Rapid and Improved Methods of Soap Analysis[*]

W. HAWARD HUNT and M. H. NEUSTADT
Production and Marketing Administration, United States Department of Agriculture
Washington 25, D. C.

SINCE 1941 the Grain Branch of the Production and Marketing Administration, United States Department of Agriculture, has been responsible for the large-scale inspection and testing for compliance with contract specifications of soap products purchased by various Federal agencies for domestic and foreign use. The methods of testing specified in the Federal and other specifications under which the soaps are purchased are, in general, similar to or identical with the Official and Tentative Methods of the American Oil Chemists' Society. Because of the importance of prompt inspection in order to expedite deliveries of soap, particularly under wartime conditions, modifications in technique have been applied to certain of the standard testing methods and in rare instances new, more rapid methods of testing giving results in agreement with the standard methods have been devised. By the use of such improvements the time required to complete inspections of soap has been materially reduced. The modified laboratory techniques and rapid testing methods developed in this work are presented herewith in the belief that they may prove useful to others engaged in the routine analysis of soap products.

Preparation of Samples

Portions of samples for analysis, obtained in accordance with the official method by shaving thin slivers of soap from the cakes with a spatula or by putting the soap through a meat chopper, were not wholly satisfactory, as the soap thus prepared was in a form difficult to handle in weighing, in making moisture determinations, and in dissolving in alcohol or water. Grating the cake of soap with an ordinary metal kitchen vegetable grater having holes approximately 3 mm. in diameter was found (1)[1] to be an ideal procedure for obtaining samples in a form easy to handle for all the required analyses. This procedure is of particular value in the moisture determination method described later and for rapidly dissolving soap samples in alcohol or water. In the case of solid, barreled soap, it is necessary to use a piston-type trier to obtain sections of the soap for grating.

Moisture

Moisture in soap can be determined rapidly and accurately by a modification previously described by the authors (1) of the method of Matt (2). The method consists of placing a 3- to 5-gram portion of the grated sample into a tared Petri dish, of weighing it accurately, and drying it at 100° C. in a vacuum oven at a pressure of 100 mm. or less of mercury for 1 hour. The dish is then removed from the oven, cooled in a desiccator, and loss in weight determined.

Moisture of soap flakes and soap powder may be obtained in a similar manner except that it is unnecessary to grate or otherwise prepare the sample. For shaving creams, a thin film of not more than 2 to 3 grams should be spread on the bottom of a Petri dish.

Repeated checks have shown (Table 1) that moistures obtained in this manner are completely reliable and check accurately with the usual methods of drying to constant weight in the air oven at 105° C. or by toluene distillation. The vacuum-oven method yields results in 1 hour, whereas, by the distillation method 3 hours are necessary and by the air-oven 17 hours are necessary for a moisture determination.

TABLE 1

Comparison of Moisture Determination by the Official Air-Oven Method and the Proposed Vacuum Oven Method

Sample	Percent Moisture		Difference
	Air Oven (A)	Vacuum Oven (V)	V—A
Milled Toilet Soap	12.15	12.30	+.15
	13.50	13.26	—.24
	11.85	12.28	+.43
	11.81	12.24	+.43
	8.64	8.48	—.16
	13.00	13.02	+.02
Barreled Toilet Soap	35.05	35.09	+.04
	34.07	33.96	—.11
	34.48	34.46	—.02
	44.26	44.14	—.12
	35.92	36.21	+.29
Laundry Soap	36.81	37.04	+.23
	44.79	45.18	+.39

