worthwhile, a comparison was made. The walls of the experimental booth were reversed, coated with white paint, and a white paper placed over the blackened top of the colorimeter. The booth was illuminated with a 300 watt light which reflected 100 foot candles at the eyes of the color reader. This seems high, but it has been observed in some color reading stations facing windows. Three sets of readings were made in this booth with high illumination—one with the plain white walls, one with a red paper 10 in. by 15 in.—Munsell color 5R 5/14 placed in front of the reader who gazed at it for ten seconds before making a reading, and one with a green paper of the same size, Munsell color GY 5/10 similarly used.

Six readers participated; two read colors as a matter of daily routine, two read colors infrequently, and two have read colors but are considerably out of practice. One set of readings was made with the booth rebuilt and fixed for low level illumination. The results were as follows, the average of all six observers being the figure given:

Oil.	Description of Oil	High Illumination White	Red	Green	Low Illumination
1.	Light refined cottonseed oil........	5.82	5.92	5.82	5.58
2.	Dark refined cottonseed oil.........	10.15	10.22	10.17	10.05
3.	Refined and bleached soybean oil...	5.83	6.07	5.9	5.62
4.	Dark refined cottonseed oil.........	6.98	7.10	7.02	6.88
5.	Light refined cottonseed oil	5.45	5.78	5.53	5.45
6.	Refined soybean oil	8.45	8.38	8.32	7.86

These are shown graphically in Figure 3. It is evident that the red makes the reading high and the low illumination gives a consistently lower reading than the high one, even when the red paper is not used. There was one respect in which the low illumination was a disappointment. It was hoped that the several observers' readings on an oil would scatter less from the mean when the low illumination was used. This was not the case; the average co-efficient of variation was 6.6% for both the high white and the low. The low level is much more comfortable, however.

It is recommended that the members of the Society try color reading booths as described and from their experience recommend a standard for Lovibond color readings.

UNSAPONIFIED AND UNSAPONIFIABLE DETERMINATIONS AS APPLIED TO INCOMPLETELY SAPONIFIED SOAPS

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Abstract

Unsaponified and unsaponifiable determinations were made on toilet bar soap, potash vegetable oil paste soap, yellow laundry soap and hardwater cocoa bar soap according to the method of (1) the American Oil Chemists' Society, and (2) the Society of Public Analysts (British). The results obtained by the two methods were comparable for toilet bar soap, potash vegetable oil paste soap and yellow laundry soap. The unsaponifiable matter in hardwater cocoa bar soap, however, appeared considerably lower when determined by the A. O. C. S. method than when determined by the S. P. A. method. Extraction of unsaponified matter in the former method is by petroleum ether; in the latter method by ethyl ether. In order to determine whether the difference in results could be traced to the difference in solvents, extraction with petroleum ether in the A. O. C. S. method was followed by extraction with ethyl ether. The weight of unsaponified matter (50 gram sample) was increased thereby from 0.791 g. to 1.423 g. The saponification value of the ethyl ether extract under the A. O. C. S. method tended to show that practically all of the additional material extracted with ethyl ether was made up of mono and diglycerides with the mono predominating.

OUR work on the determination of unsaponified and unsaponifiable matter of incompletely saponified soaps was prompted by making a comparison in our laboratory between the American Oil Chemists' Society methods (1) and the Society of Public Analysts (British) (2). The British proposed methods were contained in a report entitled "The Determination of Unsaponified Fat in Soaps" and submitted by the Sub-Committee on the Determination of Unsaponifiable Matter in Oils and Fats and of Unsaponified Fat in Soaps to the Analytical Methods Committee of the Society of Public Analysts.

In this investigation, the S.P.A. Sub-Committee made a survey of the various published methods and noted that "none was found to be wholly satisfactory." The extraction of dried and powdered soaps with a solvent was found to be quite unreliable since it was impossible to extract all the fat by any dry process. Consideration was given to published methods using weight extractions with ether and petroleum ether but, in the opinion of the Sub-Committee, the conditions for extraction stipulated therein were insufficient for complete extraction. The Sub-Committee "considers that it is essential to use ether, notwithstanding its greater solvent power for soap, rather than petroleum spirits."

