient of the sample to yield at least three grams of alcohol-insoluble material. Digest the sample with 100 ml. of 95% ethyl alcohol in a 250 ml. beaker on a steam bath until all of the soap is dissolved. Filter the solution through a tared Gooch crucible. If desired a crucible with a sintered filtering surface may be employed instead of the usual Gooch. A Selas crucible, Grade 4010, is recommended. Wash the beaker and the insoluble material with hot alcohol until free of soap.

Dry the Gooch in an oven at 105°C. to constant weight. Cool in a desiccator and weigh. Calculate the percent of alcohol-insoluble present in the sample.

Transfer as much of the alcohol-insoluble matter as possible, without disturbing the asbestos mat, to a small weighing bottle. The use of a crucible with sintered bottom avoids danger of including asbestos fibers with the sample.

Determine the total CO_2 content on a small portion of the alcohol-insoluble material by the official method of the A. O. C. S. (8).

Weigh another portion of the alcohol-insoluble material (0.2 to 0.3 gram) into a platinum crucible and heat at 260° ± 10°C. for one-half hour. The crucible may be partially imbedded in a sand bath maintained at 260°C. or it may be heated in a muffle. It is important that the contents of the crucible be maintained

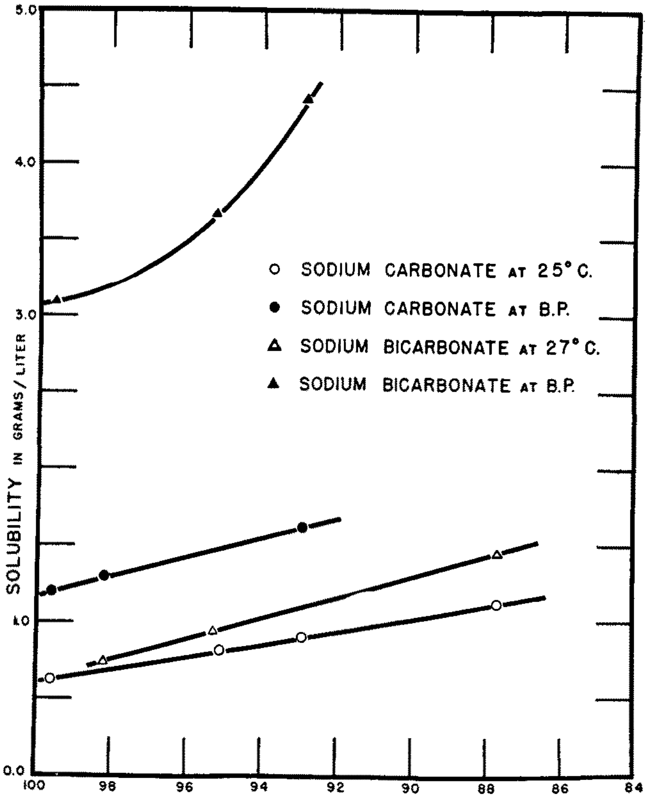

FIG. 2. Solubility curves for Na_2CO_3 and $NaHCO_3$ in various concentrations of methyl alcohol and water.

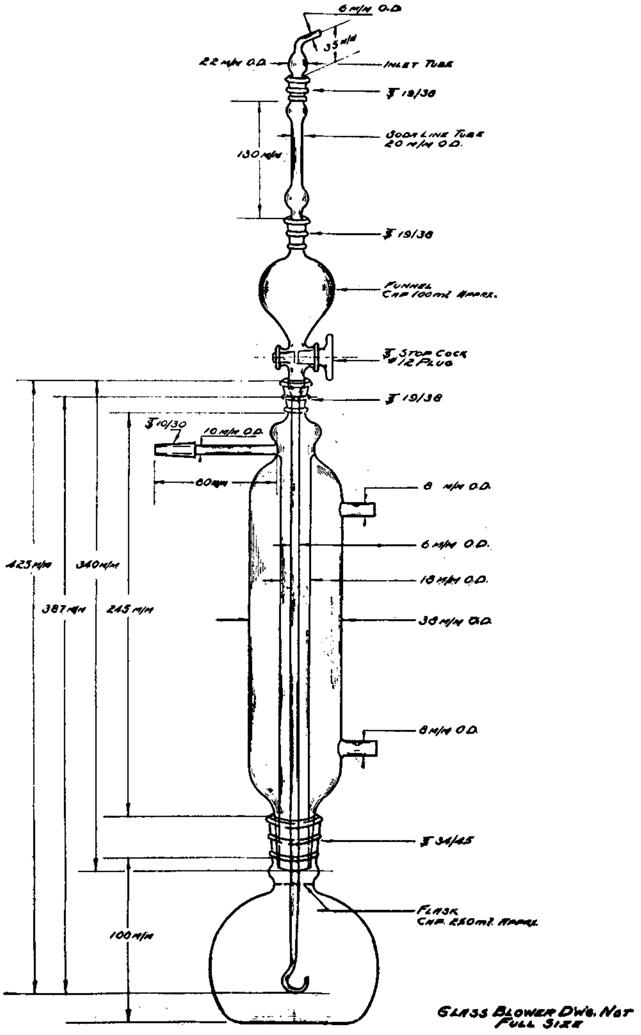

FIG. 3. Constructional details of CO_2 apparatus.

