crease in PV and a broad band which increased with increasing PV until it resolved into a true maximum at 3430 cm^{-1}. Reduction of typical oxidized samples with KI reagent resulted in disappearance of the 3430 cm^{-1} band and appearance of a new band above 3500 cm^{-1}. The band at 3430 cm^{-1} was attributed to —OOH groups associated by hydrogen bridging. The band at 3467 cm^{-1} and the band appearing above 3500 cm^{-1} were attributed to —OH groups, the band at the higher frequency resulting directly from reduction of a hydroperoxide.

Absorption due to ketone and aldehyde carbonyl groups appeared only as an indefinite shoulder on the band due to the ester carbonyl. These were resolved by using the intensity of the sample with PV 1 as I_0 and that for the oxidized samples as I. A plot of Log I_0/I then revealed three maxima. These indicate the presence of two and possibly three carbonyl containing substances other than the ester carbonyl in autoxidized methyl linoleate.

Absorption in the two critical frequency ranges of fractions of autoxidized methyl linoleate eluted from an adsorption column correlate with interpretations made from ultraviolet absorption studies of the same substances.

REFERENCES

1. Gamble and Barnett, Ind. Eng. Chem., *32*, 375 (1940).
2. Dugan, Beadle, and Henick, J. Am. Oil Chemists' Soc., *25*, 153 (1948).
3. Farmer, Trans. Faraday Soc., No. 286, *42*, 228 (1946).
4. Swift and Dollear, J. Am. Oil Chemists' Soc., *25*, 52 (1948).
5. Barnes, Liddel, and Williams, Ind. Eng. Chem. Anal. Ed., *15*, 659 (1943).
6. Swift, Dollear, and O'Connor, Oil and Soap, *23*, 355 (1946).
7. Bolland and Koch, J. Chem. Soc., 445 (1945).
8. Bergstrom, Arkiv. Kemi, Mineral Geol., *21A*, No. 14, 1 (1945).
9. Holman, Arch. Biochem. *15*, No. 3, 403 (1947).
10. Bergstrom, Arkiv. Kemi, Mineral Geol., *21A*, No. 15, 1 (1945).
11. Lundberg and Chipault, J. Am. Chem. Soc. *69*, 833 (1947).
12. Barnes, Gore, Stafford, and Williams, Anal. Chem. *20*, 402 (1948).
13. Honn, Bezman, and Daubert, J. Am. Chem. Soc. *71*, 812 (1949).

Determination of Bicarbonate in Soap Products

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CONTINUED need for the accurate determination of bicarbonate in the presence of carbonate and alkali salts such as phosphates and silicates has led to the development of an improved procedure yielding quicker and more accurate results than can be obtained by the procedure originally described by Blank and Boggie (1). The latter procedure, as emphasized in the original paper, is subject to errors due to the solubility of bicarbonate in alcohol and to the decomposition of bicarbonate during the process of isolating the alcohol insoluble material required for the determination.

The method described herewith permits the determination of bicarbonate and carbonate directly in the presence of soap, thus avoiding any loss of bicarbonate due to solubility in alcohol or in virtue of its inherent instability.

Principle of Method

Essentially the method consists in heating the sample containing bicarbonate and carbonate to 200°C. for one-half hour in a dry flask connected to the usual carbon dioxide train. After obtaining the increase in weight of the carbon dioxide absorption tube due to the CO_2 liberated by the decomposition of the bicarbonate, water is added to the contents of the flask to dissolve the sample, the residual carbonate is decomposed by the addition of 20 ml. 1:1 HCl and the CO_2 is evolved by heating as described in the official method of the A.O.C.S. (2).

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. Each gram of $NaHCO_3$ present yields 0.107 grams of H_2O.

The temperature at which $NaHCO_3$ is quantitatively decomposed has been variously reported (3, 4). More recently Waldbauer, McCann, and Tuleen (5) conclude that any sample of $NaHCO_3$ heated above 150°C. is completely converted into the carbonate. This temperature is considerably less than that formerly regarded as necessary for the quantitative conversion. It has been found in this laboratory that a temperature of 200°C. for a period of one-half hour is sufficient to accomplish the conversion to the extent of about 98%. Figure 1 presents a plot of per cent loss of CO_2 from $NaHCO_3$ against time in minutes at the two temperatures of 150°C. and 200°C.

Apparatus

The apparatus employed in this determination may be any one of the usual CO_2 trains (1, 2, 6) with but one difference. In this procedure the CO_2 evolution flask is heated by means of an electric heating mantle of the usual laboratory type, connected to a pyrometer so that the temperature can be controlled to 200 ± 10°C.