The procedure of extraction by the S.P.A. method is faster than the A.O.C.S method since there are only three extractions made in the S.P.A. method as compared to seven in the A.O.C.S. procedure. The S.P.A. method specifies the use of separatory funnels whereas the A.O.C.S. stipulates extraction cylinders.

According to the S.P.A. method, not more than 0.1 cc. of N/10 NaOH should be required to neutralize the dried extract. If the titration is greater than 0.1 cc., then supposedly the method has not been effectively carried out and the test should be repeated. On the soaps we tested it was practically impossible to have the titrations of the dried extracts as low as 0.1 cc., although the highest titration of any sample was 0.4 cc. and the average of all samples was about 0.3 cc.

Basically, the main difference between the two methods is the solvent used, ethyl ether in the S.P.A. method and petroleum ether in the A.O.C.S. method.

In making our comparison between the British proposed methods and the A.O.C.S. methods for unsaponified and unsaponifiable, we tested the following four types of soaps:

1. Toilet Bar Soap.
2. Potash Vegetable Oil Paste Soap.
3. Yellow Laundry Bar Soap.
4. Hardwater Cocoanut Oil Bar Soap (incompletely saponified).

Below is a tabulation (Table No. 1) showing results obtained on the above four soaps using both methods:

TABLE NO. 1

Soap	Method	Unsaponified plus Unsaponifiable Matter Tests	Unsaponified plus Unsaponifiable Matter Avg.	Unsaponifiable Matter Tests	Unsaponifiable Matter Avg.	Unsaponified Matter
Toilet Bar Soap	(A. O. C. S.)	0.38% 0.40	0.39%	0.20% 0.36	0.28%	0.11%
	(S. P. A.)	0.44 0.38	0.41	0.28 0.36	0.32	0.09
Potash Vegetable Oil Paste Soap.....	(A. O. C. S.)	0.78 0.74	0.76	0.56 0.60	0.58	0.18
	(S. P. A.)	0.90 0.76	0.83	0.74 0.66	0.70	0.13
Yellow Laundry Soap..	(A. O. C. S.)	1.92	1.92	1.52 1.50	1.51	0.41
	(S. P. A.)	2.00 2.02	2.01	1.48 1.58	1.53	0.48
Hardwater Cocoa Bar No. 1...	(A. O. C. S.)	2.78 2.72	2.75	0.22 0.38	0.30	2.45
	(S. P. A.)	4.08 4.28	4.18	0.08 0.16	0.12	4.06
Hardwater Cocoa Bar No. 2...	(A. O. C. S.)	3.10 3.10	3.10	0.12 0.14	0.13	2.97
	(S. P. A.)	4.46 4.42	4.44	0.12 0.18	0.15	4.29

It will be noted that the two methods gave comparable results on both unsaponified and unsaponifiable matter on the toilet bar soap, potash vegetable oil paste soap and yellow laundry bar soap. However, the unsaponified results obtained on two samples of hardwater cocoanut oil soap were not in close agreement when tested by the two methods, the S.P.A. method giving results considerably higher than those obtained with the A.O.C.S. method.

The hardwater cocoanut oil soaps used in these determinations represent typical soda-cocoanut oil soaps, incompletely saponified, made by the cold soap process. It is common practice to manufacture these soaps with a residual free fat content ranging in the neighborhood of 2 to 5 per cent.

Inasmuch as such a wide variation was obtained between the two methods on the incompletely saponified soaps, further studies were undertaken to account for these differences. Another sample of hardwater cocoanut oil soap was tested, using the two methods in question. Moreover, after running through the standard method of extracting with petroleum ether in the A.O.C.S. procedure, the same sample was further extracted using ethyl ether as in the S.P.A. method. Also, saponification values were determined on the free fat extraction in an attempt to determine if mono and diglycerides which might be present in the soap were responsible for the marked differences in results obtained by the two methods. (Table No. 2.)