at 260°C. for at least one-half hour not including the time required to bring the heating medium to the proper temperature. After the heating period allow the crucible and contents to cool in a desiccator. When cooled to room temperature transfer all of the ignited material to the evolution flask of a CO_2 train and determine the total CO_2 content by the official method of the A. O. C. S. (9). In calculating the % CO_2 after ignition it is necessary to use the original weight of the alcohol-insoluble before ignition.

Calculate the percentage of bicarbonate present by means of the following mathematical relationship:

$$\left(\begin{array}{l}\%\ CO_2\ \text{present}\\ \text{in alcohol-insoluble}\\ \text{before ignition}\end{array} - \begin{array}{l}\%\ CO_2\ \text{present in}\\ \text{alcohol-insoluble}\\ \text{after ignition}\end{array}\right) \times 3.8184 = \begin{array}{l}\%\\ NaHCO_3\ \text{present in}\\ \text{alcohol-insoluble}\end{array}$$

Then,

$$\%\ NaHCO_3 \times 0.5238 = \%\ CO_2$$

And,

$$\left(\begin{array}{l}\%\ CO_2\ \text{present}\\ \text{in alcohol-insoluble}\\ \text{before ignition}\end{array} - NaHCO_3\ \text{as}\ \%\ CO_2\right) \times 2.4090 =$$
$$\%\ Na_2CO_3\ \text{present in alcohol-insoluble}$$

The percentage values obtained for the amount of $NaHCO_3$ and Na_2CO_3 in the alcohol-insoluble are converted to the sample basis "as received" by multiplying by the percent alcohol-insoluble present in the sample.

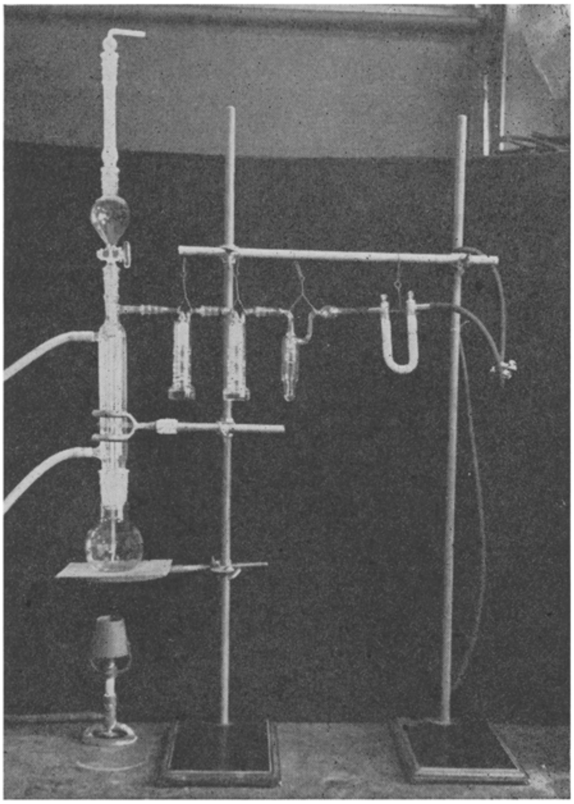

FIG. 4. Modified train for the determination of carbonaters by evolution.

The alternative method, which may suggest itself, of determining the amount of $NaHCO_3$ present by calculation from the loss in weight before and after ignition is very inexact and cannot be recommended. The loss in weight is invariably too high by an amount corresponding to the loss of adsorbed and hydrated moisture which is liberated due to the temperature difference between drying at 105°C. and igniting at 260°C.

Description of Apparatus

During the course of this work innumerable CO_2 determinations were run using the Knorr type (10) carbon dioxide apparatus. Certain unfavorable characteristics of this apparatus led to the design described in this paper. The chief defects of the Knorr apparatus are the fragility of the side arm condenser and the fact that the narrow condenser tube gives rise to back pressure which frequently during the final boiling out of the CO_2 causes the liquid in the flask to rise into the dropping funnel. In the present modification of the apparatus the large diameter and extensive cooling area of the condenser tube prevent the building up of any pressure and the contents of the flask can be boiled as vigorously as desired without danger of accident or loss of CO_2.

The design and constructional details of the apparatus are shown in Fig. 3. The drawing shows only the evolution end of the apparatus. The balance of the train extends from right to left and consists, in the respective order named, of two sulfuric acid dryers (Bowen absorption bulbs), a bubble counter, and the carbon dioxide absorption tube (packed with Ascarite and indicating Drierite) attached to the bubble counter. The sulfuric acid dryers and bubble counter are provided with standard-taper joints (10/30) and consequently, the apparatus is composed entirely of glass with the exception of a short length of rubber tubing connecting the absorption tube to the bubble counter.

