

# Soap Analysis

# Committee Report

Methods for Unsaponified and Unsaponifiable Material  
Reviewed and checked by Co-operative Analyses

By H. P. TREVITHICK, *Chairman*

IN 1922, a complete set of soap methods adopted by a committee consisting of representatives of various soap manufacturers and the Bureau of Standards, etc., under the leadership of Archibald Campbell. These methods were given to this committee for review.

The most pressing problems apparently were the determinations of the unsaponifiable and unsaponified matters in soap samples. The methods prescribed the use of ethyl ether in these tests. The use of this solvent has very many disadvantages: first, the soap is soluble in the solvent, and is carried into the other solution, from which it must be removed by washing with water, but then the water washings must be extracted again: second, it is very apt to cause troublesome emulsions which are very difficult to break: third, due to the fact that alcohol and ether readily dissolve in each other in all proportions, the soap solution must be an aqueous one, free from alcohol. This causes hydrolysis of the soap, and consequent liberation of fatty acids and caustic, the fatty acids dissolving in the solvent and thus going into the extract. The weight of this extract must be corrected, by dissolving in petroleum ether to ensure freedom from soap (this ingredient must be weighed and allowed for if present) and then titrating with caustic alkali in neutral alcohol solution to obtain the correction for fatty acid content. This last correction frequently is so large that it represents 80 or 90% of the total residue, and in our opinion, is so large that it destroys practically the value of the whole test.

Petroleum ether does not have these disadvantages, as soap is only slightly soluble in it, hydrolysis in the 50% alcoholic solution is almost negligible, and emulsions are not easily formed. It is also the standard solvent in the

F. A. C. methods for fats and greases. We, therefore, decided to check this method on soap.

Two samples of soap, a straight tallow soap, and the same tallow soap containing 20% rosin, were prepared by one of our members, Mr. W. A. Peterson, and mailed to the members with instructions to make the following tests on each:

A—Determine the unsaponified plus unsaponifiable by petroleum ether by the method of the Committee on the Analysis of Commercial Oils and Fats of The American Oil Chemists' Society and the American Chemical Society, usually referred to as the F. A. C. Committee.

B—After completing the extraction, remove the alcohol by evaporation, redissolve the soap in water, and extract three more times with ethyl ether, correcting the extracts for any fatty acids and soap present.

C—Determine the same constituents by the straight method as prescribed by the American Chemical Society method using ethyl ether and making the usual corrections.

Of course, it was not necessary to saponify the sample in any of these tests above, but simply to start by dissolving the soap in the required solvent and then to extract.

Then determine the unsaponifiable matter by the same three methods, A, B and C, of course, saponifying the soap, etc. Also the moisture content was to be determined.

The results of these tests by 7 analysts are shown in Tables I to IV. Four of the members of the committee have not yet been able to complete the work for various reasons. Each table shows the average value, and the maximum and minimum values for each column, and the gross and corrected or net figures for each test as reported.

It is seen that the "F. A. C." method gives quite concordant and consistent results in all four tables, the deviations being not more than would be expected from the work of different collaborators, in most cases the corrections necessary being minor. In this test, the material is extracted from a 50% alcohol solution which tends to depress, if it does not completely eliminate, hydrolysis of the soap.

The additional extractions with ethyl ether, the results being shown in the 3rd and 4th columns, gave rather fantastic results, the gross results varying from 0.20 to 3.81 on Table I, 0.12 to 1.60 on Table II, 1.29 to 4.74 on Table III, and 0.74 to 1.98 on Table IV, while the net corrected values ran 0.0 to 0.25 on Table I, 0.0 to 0.25 on Table II, 0.0 to 0.94 on Table III, and 0.0 to 0.74 on Table IV, the corrections being many times the net results in most cases, so that it seems probable that the net results should be negligible in all cases.

The results by the straight official method as at present prescribed also show very large corrections, the gross values varying from 1.86 to 2.93 on Table I, and from 2.89 to 6.53 on Table III. The net values also show large variations, which are due we believe to the difficulties inherent in the method, the length of time required (several days) and the number of pieces of apparatus required, with consequent enhanced chances of loss, spillage, etc.

In all four tests, the petroleum ether extract seems somewhat less than the ethyl extract, but this may be partially due to the fact that the corrections as applied to the ethyl ether method are not sufficiently exact. Further, we believe that no method should be adopted where the corrections are much larger than the net results, as the chances of errors creeping in are too great.

We, therefore, recommend that these methods for the determination of unsaponifiable, unsaponified plus unsaponifiable, and unsaponified saponifiable matter be rewritten to agree with the F. A. C. procedure.