Procedure

Weigh 2.5 to 3.0 grams of the sample into a 300-ml. CO_2 evolution flask. Attach the flask to a carbon dioxide train and bring the absorption tube to constant weight by the slow passage of air through the train for 10 to 15 minutes. When the absorption tube has attained constant weight, attach it to the train and maintain the evolution flask at a constant temperature of 200° ± 10°C. for one-half hour. Turn off the current and continue to draw CO_2 free air through the apparatus for an additional 20 minutes, at the end of which time detach the absorption tube and weigh. The percentage of $NaHCO_3$ present in the original sample may be calculated as follows:

$$\frac{\text{Weight of } CO_2 \times 3.8184 \times 100}{\text{Sample Weight}} = \%\ NaHCO_3$$

Replace the absorption tube in the train. Add distilled water through the entrance funnel attached to the evolution flask until the level is slightly above the lower end of the entry tube. It may be necessary to apply slight suction through the train to accomplish this operation.

Add 20 ml. of 1:1 HCl containing a few drops of methyl orange indicator to the sample in the flask. If the solution in the flask is not distinctly acid, add sufficient additional 1:1 HCl to bring the solution to distinct acidity. Increase the electric current until smooth boiling is effected. After boiling is initiated, the power may be decreased to the point at which it is just sufficient to maintain steady boiling. Boil the solution for 10 to 15 minutes. Turn off the current and continue to draw CO_2 free air through the apparatus for an additional 30

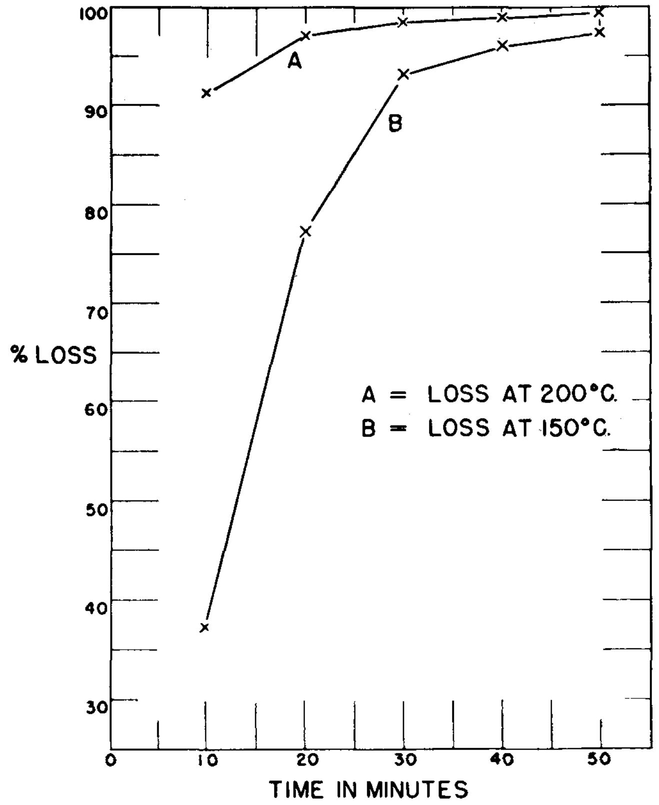

FIG. 1.

minutes, at the end of which interval detach the absorption tube and weigh. The difference between the weights of CO_2 obtained by acid evolution and by heat evolution represents the weight of CO_2 equivalent to the Na_2CO_3 in the sample. The percentage of Na_2CO_3 present in the original sample may be calculated as follows:

$$\frac{\text{Weight of } CO_2 \text{ equivalent to } Na_2CO_3 \text{ originally present} \times 2.409 \times 100}{\text{Sample Weight}} = \%\ Na_2CO_3$$

Results

In order to check the accuracy of the method when dealing with $NaHCO_3$ alone, a series of determinations were run employing $NaHCO_3$ of 99.80% purity. The average of six determinations gave a value of 99.61%. This compares favorably with the value 99.80% obtained by evolution employing HCl to decompose the sample.

Values obtained by evolution and by differential titration (7) for $NaHCO_3$ in the presence of Na_2CO_3 are given in Table I. Extreme care is necessary to obtain reproducible results in the differential titration method. The sum of the results in Table I for $NaHCO_3$ and Na_2CO_3 obtained by titration varies from a high of 99.77 to a low of 98.29. The sum of the Na_2CO_3 and $NaHCO_3$ results by evolution vary from a high of 100.45 to a low of 98.75. The accuracy of the results obtained by evolution appears to decrease as the amount of $NaHCO_3$ present decreases. The results given in Table II would indicate that the results for $NaHCO_3$ by titration and by evolution are of an approximately equal degree of accuracy.