A photograph of the complete apparatus is shown in Fig. 4.

Results

This method has been in use for several years. The values given in Table II have been selected from a large number of determinations run in this laboratory.

TABLE II

Bicarbonate Content of Various Commercial Soaps (As Received Basis)

Sample Description	Sodium Carbonate Present	Sodium Bicarbonate Present
	Pct.	*Pct.*
Granulated soap	0.55	11.30
Granulated soap	0.62	2.83
Sprayed soap	1.46	1.16
Industrial cleanser	48.04	7.03
Scouring cleanser	30.16	34.44
Soap powder	0.55	3.93
Synthetic detergent	8.60	13.50
Hand soap	3.26	3.32
Special industrial soap	48.90	9.39

As a check on the accuracy of the method the work summarized in Table III was initiated. In this work known amounts of $NaHCO_3$ and Na_2CO_3 were added to various types of soaps and the percentage recovery determined.

TABLE III

Recovery of Sodium Bicarbonate Added to Various Commercial Soaps

Sample	Original Sample		Pct. Na_2CO_3 Added to Sample	Pct. $NaHCO_3$ Added to Sample	Recovery	
	Pct. Na_2CO_3	Pct. $NaHCO_3$			Pct. Na_2CO_3	Pct. $NaHCO_3$
Sprayed Soap I	2.18	1.50	4.00	4.00	5.62	6.03
Sprayed Soap II	1.87	6.28	4.00	4.00	5.65	10.40
Sprayed Soap III	1.27	0.00	0.00	11.20	1.30	10.38
Sprayed Soap IV	10.85	4.00	17.45	51.30	30.00	53.00
Sprayed Soap V	26.71	0.00	9.72	33.05	40.60	32.15
Kettle Soap I	0.96	0.00	14.29	14.29	15.25	13.55

Reproducibility of Results

It has already been noted that this method, assuming the analytical operations to be above reproach, is subject to introduced errors due to the fact that bicarbonates are slightly soluble in alcohol and also to the fact that in order to calculate the bicarbonate content an inordinately large factor of 3.8184 is employed. None the less in view of the fact that no other method is known at present for determining the bicarbonate content of a soap the inaccuracy of the present method is to some extent discountable in view of the knowledge derived from its use. It is true, too, that although repeat determinations may sometimes differ by as much as 5% in respect to the bicarbonate content, it must be remembered that the percentages of bicarbonate and carbonate are calculated on the basis of 100% alcohol-insoluble. Since the alcohol-insoluble in most soaps is appreciably low, on the average ranging from a negligible amount to 25 or 30%, the differences between repeat values on the values for carbonate and bicarbonate become appreciably smaller when calculated to the "as received" basis.

The errors introduced into the procedure lead to the finding of small amounts of bicarbonate in nearly all soaps. Consequently use of this method is indicated only when indirect evidence, such as the alkali balance, indicates that appreciable amounts of sodium bicarbonate may be present.

The values given in Table IV illustrate the discrepancies that errors incurred in the determination of CO_2 content induce in the results calculated as percentages of Na_2CO_3 and $NaHCO_3$. Although the repeat values for the CO_2 content, both before and after ignition, agree very closely, the effect on the final result of small errors in these determinations is clearly discernible.

TABLE IV

REPRODUCIBILITY OF RESULTS

Effect of Errors in Determination of CO_2 Content on Results Calculated as Percentages of Na_2CO_3 and $NaHCO_3$

Sample Designation	CO_2 content before ignition	CO_2 content after ignition	% Na_2CO_3 present calculated	% $NaHCO_3$ present calculated
Sprayed soap 1	5.26	3.64	4.87	6.19
Sprayed soap 1	5.09	3.69	5.52	5.35
Sprayed soap 2	3.35	1.99	1.52	5.19
Sprayed soap 2	3.39	2.00	1.47	5.31
Sprayed soap 2	3.38	2.03	1.64	5.15
Sprayed soap 3	15.16	13.44	28.23	6.57
Sprayed soap 3	15.26	13.52	28.38	6.64
Sprayed soap 4	17.44	12.82	19.75	17.64
Sprayed soap 4	17.24	12.73	19.80	17.22
Sprayed soap 4	17.49	12.62	18.67	18.60

Summary

A method has been presented for the determination of bicarbonates in soap products based on the quantitative loss of CO_2 which occurs when bicarbonates are heated to 260°C. for 30 minutes. The method is subject to errors arising from the solubility of sodium bicarbonate in alcohol and the use of a large mathematical factor in calculating the bicarbonate content. In the absence of a more exact method the procedure gives results which are of great interest and value in soap analysis.

Acknowledgments

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