Total Matter Insoluble in Alcohol

It has been found that a fritted glass Gooch crucible is more satisfactory to use than an ordinary Gooch crucible with an asbestos mat in the determination of total matter insoluble in alcohol. Ace "E" crucibles are used by the authors in this determination for toilet soap and Ace "D" crucibles for laundry soap. These crucibles can be readily cleaned with a test tube brush having bristles at the tip parallel to the shaft. If such a brush is cut off about 2 inches back from the tip and inserted into the chuck of an electric stirrer, an excellent mechanical cleaner is made available. The crucibles are partially filled with hot, soapy water and pushed up against the rotating brush tip. (Care should be exercised not to use the brush after the bristles have worn down, as the wire tip will damage the fritted glass.) The crucibles are first "reverse" washed over a suction flask with hot tap water and then washed upright with boiling, distilled water. Ultramarine, used to color "blue streaked" or "blue mottled" soaps, can be readily removed from the crucibles by immersing them in 6N hydrochloric acid. If the crucibles should have matter on them not removed in the ordinary washing operation, they may be boiled in alcoholic potash solution. This method should not be followed often, however, as the alkali will attack the fritted glass and enlarge the pores.

Matter Insoluble in Water

In testing any commodity for compliance with a requirement having a maximum limit it is frequently possible to save considerable time by using a simplified testing method known to give a result equal to or greater than that given by the official method. If the result of such a test is equal to or lower than the maximum limit permitted by the specification, the

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[1] Numbers in parentheses refer to literature citations.

requirement in question is met and no further test for compliance with that requirement need be made. Such is the case in testing soap for matter insoluble in water. The matter insoluble in alcohol, after weighing, is washed with boiling water in the fritted glass crucible on the suction flask. Higher results are obtained by this method than with the official method, but when the value obtained is below the maximum limit permitted by the specifications, it is not necessary to resort to the official method. If the amount of water-insoluble material is small and a saving of time is desirable, oven drying of the water-insoluble matter can be eliminated by following the boiling water treatment with a rinse of 95 percent alcohol, allowing suction to continue 3 or 4 minutes and then weighing the crucible with its contents. We have found that the longer the soap sample is in contact with alcohol the greater will be the amount of water-insoluble matter. Accordingly, the rapid method for dissolving the soap in alcohol, described below, is of considerable significance.

Total Anhydrous Soap

The official method for determining the percentage of anhydrous soap in soap containing large amounts of soluble silicates and soap products containing a high percentage of finely divided material insoluble in water is equally applicable to all types of soap except those high in alcohol soluble salts, with a considerable saving in time and effort over the longer method because it is necessary merely to evaporate the filtrate from the matter insoluble in alcohol and to dry and weigh. Furthermore, the results obtained by this method compare favorably with those obtained by using the official method for anhydrous soap, as is evident from Table 2.

TABLE 2

Anhydrous Soap Values as Determined by the Fatty Acid Titration Method (Official) and by the Evaporation of the Filtrate From the Matter Insoluble in Alcohol

Sample	Percent Anhydrous Soap		Difference
	Fatty Acid Method (Official)	Alcohol Insoluble Filtrate Method	AIFM—FAM
Toilet Soap	69.2	69.1	—.1
	61.4	61.3	—.1
	61.2	61.6	+.4
	69.2	68.9	—.3
Laundry Soap	48.6	48.3	—.3
	66.6	66.2	—.4
	66.4	67.0	+.6
	66.6	66.9	+.3

As mentioned previously, it is important that water-soluble matter should have no more contact with alcohol than is necessary to effect solution. Slivers of soap obtained by slicing, or masses obtained from ground samples, when digested in alcohol will require about 5 to 6 hours or longer to disintegrate. However, a finely grated sample when stirred with an air-powered stirrer will completely disintegrate in 5 minutes or less. A stirring rod may be made in the laboratory by flattening and turning to a right angle the end of a glass rod and then giving it sufficient pitch so as to agitate the soap thoroughly on the bottom of the beaker. To avoid evaporation and to catch spray thrown up by the stirrer a watch glass with a hole in the center is used as a cover. An expedient method for rapid evaporation of alcohol solutions is to place the beaker of solution on the steam bath in a hood with considerable steam turned on and to close the door to within an inch or so of the bottom of the hood. This will create a strong air current over the beaker and will evaporate the alcohol rapidly. It is preferable to dry the anhydrous soap from shaving cream and similar types of soap in the 100° C. vacuum oven. The ordinary air oven at 100° C. to 105° C. is satisfactory for other types of soap.