The methods, as we suggest them, are as follows:

### Soap Analysis

#### Unsaponified & Unsaponifiable Matter:

##### Extraction Cylinder:

The cylinder shall be a 250 cc. glass stoppered cylinder about 35 mm. ( $1\frac{3}{8}$ " in diameter and about 30 cm. (12" high.

##### Petroleum Ether:

Redistilled petroleum ether, American Oil Chemists' Society specifications, shall be used. A blank must be made by evaporating 250 cc. with about 0.25 gram of stearin or other hard fat (previously brought to constant weight by

heating) and drying as in the actual determination. The blank must not exceed a few milligrams.

##### Determination:

Weigh 5 grams ( $\pm 0.2$  gram) of the prepared sample into a 250 cc. Erlenmeyer flask or beaker which contains approximately 0.1 gram bicarbonate of soda, and dissolve in 100 cc of 50% redistilled ethyl alcohol. Warm and shake to effect solution, keeping the temperature under 60° C., and filter off any undissolved residue on a Gooch crucible with an asbestos pad or in a funnel using an asbestos pad deposited on a perforated porcelain disc. Wash three times with hot 50% alcohol and then with 5 cc. of hot 95% alcohol. Wash with a small amount of petroleum ether to remove any traces of unsaponified and unsaponifiable. Transfer the entire alcohol — water and ether filtrate to the extraction cylinder and make up to the 160 cc. mark with 50% redistilled ethyl alcohol. Add 50 cc. of petroleum ether, shake vigorously for one minute and allow to settle until both layers are clear. The volume of the upper layer should be about 40 cc. Draw off petroleum ether layer as closely as possible by means of a slender glass siphon, into a separatory funnel of 500 cc. capacity. Repeat the extraction at least six times using 50 cc. of petroleum ether each time. Wash the combined ether extracts in a separatory funnel first with a mixture of 15 cc. of N/10 sodium hydroxide solution and 15 cc. of 95% alcohol, and then three times with 25 cc. portions of 10% alcohol, shaking vigorously each time. Transfer the petroleum ether extract to a beaker and evaporate the petroleum ether on a steam bath in an air current.

Test the residue for solubility with 50 cc. of petroleum ether at room temperature. Filter and wash free from the insoluble residue, if any; evaporate and dry in the same manner on the steam bath in a current of air, and finally in an air oven at 101° C. for 30 minutes. Weigh and return to the oven, re-weighing at 15 minute intervals until constant weight is reached. Take up the residue in 50 cc. of warm ethyl alcohol, neutralized to phenolphthalein, titrate to the same color as original neutral alcohol with N/25 sodium hydroxide solution and calculate to oleic acid. Deduct this figure from the gross weight previously found and report as "Unsaponified and Unsaponifiable Matter."

NOTE: Any blank from the petroleum ether must be deducted from the weight before calculating the unsaponified and unsaponifiable matter.

NOTE: Any free fatty acids in the soap. (titrated in 50% alcohol solution and calculated to oleic acid) must be added to the corrected figure for "Unsaponified and Unsaponifiable Matter."

Unsaponifiable Matter:

Determination:

Weigh 5 grams ( $\pm 0.2$  gram) of the prepared sample into a 200 cc. Erlenmeyer flask. Add 30 cc. of redistilled 95% ethyl alcohol and 5 cc. of 50% aqueous potassium hydroxide and boil the mixture for one hour under a reflux condenser. Transfer to the extraction cylinder and wash to the 40 cc. mark with redistilled 95% ethyl alcohol. Complete the transfer, first with warm then with cold water till the total volume is 80 cc., and finally with a small quantity of petroleum ether. Cool the cylinder and contents to room temperature and add 50 cc. of petroleum ether; and then proceed with the extraction as outlined above under "Unsaponified and Unsaponifiable Matter," except the alkaline wash may be omitted; weigh the resi-

due and correct for fatty acids in the usual manner. Report the result as "Unsaponifiable Matter."

From the total Unsaponified and Unsaponifiable Matter figure as found above, deduct the Unsaponifiable figure and report as "Unsaponified Matter."

The Committee wishes to emphasize the necessity of thorough and vigorous shaking in order to secure accurate results. The two phases must be brought into the most intimate contact possible; otherwise low and disagreeing results may be obtained.

NOTE: The above method will not remove all the unsaponifiable matter in soaps to which lanolin has been added. Many more extractions are required when substances of this nature are present.