The values in Table II demonstrate that the recovery of known added amounts of $NaHCO_3$ and Na_2CO_3 to various soap products is analytically satisfactory.

TABLE I

Comparison of the Evolution and Differential Methods for the Determination of $NaHCO_3$ in the Presence of Na_2CO_3

Determination No.	Sample	Recovery			
		$NaHCO_3$		Na_2CO_3	
		Evolution	Titration	Evolution	Titration
1	$NaHCO_3$-Na_2CO_3 Mixtures	71.81	71.57	28.64	28.20
2		60.73	59.93	39.33	38.71
3		39.03	38.73	61.01	60.52
4		15.21	15.30	84.11	84.16
5		7.59	7.26	91.16	91.03

Table III shows the reproducibility that may be expected when soaps containing both $NaHCO_3$ and Na_2CO_3 are analyzed in duplicate. It should be noticed that a synthetic detergent is included. The above described procedure is applicable to synthetic detergents in general.

Discussion

It has been found that most sprayed soaps contain small amounts of $NaHCO_3$ even though it may not have been added originally. Such soaps almost invariably contain pyrophosphate. Preparation of the latter on an industrial scale involves the heating of Na_2HPO_4 and inasmuch as the conversion is not quantitative, some Na_2HPO_4 is usually found associated with commercial grades of $Na_4P_2O_7$. Bayliss (8) has indicated that under certain conditions Na_2HPO_4 will react with H_2CO_3 to give $NaHCO_3$. It is possible that this reaction takes place during the process of spraying a soap, thus leading to the presence of small amounts of $NaHCO_3$ in many sprayed soaps.

TABLE III

Reproducibility Obtainable in the Analysis of Soaps and Synthetic Detergents for $NaHCO_3$ and Na_2CO_3

Determination Number	Sample Designation	$NaHCO_3$ Content		Na_2CO_3 Content	
		Initial Detm.	Replicate Detm.	Initial Detm.	Replicate Detm.
1	Sprayed Soap C	0.83	1.00	8.43	7.96
2	Sprayed Soap D	1.04	1.16	Nil	Nil
3	Soap Powder A	18.64	18.49	35.23	35.20
4	Soap Powder B	3.37	3.45	43.81	43.74
5	Synthetic Detg.	28.90	29.80 29.30	Nil	Nil Nil

The method described in this paper is generally applicable to the analysis of $NaHCO_3$ and Na_2CO_3 in

TABLE II

Recovery of Known Amounts of $NaHCO_3$ and Na_2CO_3 Added to Various Soap Products

Determination No.	Sample Designation	Original Sample		Added		Found (Total)		Recovered	
		$NaHCO_3$ %	Na_2CO_3 %	$NaHCO_3$ %	Na_2CO_3 %	$NaHCO_3$ %	Na_2CO_3 %	$NaHCO_3$ %	Na_2CO_3 %
1	Soap Powder A	18.64	35.23	16.10	11.26	34.70	46.66	16.06	11.43
2	Soap Powder B	3.37	43.81	13.92	15.18	17.23	59.13	13.86	15.32
3	Sprayed Soap A	0.23	2.80	13.79	9.31	13.86	12.19	13.63	9.39
4	Sprayed Soap B	0.10	1.64	15.98	8.30	15.80	10.27	15.70	8.63
5	Sprayed Soap C	0.83	8.43	20.01	0.00	20.80	8.52	19.99	0.09

the presence of a wide variety of alkaline salts. Snell and Biffen (9) have described the possible combinations of 12 commercially available alkaline salts. It should be recognized that most of these combinations can be analyzed by this procedure for both carbonate and bicarbonate content.

Summary

Sodium bicarbonate can be determined directly in the presence of sodium carbonate and soap by heating the mixture under controlled conditions. The carbon dioxide liberated by heating is estimated gravimetrically and calculated to sodium bicarbonate. The balance of the carbon dioxide content of the sample is liberated by acid, estimated gravimetrically, and calculated to sodium carbonate. The procedure is applicable in the presence of synthetic detergents. It is rapid and yields accurate results.