Chloride

Since the alcohol method is used for anhydrous soap, chlorides are determined on the acid water solution which remains after the extraction of the fatty acids in our modification of the rosin determination. It has been found that neither ether nor fatty acids that may be left in the acid water solution will affect the end point of the titration, but that exact neutrality to methyl orange is very essential. This is conveniently accomplished by titration with about 2N chloride-free alkali.

Unsaponified and Unsaponifiable Matter

The determination of unsaponified matter in hard-milled toilet soap has, at times, caused considerable difficulty, particularly with respect to obtaining satisfactory duplicate results. Finally, it was found that with the official method minute amounts of soap were often dissolved in the petroleum ether used for the extraction and carried through with the unsaponifiable and/or unsaponified matter. When this dissolved soap was precipitated as the lead soap with basic lead acetate from the petroleum ether solution, better duplicate checks were obtained. Instances still occurred, however, when replicates were at variance and it was concluded that complete extractions were probably not obtained by either the use of the separatory funnel or a cylinder for extraction. Liquid extractors were tried with excellent results as shown in Tables 3 and 4. The type of extractor used is the one designed for the extraction of liquid by means of ether in which the distributing tube contains an integral fritted glass disc.

TABLE 3

Comparison of Extractability of Unsaponified and Unsaponifiable Matter in Soap With a Separatory Funnel and a Liquid Extractor

	Weights in grams[1]			
	Separatory Funnel		Liquid Extractor	
	1st Test	2nd Test	1st Test	2nd Test
Unsaponified plus unsaponifiable matter	0.0399	0.0548	0.0606	0.0591
Unsaponifiable matter	.0363	.0449	.0454	.0470
Unsaponified matter	.0036	.0099	.0152	.0121

[1] Each value represents the average of duplicate simultaneous determinations.

TABLE 4

Study of the Recovery of Unsaponified and Unsaponifiable Matter Added to Soap Using a Separatory Funnel and a Liquid Extractor

	Weights in grams			
	Separatory Funnel		Liquid Extractor	
	1st Test	2nd Test	1st Test	2nd Test
Unsaponified and unsaponifiable matter present in soap (by analysis)	0.0548	0.0548	0.0606	0.0606
Unsaponified and unsaponifiable matter added[1]	0.0519	.0354	.0359	.0325
Total unsaponified and unsaponifiable matter	.1067	.0902	.0965	.0931
Total unsaponified and unsaponifiable matter recovered	.0981	.0773	.0950	.0913
Percentage recovery	91.9	85.7	98.4	98.1

[1] Unsaponified matter is oleic acid; unsaponifiable matter is mineral oil.

In using liquid extractors the official procedure is followed to the point of transferring the soap solution to the extraction cylinder. At this point the transfer is made to the liquid extractor and petroleum ether is added to just below the side arm. A 250-ml. Erlenmeyer flask, containing a small quantity of petroleum ether, is connected to the side arm and the extraction started. Extraction is carried on for one hour and then the contents of the extractor are transferred quantitatively to a 500-ml. separatory funnel, allowed to separate, and the soap solution drained. By gently swirling the solvent, any whitening agent, or other insoluble material originally present in the soap, can be forced to the bottom of the funnel and drawn off. Then the contents of the Erlenmeyer flask are transferred quantitatively to the separatory funnel. Approximately 10 ml. of a saturated solution of basic lead acetate $[Pb(C_2H_3O_2)_2 \cdot Pb(OH)_2 \cdot H_2O]$ are added. If the immediate precipitate is heavy it is drawn off without shaking. This step is repeated until there is only a slight precipitate and then the funnel is shaken vigorously for 30 seconds, the water layer drained, and the process repeated with another 10-ml. portion, after which the petroleum ether extract is washed 3 times with about 25 ml. of 10 percent ethyl alcohol. The petroleum ether extract is then transferred to a 300-ml. Erlenmeyer flask containing about 15 grams anhydrous sodium sulfate to remove moisture, swirled 5 minutes, and filtered into a tared Soxhlet flask if the solvent is to be recovered (otherwise into a tared beaker), and evaporated to dryness.