Respectfully submitted;

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TALLOW SOAP  
UNSAAPONIFIED PLUS UNSAPONIFIABLE  
(Table I)

ANALYST	F. A. C.		Add'l Ethyl Ether		American Chemical Society	
	Gross	Net	Gross	Net	Gross	Net
No. 1. ....	0.90	0.34	0.13	0.06	—	—
	0.97	0.35	0.27	0.11	—	—
No. 2. ....	0.36	0.31	0.76	0.26	2.86	1.23
	0.36	0.31	0.90	0.23	3.00	1.08
No. 3. ....	0.51	0.40	1.20	0.10	—	—
	0.48	0.40	1.25	0.09	—	—
No. 4. A. (5 extractions)	—	0.25	—	0.0	—	0.22
	—	0.26	—	0.0	—	0.24
	—	0.26	—	0.0	—	0.26
	—	0.26	—	0.0	—	0.27
B. (7 extractions)	—	—	—	—	—	—
C. (Stokes Flask used)	—	—	—	—	—	—
	—	0.28	—	0.0	—	—
	—	0.26	—	0.0	—	—
	—	0.27	—	0.0	—	—
	—	0.28	—	0.0	—	—
No. 5. ....	0.42	0.37	0.32	0.05	2.14	0.54
	0.35	0.30	0.35	0.06	1.58	0.27
No. 6. ....	0.56	0.23	3.81	0.07	1.89	0.35
No. 7. A. ....	0.32	0.29	—	—	—	0.68
	0.32	—	—	—	—	0.77
B. ....	0.32	0.30	—	—	—	—
	0.34	—	—	—	—	—
AVERAGE .....	0.49	0.31	1.28	0.08	2.23	0.58
MAXIMUM .....	0.94	0.40	3.81	0.25	2.93	1.16
MINIMUM .....	0.32	0.23	0.20	0.00	1.86	0.25

TALLOW SOAP  
UNSAAPONIFIABLE  
(Table II)

ANALYST	Moisture	F. A. C.		Add'l Ethyl Ether		American Chemical Society	
		Gross	Net	Gross	Net	Gross	Net
No. 1. ....	2.77	0.30	0.25	0.10	0.05	—	—
		0.30	0.25	0.13	0.06	—	—
No. 2. ....		0.26	0.18	0.74	0.28	1.30	1.19
		0.26	0.19	0.66	0.22	1.22	1.13
No. 3. ....	3.45	0.32	0.32	0.83	0.02	—	—

Table II—Continued

		0.29	0.29	0.73	0.08	—	—
No. 4. A. (5 extractions)		—	0.24	—	0.0	—	0.20
		—	0.24	—	0.0	—	0.23
		—	0.24	—	0.0	—	0.24
		—	0.24	—	0.0	—	0.25
B. (7 extractions)							
C. (Stokes Flask used)							
	(5 extractions)						
	3.58	—	0.26	—	0.0	—	—
	3.56	—	0.24	—	0.0	—	—
	3.59	—	0.25	—	0.0	—	—
		—	0.26	—	0.0	—	—
No. 5. ....	3.55	0.24	0.24	1.97	0.08	1.22	0.32
	3.49	0.27	0.27	1.22	0.03	1.42	0.37
No. 6. ....		0.48	0.18	0.42	0.09	0.48	0.09
No. 7. A. ....	2.52	0.29	—	—	—	—	—
	2.60	0.28	0.29	—	—	—	0.50
B. ....		0.26	—	—	—	—	—
		0.28	0.27	—	—	—	—
C. ....		0.24	—	—	—	—	—
		0.28	0.26	—	—	—	—
AVERAGE .....	3.18	0.32	0.25	0.72	0.07	1.02	0.47
MAXIMUM .....	3.59	0.48	0.31	1.60	0.25	1.32	1.16
MINIMUM .....	2.56	0.26	0.18	0.12	0.00	0.48	0.09

ROSIN TALLOW SOAP  
UNSAAPONIFIED PLUS UNSAAPONIFIABLE  
(Table III)

ANALYST	F. A. C.		Add'l Ethyl Ether		American Chemical Society	
	Gross	Net	Gross	Net	Gross	Net
No. 1. ....	1.77	1.60	1.10	0.84	—	—
	1.73	1.66	1.47	0.94	—	—
No. 2. ....	1.58	1.54	1.80	0.90	6.48	2.81
	1.62	1.56	1.78	0.98	6.58	2.80
No. 3. ....	1.83	1.67	2.44	0.58	—	—
	1.83	1.67	—	—	—	—
No. 4. A. (5 extractions)						
	—	1.51	—	0.02	—	1.66
	—	1.60	—	0.03	—	1.66
	—	1.60	—	0.02	—	1.67
	—	1.68	—	0.03	—	1.68
B. (7 extractions)						
	—	1.67	—	—	—	—
	—	1.63	—	—	—	—
	—	1.65	—	—	—	—
	—	1.64	—	—	—	—
C. (Stokes Flask used)						
	(5 extractions)					
	—	1.60	—	0.0	—	—
	—	1.61	—	0.0	—	—
	—	1.63	—	0.0	—	—
	—	1.64	—	0.0	—	—
No. 5. ....	1.44	1.23	2.62	0.62	3.40	1.80
	—	—	—	—	3.40	1.80
No. 6. ....	1.62	1.31	4.74	0.66	2.89	2.49
No. 7. A. ....	1.16	—	—	—	—	—
	1.08	1.04	—	—	—	2.72
B. ....	1.10	—	—	—	—	—
	1.08	1.00	—	—	—	2.75
AVERAGE .....	1.49	1.43	2.58	0.53	4.27	2.37
MAXIMUM .....	1.83	1.67	4.74	0.94	6.53	2.81
MINIMUM .....	1.09	1.00	1.29	0.00	2.89	1.67

