frequent stirring. Solutions were then filtered and the filtrate taken down to dryness and the residue weighed. Using this procedure, the solubility of the sample of mixed mono and diglycerides made from tallow was as follows:

Petroleum Ether	41.5%
Ethyl Ether	92.0

The solubility of the mono stearin was as follows:

Petroleum Ether	17.0%
Ethyl Ether	95.0

The solubility of the mono stearin appears to coincide with our data relative to the solubility of the unsaponified matter in incompletely saponified soap.

In view of the data given, it would appear desirable that the Soap Analysis Committee of the A.O.C.S. give consideration to suitable changes in the present standardized procedure for unsaponified matter in the incompletely saponified cold process type soaps.

REFERENCES

[1] Oil and Soap, 11, 90 (1934). Standard Methods for the Sampling and Analysis of Commercial Soap and Soap Products.

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THE DETERMINATION OF COMBINED CARBON DIOXIDE IN SOAPS AND OTHER DETERGENTS

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Abstract

An evolution method for the determination of combined carbon dioxide is described in which the gas is liberated in a closed, partially evacuated system and immediately absorbed in an excess of alkaline solution. Unconsumed absorbent is titrated. The method is suggested as appreciably simpler and easier than the "train" method, without sacrifice of accuracy. Examples are cited of application to a variety of detergents. Confirmatory results from other laboratories are included.

MANY soaps contain significant quantities of alkali in excess of the amount required to exactly neutralize their fatty acids. Among the several forms in which this excess alkali may be found are the combinations with carbonic acid as carbonate and bicarbonate. The soap analyst is therefore frequently confronted with the necessity of determining carbon dioxide in soaps and other detergents in order that the alkali may be allocated to its true form of combination.

Carbon dioxide in soaps is usually determined by means of the absorption train which, even in its simplest form, is a somewhat complicated set of coordinated apparatus. The principles upon which the absorption train is based are beyond criticism. Its satisfactory application to soap and detergent analysis depends upon special experience with the method.

The desirability of a simpler procedure adapted to work in our field induced us to make some experiments which have resulted in a method for determining carbon dioxide in detergents, which, it is believed, is easier and more certain in inexperienced hands. This method is based on the principle that in a closed system from which air has been exhausted, carbon dioxide may be set free and distilled from an evolution flask into a receiver containing a measured quantity of an alkaline absorbent. The excess of absorbent may be accurately titrated with a solution of sodium bicarbonate. The loss of alkalinity is equivalent to the carbon dioxide taken up. The apparatus consists of two Pyrex flasks, each of which is equipped with a two-hole stopper and a small separatory funnel through which reagents are introduced.

Referring to Figure 1 herewith, "A" is a round-bottom heavy Pyrex long-neck flask of one liter capacity, furnished by the Corning Glass Works. It corresponds to a standard distilling flask without the side arm. We have found it convenient to work with the same size evolution flask in all cases, operating at the same liquid level, and varying only the quantity of sample taken. This should be such as will contain about 150 to 200 milligrams of CO_2. Beside the separatory funnel the stopper of Flask "A" carries a small calcium chloride tube which serves as a spray trap.

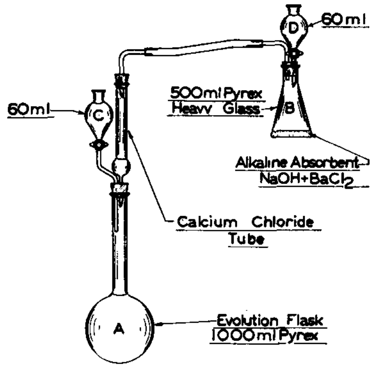

FIGURE I

Flask "B" is of heavy Pyrex glass and contains the alkaline absorbent solution. Both flasks are held in suitable clamps on the same support. The connecting rubber tube is sufficiently thick walled to avoid collapse when air is exhausted from the apparatus. This tube is conveniently about six to eight inches long. Flask "A" is heated by a small electric heater with a sliding rheostat.