It has been found in this laboratory that traces of solvent in contact with extracted material in a Soxhlet flask can be removed by connecting a two-hole rubber stopper, or a one-hole rubber stopper with a V-notch on a side, to the flask and connecting a vacuum line to a tube through one hole while the flask is kept warm. In this way while there is a partial vacuum over the material there is a constant circulation of air through the other opening. This method has been found more satisfactory than allowing vapors to evaporate spontaneously on a steam bath or in an oven. After a minute or so of this, the flask with its contents is dried in a 100° C. air oven for one-half hour or longer to constant weight. Care must be taken not to produce a static electric charge on the flask by rubbing with a towel, or significant errors in weight will occur.

Rosin

An easier and more rapid method than the official method for preparing the fatty acids for the rosin determination is to dissolve 10 grams of soap in about 300 ml. of boiling water and then to separate the fatty acids with about 5 ml. of 1:1 H_2SO_4 (until no more suds and/or turbidity exists). While the fatty acids are still liquid they are transferred to a 500-ml. separatory funnel and cooled to below 25° C. The fatty acids are extracted with 50 ml. of ethyl ether after first washing the residue in the beaker into the separatory funnel with the ether. The aqueous portion is drawn off into the original beaker and the ether extract transferred to another separatory funnel. Three more extractions are made with 30-ml. portions of ether and all the ether extracts are collected in one separatory funnel. The aqueous solution is reserved for chloride determinations as described previously. The combined ether extracts are washed with 25-ml. portions of distilled water containing methyl orange (3 ml. of 1 percent solution per liter) until neutral. The ether extract is transferred to a 250-ml. Erlenmeyer flask containing about 15 grams of anhydrous sodium sulfate to remove moisture, swirled 5 minutes, filtered into a tared Soxhlet flask, and the solvent recovered. Removal of the last traces of ether is accomplished by connecting the flask to a vacuum line as mentioned above, and then drying in a 100° C. oven for one-half hour. After cooling and weighing, 10 ml. of naphthalene-beta-sulfonic acid (an adequate amount for soaps having less than 25 percent rosin) and 15 ml. of methyl alcohol are added. A blank is run in the same way and the determination is continued as outlined in the official method.

Titer Test

The only variation made in this test is the development of a mechanical vertical stirrer having a windshield wiper motor as the source of power. This device is the subject of a brief article now being published elsewhere. The mechanical stirrer furnishes a precise and uniform stirring rate and frees the operator from the fatigue induced by hand stirring.

REFERENCES

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Kenaf Seed Oil[*]

MARIO LEWY[1]

Introduction

KENAF (*Hibiscus cannabinus* L.) belongs to the Malvaceae family. It is an annual plant, native of India and is extensively cultivated for its fibers which are in many characteristics comparable to jute fiber. Under favorable conditions the plant reaches 12 to 14 feet in height and its characteristic large flowers are yellowish with crimson centers. Kenaf was introduced to El Salvador several years ago when a few seeds were brought in from Java. From this original source the plant has spread throughout Latin America.

When introduced to El Salvador, the plant was considered erroneously to be Roselle (*Hibiscus sabdariffa var. altissima*) (2) but it was later identified as *Hibiscus cannabinus* L. (7). Two varieties, vulgaris and viridis make up the plant material being cultivated in Latin America.

Kenaf is a quick growing plant. Usually the fiber may be extracted about 90 days after planting. It may be impracticable to obtain both a seed crop and

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