ROSIN TALLOW SOAP  
UNSAAPONIFIABLE  
(Table IV)

ANALYST	Moisture	F. A. C.		Add'l Ethyl Ether		American Chemical Society		
		Gross	Net	Gross	Net	Gross	Net	
No. 1. ....	0.20	1.60	1.45	0.77	0.74	—	—	
		1.60	1.40	0.73	0.73	—	—	
No. 2. ....		1.36	1.30	1.32	0.74	2.80	1.32	
		1.42	1.39	1.24	0.70	2.50	1.19	
No. 3. ....	0.60	1.63	1.61	1.43	0.53	—	—	
		1.61	1.58	1.97	0.67	—	—	
No. 4. A. (5 extractions)		—	1.51	—	—	—	1.60	
		—	1.50	—	—	—	1.59	
		—	1.54	—	—	—	1.66	
		—	1.57	—	—	—	1.66	
B. (7 extractions)		—	1.60	—	—	—	—	
		—	1.61	—	—	—	—	
		—	1.60	—	—	—	—	
		—	1.60	—	—	—	—	
C. (Stokes Flask used) (5 extractions)		—	1.52	—	0.0	—	—	
	0.84	—	1.55	—	0.0	—	—	
	0.83	—	1.57	—	0.0	—	—	
	0.85	—	1.58	—	0.0	—	—	
		—	1.58	—	0.0	—	—	
No. 5. ....	0.74	1.06	1.06	2.47	0.23	2.97	1.62	
	0.60	0.91	0.91	1.49	0.23	2.87	1.47	
No. 6. ....		1.25	1.06	0.74	0.15	1.58	0.94	
No. 7. A. ....	1.54	0.90	—	—	—	—	—	
	1.50	0.84	0.87	—	—	—	1.72	
B. ....		0.86	—	—	—	—	—	
		0.84	0.85	—	—	—	—	
		(on dried soap) (with ethyl ether)				Gross 0.91	Net 0.83	
AVERAGE .....	0.78	1.22	1.28	1.09	0.41	2.02	1.42	
MAXIMUM .....	1.54	1.60	1.60	1.98	0.74	2.82	1.62	
MINIMUM .....	0.20	0.85	0.85	0.74	0.00	1.58	0.94	

Butter consumption in Netherlands was 12% greater in 1930 than in 1929. This information, Commercial Attache Van Wickel, The Hague, furnishes in a recent report based on official Dutch statistics. Per capita consumption of margarine fell off .3 of a kilogram to 8.9 kilograms, from 1929 to 1930, whereas butter increased per capita .6 of a kilogram. The consumption of animal fats in the manufacture of margarine in 1930 was 71,035 metric tons, or nearly three times the quantity that entered into margarine in 1926 and approximately 50% more than the consumption in 1929. In the case of vegetable oils, consumption dropped from 118,000 metric tons in 1928 to 68,000 metric tons last year. There was a decline of 33 1/3% between the years 1929 and 1930 in the use of vegetable oils.

Because of the average retail price of butter, the terms of percentage of prices prevailing for the period 1921-1925 dropped from the index figure of 90 in 1929 to 76 in 1930, whereas margarine underwent no downward revision. Consumption of the latter product was affected to the extent of a drop of 2%.

A large sugar company in the Matanzas Province is contemplating the planting of approximately 10,000 acres in sunflowers after the present grinding season is over. The company in question intends to process the resulting production of sunflower seeds themselves for the extraction of oil. No information is as yet available as to whether the oil will be exported to northern markets or whether it will be sold to the local manufacturers of vegetable compounds.

Due to the large surplus of soya beans North Manchuria officials are advocating that the farmers plant larger crops of wheat, kaoliang, and millet and decrease soya bean acreage. Reports conflict as to what extent these instructions have been followed by the farmers. The cable reports that farmers are adverse to planting wheat on account of the great hazard due to fall rains preventing maturity, therefore they are counting on planting beans in spite of advice of Government. Present estimates indicate soya bean acreage will be equal or slightly smaller than past year with slight increase in acreage of wheat, kaoliang and millet.