The solutions required are:

1. N/4 HCl
2. Alkaline absorbent solution.—This is prepared by mixing equal volumes of normal caustic soda (carbonate-free) and normal barium chloride and settling over night. It is quite constant in strength; with reasonable avoidance of exposure to air its strength holds from month to month.
3. Normal barium chloride solution.
4. Sodium bicarbonate solution, 22 grams per litre. This is best made up in moderate amounts, say a week's supply at a time. Its strength diminishes in keeping and must be checked daily against the alkaline absorbent solution.

As an example of the procedure, the determination of combined CO_2 in a toilet soap will be described. This grade will ordinarily contain a relatively small amount of alkali carbonate and 50 grams of the divided sample should be weighed into a flask "A," about 350 ml. of boiled distilled water are added, and the flask is heated over steam until the soap is dissolved, then cooled until slightly warm to the hand. Twenty grams of crystallized magnesium chloride are dissolved in 30 ml. of boiled distilled water and added to the soap solution, which is now thoroughly cooled. A few glass beads are put into the flask and a piece of copper wire is placed vertically in the flask with the object of preventing violent bumping when the solution is boiled. The apparatus is now connected with an aspirator pump through "D" and the air is pumped out. Three minutes usually suffices.

At the suggestion of Mr. W. W. Walton of Mr. Smither's laboratory at the United States Bureau of Standards, a mercury manometer may be connected permanently into the line between "A" and "B" to indicate the pressure inside the apparatus throughout the test. A suitable volume of absorbent solution (in this case 25 ml.) is measured into "D" and introduced into "B," rinsing "D" with boiled distilled water. Air must not be allowed to enter "B" while introducing the absorbent.

HCl 1:3 which has been colored with methyl orange indicator is introduced into "A" through funnel "C" until an acid reaction is obtained, avoiding a large excess of acid. If the sample is known to contain considerable carbonate, the acid should be added slowly, and the Flask "A" gently swirled between additions.

We have found that the addition of trichlor benzol to the evolution flask after the soap has been decomposed with acid and after boiling has proceeded a few minutes, has the effect of hastening liquefaction of the fatty acids. For a 50 gram sample of soap we would take 25 ml. of trichlor benzol; for smaller samples, proportionate quantities. Trichlor benzol (1-2-4 isomer made by the Hooker Electrochemical Company) has a boiling point about 213° C. Its specific gravity is about 1.47. It serves admirably to carry down the fatty acids which finally all sink to the bottom of the aqueous liquid and remain there when the flask is filled with hot water at the end of a determination. This avoids annoyance in cleaning greasy material from the apparatus after use.

The contents of "A" are now heated to boiling under the reduced pressure existing in the system and maintained under ebullition about ten minutes. The boiling time must, of course, be sufficient to drive the CO_2 out of the solution. This may be judged after a few trials by noting the character of the boiling in "A" and noting also the appearance of the solution in "B"; that is to say, it is apparent to the eye when the gas has ceased to come over into "B." Boiled distilled water of about the same temperature (140°-150°F) as the contents of flask "A" as evident to the hand is now introduced through funnel "C" into "A" until it is practically filled. Any residuum of gas in "A" will be forced over into "B." After a few minutes to complete absorption, CO_2 free air (air passing a caustic soda wash bottle) is admitted through "D" until atmospheric pressure is restored.

Flask "B" is now disconnected and cooled thoroughly, 20 ml. of normal barium chloride solution are added to the solution, which is then titrated with the bicarbonate solution in the presence of phenolphthalein indicator. The titration represents residual alkalinity of the absorbent. A measured volume of alkaline absorbent solution corresponding to that introduced into "B" at the beginning of the test is titrated with N/4 HCl. The relation of the alkaline absorbent to the bicarbonate solution is established by measuring 10 ml of the former into a flask, adding 20 ml of normal barium chloride solution and titrating with the bicarbonate solution. From this is calculated the value of the bicarbonate solution in terms of N/4 HCl. Finally the residual alkali in "B" is deducted from the alkali added at the beginning of the test, the difference representing the CO_2 in terms of N/4 HCl.