REFERENCES

1. Blank and Boggie, Oil and Soap *20*, 125 (1943).
2. Official and Tentative Methods of the American Oil Chemists' Society, 2nd Edition, Official Method Da 19a-42, The American Oil Chemists' Society, Chicago (1946).
3. Kolthoff and Furman, "Volumetric Analysis," Vol. 2, p. 88, John Wiley and Sons, Inc., New York (1929).
4. Hillebrand and Lundell, "Applied Inorganic Analysis," p. 137, John Wiley & Sons, Inc., New York (1929).
5. Waldbauer, McCann, and Tuleen, Ind. Eng. Chem., Anal. Ed. *6*, 336 (1934).
6. Official and Tentative Methods of Analysis of the A.O.A.C., 5th Edition, p. 186, Washington, D. C. (1940).
7. Smith "Analytical Processes," 2nd Edition, p. 238, Edward Arnold & Co., London (1940).
8. Bayliss, "Principles of General Physiology," 4th Edition, p. 196, Longmans, Green and Co., Ltd., London (1927).
9. Snell and Biffen, "Commercial Methods of Analysis," 1st Edition, p. 254, McGraw-Hill Book Co., Inc., New York (1946).

The Use of Antioxidants in Potato Chipping[1]

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ONE of the most interesting developments in the food field in recent years has been the rapid growth of the potato-chipping industry. Although for some time the cooking of potato chips seemed a logical application for antioxidants, there was no antioxidant available which possessed the ability to "carry through" the frying process. The announcement of butylated hydroxyanisole (2, 3) last year and the demonstration that it possessed remarkable "carry-through" properties in animal fats made available an antioxidant suitable for conducting a study on prolonging the shelf life of potato chips. Accordingly we have undertaken this study in our laboratory and in a local commercial potato-chipping plant.

Preliminary work on the effectiveness of butylated hydroxyanisole and combination antioxidants containing butylated hydroxyanisole were conducted in a laboratory fryer which holds one pound of fat. The temperature of the electrically-heated fryer is controlled by means of rheostats. In each experiment 100 grams of sliced potatoes were fried in one pound of fat. The frying was done in small portions, and the stability studies were made on the last 50 grams fried in each lot. No additions of fat were made in any of these experiments. The large-scale experiments were carried out in a commercial fryer of 600 pounds capacity. This was a batch fryer, and it was necessary to add between 50 and 100 pounds of fat daily, depending upon the amount of potatoes fried. In the large-scale experiments up to 5,000 pounds of potatoes were fried before the fryer was emptied and the fat discarded.

Since this study was concerned with the shelf life of potato chips, the bulk of our data consists of results from Schaal Oven (1) studies on the chips themselves.[3] We also investigated the stability of the frying fats by means of the Active Oxygen Method (5) in an attempt to find out how their stability changed with usage. The data obtained in one series of commercial runs are shown in Figure 1. An examination of Figure 1 reveals an apparent decrease in the quality of the fat, as shown by the Schaal tests on the potato chips, and an apparent increase in the quality of the fat, as shown by the Active Oxygen Method tests on the frying fat itself. This contradictory data indicates again the fact that the value of the Active Oxygen Method (A.O.M.) is dependent largely upon the previous history of the fat. Although the A.O.M. is usually applicable to the evaluations of "fresh" fats, this method is not truly indicative of the conditions of fats which have been subjected to high temperature frying over long periods of time.

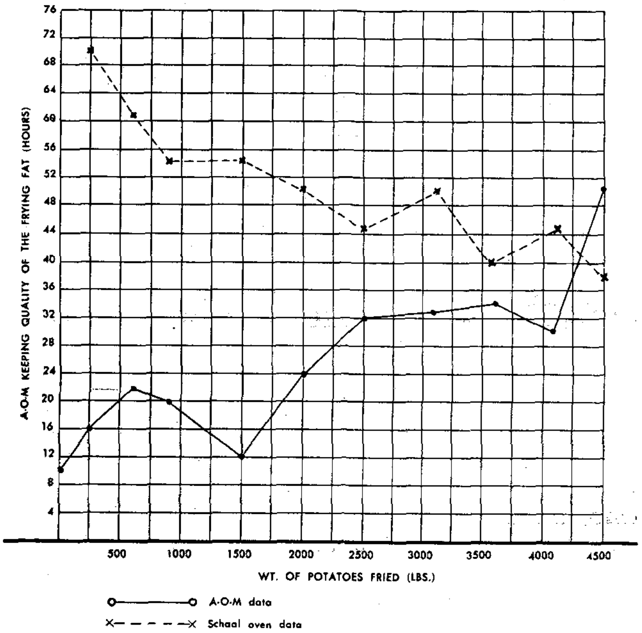

FIG. 1. Relatons of A.O.M. values of frying fats to chip stability. Fat mixture of 60% vegetable shortening—40% lard containing 0.020% butylated hydroxy anisole. Active oxygen method to a peroxide value of 20.

We also made attempts to determine the consump-

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[2] Tennessee Eastman Corporation, Kingsport, Tenn.

[3] The Schaal Oven Tests were conducted at 145°F.