TABLE NO. 2

Method	Unsaponifiable Matter	Unsaponified Matter	Saponification Value of Unsaponified Matter
A. O. C. S.—			
(a) Petroleum Ether	0.11%	2.71%	228.2
(b) Ethyl Ether*	....	1.46	172.8
Total........		4.17%	208.8 (Calc.)
S. P. A.	0.15%	4.18%	216.0

*Additional extract with Ethyl Ether.

The saponification values given above apply to the unsaponified matter, correction being made for unsaponifiable matter present in the extracts. The calculated saponification value of the unsaponified matter in the A.O.C.S. method is 208.8 as against 216.0 in the S.P.A. method. The saponification values were determined on the extracted material which in each case represented an unusually small amount on which to make this determination.

In order to substantiate our findings and also to minimize the possibility of error in the determination of the saponification value of the extracted fractions, a much larger sample (50 grams) of hardwater cocoanut oil soap was used in both the A.O.C.S. and S.P.A. methods with the results shown in Table 3.

TABLE NO. 3

A. O. C. S. METHOD OF EXTRACTION

(50 g. sample)

	Unsaponified plus Unsaponifiable Matter Weight	Unsaponified plus Unsaponifiable Matter %	Unsaponifiable Matter Weight	Unsaponifiable Matter %	Unsaponified Matter Weight	Unsaponified Matter %	Saponification Value
Petroleum Ether Extract..	0.895 g.	1.79	0.104 g.	0.21	0.791 g.	1.58	228.7
Additional Extraction with Ethyl Ether	......	...	......	...	0.632	1.26	182.0
Total of both Petroleum and Ethyl Ether Extractions	......	...	......	...	1.423	2.84	208.0
S. P. A. METHOD (50 g. sample)							
Ethyl Ether Extraction...	1.437 g.	2.87	0.110 g.	0.22	1.327 g.	2.65	208.5

Summarizing table No. 3 we show below a comparison of the results obtained by the two methods on the same sample of hardwater cocoa soap.

TABLE NO. 4

	A. O. C. S.	S. P. A.
Total Unsaponified plus Unsaponifiable	3.05%*	2.87%
Unsaponifiable	0.21	0.22
Unsaponified	2.84	2.65
Saponification Value of Unsaponified	208.0	208.5

*Combined Petroleum and Ethyl Ether Extraction.

The saponification value of the ethyl ether extract under the A.O.C.S. method would tend to show that practically all of the material extracted with ethyl ether was made up of mono and diglycerides with the mono predominating. This statement is based on the fact that the saponification value drops rapidly from a tri-glyceride to the di and monoglycerides. For example we give the following:

	Sap. Value
Trilaurin—$C_3H_5(O.C_{12}H_{23}O)_3$	264
Dilaurin—$C_3H_5(O.C_{12}H_{23}O)_2(OH)$ ..	243
Monolaurin—$C_3H_5(O.C_{12}H_{23}O)(OH)_2$	204

In regard to the solubility of di and mono glycerides in petroleum and ethyl ether, we have made some solubility tests using a sample representing mono and di glycerides (approximately 90 per cent mono) of tallow and also a sample of mono stearin.

0.2 gram samples were placed in 250 cc. each of petroleum and ethyl ether and these solutions were allowed to stand at room temperature for approximately two hours with 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.

[2]Unpublished.

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.

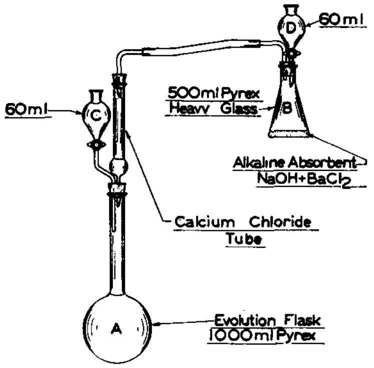

FIGURE I

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.

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