When working with built soaps, soap powders, and other detergents in which the carbonate content is appreciably higher than in the toilet soap exemplified above, precaution must be taken to avoid decomposition of bicarbonate which may be present. Built soaps containing soda ash have been found in recent investigations in our laboratory to add CO_2 under normal atmospheric exposure over a 14-day period until the sesqui carbonate was formed, when atmospheric carbonation practically ceased.

Built soaps containing silicate carbonated much more rapidly than the comparable product built with soda ash, and silica was liberated in the product.

Products of this type should be dissolved in cold boiled distilled water. Before exhausting the apparatus, some of the alkaline absorbent (carbonate-free) should be added to the contents of flask "A" to convert any bicarbonate to normal carbonate. In the presence of barium chloride it becomes even more desirable to use HCl for acidifying the sample as suggested above. Sulfuric acid does not satisfactorily decompose barium soaps nor barium carbonate.

Use of Method in Other Laboratories

The method as described above has undergone some preliminary trials in outside laboratories with encouraging results. These are presented in Table I. Reports indicate

TABLE I

RESULTS FROM OTHER LABORATORIES WITH CO_2 TEST

Material	Hooker Method	AOCS Standard Soap Method	Theoretical
Armour and Co. Laboratory—			
Soda Ash	41.36% CO_2	....	41.51% CO_2
Laundry Flakes No. 1	2.17 Na_2CO_3	2.39% Na_2CO_3	.....
Laundry Flakes No. 2	2.69 Na_2CO_3	2.90 Na_2CO_3	.....
U. S. Bureau of Standards—			
		By Train Method	
Soda Ash (not dried)	41.10% CO_2	41.10% CO_2	
	40.88	40.96	
	41.18	.....	
Cleanser (TSP + 5% rosin soap, etc.)	1.39% CO_2	1.40% CO_2	
	1.37	.....	

Sample Calculation

Weight of white floating soap taken	50.00 grams
Volume Absorbent solution used	25.00 ml
Volume Bicarbonate solution to titrate spent absorbent—	
Sample A	33.6 ml
Sample B	33.8 ml
Average	33.7 ml

10 ml Absorbent solution requires 16.2 ml bicarbonate solution,
10 ml Absorbent solution requires 20.2 ml N/4 HCl.
Hence,
10 ml Bicarbonate solution is equivalent to 12.48 ml N/4 HCl.

25.00 ml Absorbent × 2 02 =	50.55 ml N/4 HCl
33.7 ml Bicarbonate solution × 1.248 =	42.06
Acid equivalent to CO_2 evolved	8.49 ml N/4 HCl
1 ml N/4 HCl $= \frac{22}{1000 \times 4}$ gm CO_2 =	0.0055 gm
$\frac{8.49 \times 0.0055}{50.00} \times 100 =$	0.0934% CO_2

Calculated as equivalent Na_2CO_3:
$0.0934 \times 2.41 = 0.225\%$ Na_2CO_3

that the above method is found to be simpler and more rapid than the gravimetric train method, without sacrifice of accuracy. Experiments in our laboratory in applying the new method to materials other than soap products indicate that the procedure has general utility. On materials such as 50 per cent liquid caustic soda, where the carbonate content of the product as shipped is normally only 0.1-0.3% calculated as sodium carbonate, no difficulty is experienced in obtaining reproducible and accurate results. This aspect of the method has been verified by adding very small known amounts of sodium carbonate and finding the increment.

Examples of results in using the method in the examination of a variety of soap products are presented in Table II. Convenient quantities of sample are indicated in each case. The degree of agreement which may be anticipated in routine use of the method is illustrated in these results, which represent duplicate determinations in each case.

TABLE II
CARBON DIOXIDE DETERMINATIONS ON TYPICAL PRODUCTS

Product	Sample First Taken Grams	Grams CO_2	% CO_2	Calculated as Equivalent Na_2CO_3 %
C. P. Na_2CO_3	0.5206	0.2148	41.25	99.41
C. P. Na_2CO_3	0.4989	0.2074	41.57	100.18
A textile soap	25	0.0898	0.36	0.87
A textile soap	25	0.0848	0.34	0.82
A nationally advertised washing powder	3	0.1498	4.99	12.02
A nationally advertised washing powder	3	0.1500	5.00	12.06
Another nationally advertised soap powder	3	0.0623	2.08	5.02
Another nationally advertised soap powder	3	0.0616	2.06	4.97
A well known rosin soap	10	0.1273	1.27	2.96
A well known rosin soap	10	0.1274	1.27	2.96
A prominent cleanser	6	0.2162	3.60	8.67
A prominent cleanser	6	0.2168	3.61	8.70
A nationally advertised white floating soap	50	0.0474	0.095	0.23
A nationally advertised white floating soap	50	0.0460	0.092	0.22
A well known chip soap	15	0.2357	1.57	3.78
A well known chip soap	15	0.2329	1.55	3.74

Notes on the Method

Suggestion has been made that funnel "D" might be dispensed with and absorbent solution measured directly into flask "B," thus simplifying the apparatus and making it unnecessary to rinse funnel "D." Evacuation by the aspirator pump might then be made thru funnel "C." We are unable to say at this time whether the method will give the same results with this modification, but the suggestion appears to be well worth trying.

Another suggestion has been made to the effect that the spent absorbent solution be titrated directly with standard HCl instead of sodium bicarbonate solution. We have tried this variation, but in our experience the end point is not as satisfactory.

SOME NOTES ON THE DETERMINATION OF GLYCEROL IN FATS

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THE accurate and rapid determination of glycerol that can be produced by saponifying fats is of great importance to the soap and allied industries. That it is still a great vital problem is indicated by the recent articles regarding rapid saponification[1,2] and rapid determination of glycerol[3], and the activity of the Committee on Glycerol Determination.

The usual method of analysis of fats for available glycerol divides itself into three operations: saponification, oxidation, and titration or determination of excess oxidant. Each of these operations may be performed in a number of different ways, and considering the many slight variations in the various procedures an almost innumerable number of ways of performing the entire analysis are available. It is the purpose of this paper to consider briefly, first, a few of the methods:

I. The direct saponification method.

II. The method proposed by the A. O. C. S. Committee on Glycerol Determination.

III. The method involving the use of a Carius tube; also to propose and discuss a new method.

IV. The catalytic method, using stearic acid or bentonite as catalysts, and, finally, to compare the results of the analyses and the time involved.

I. The Direct Saponification Method

This method, used for fats relatively high in free fatty acids, calls for a 4-gram sample of fat to which is added 50% aqueous potassium hydroxide and distilled water, and the mixture refluxed for 1¼ hours. After addition of hot water, it is placed on the steam bath overnight. In the morning, the solution is transferred quantitatively to a 300 cc. beaker and acidified, and the fatty acids removed. The solution is cleared with aluminum sulphate and sodium hydroxide, and the glycerol determined by the iodiometric method. To an aliquot portion are added standard potassium dichromate solution and concentrated sulphuric acid. This solution is then boiled for 15 minutes and cooled. Potassium iodide solution is added and the liberated iodine is titrated with standard sodium thiosulphate solution, using starch as the indicator. This method, although it works satisfactorily for fats relatively high in free fatty acids, is entirely unsatisfactory for fats low in free fatty acids, in that the saponification is incomplete.

II. The Method Proposed by the A. O. C. S. Committee

The Glycerine Analysis Committee of the A. O. C. S. recently proposed for cooperative work a method of saponification in which 5 grams of the melted fat are mixed with 5 cc. of 50% aqueous potassium hydroxide and heated to 105° C. for four 15-minute periods. At the end of each period, thorough mixing of the fat and the potassium hydroxide is essential. Potassium dichromate is used as the oxidizing agent, the excess titrated with ferrous ammonium sulphate solution, using potassium ferricyanide as an outside indicator.

A. O. C. S. samples of refined coconut oil, cottonseed oil, hydrogenated cottonseed oil, and tallow, all high-grade, were saponified by this method and the oxidation and titration operations were done by two methods, (1) the iodiometric method for glycerol in soap and (2) that described by the committee. The results are given in Table I.