REPORT OF THE SOAP ANALYSIS COMMITTEE--1935

By M. L. SHEELY, Chairman

THE work of the Soap Committee during the present year has been directed to a continuation of the studies of several analytical determinations which have not been hitherto entirely satisfactory. It will be recalled that at the Fall meeting of the Society in 1933 a complete set of methods of soap analyses was tentatively adopted, which, with a few exceptions, were substantially the same as those adopted by the American Chemical Society Committee in 1922. These methods were published in full in the May, 1934, issue of Oil and Soap, and since that time several important revisions have been recommended and approved.

During the present year, four cooperative samples, representing various types of filled and unfilled soaps were distributed to the committee members and tests for the following requested:

1. Free caustic alkali
2. Screen analysis
3. Naphtha

As a result of this collaborative work the committee recommends:

1. That no change be made in the present method for free alkali.
2. That tentative methods for screen analysis be included in the present methods of analysis.
3. That the present tentative method for determination of *Volatile Hydrocarbon* be deleted and replaced with the method outlined in the present report.

Cooperation With American Chemical Society Committee on Soap Analysis

During the year a committee of the A.C.S. was appointed by President Roger Adams, consisting of the following members: F. W. Smither, chairman, H. P. Trevithick, C. P. Long, R. E. Divine, J. R. Powell, P. H. Walker.

Three members of this committee are members of the A.O.C.S. Soap Analysis Committee.

Our committee has indicated its desire to cooperate with the A.C.S. Committee to the fullest extent and in order to promote uniformity in methods both in the industry and by the consuming outlets, it is hoped that both committees will be able to standardize on substantially the same methods of analysis. The first steps in this direction have been taken by the chairmen of the respective committees.

The 1935 membership of the Soap Analysis Committee is as follows: F. W. Smither, H. C. Bennett, H. E. Cutts, L. F. Hoyt, W. A. Peterson, R. B. Trusler, C. P. Long, R. C. Newton, H. P. Trevithick, J. M. Burmaster, J. E. Doherty, E. L. Luckow, M. L. Sheely, chairman.

FREE ALKALI DETERMINATIONS

(All Figures Expressed as % NaOH)

Sample No. 1—Automobile Soft Soap

	A.O.C.S. Method	Modification (A)	Modification (B)
M. L. Sheely	0.03%	0.04%	0.02%
J. E. Doherty	0.00	0.01	0.00
C. P. Long	0.01	0.04	0.04
E. R. Luckow	0.03	0.03	0.02
H. C. Bennett	0.06	0.05	0.02
W. A. Peterson	0.03	0.04	0.04
R. C. Newton	0.04	0.05	0.05
H. E. Cutts	0.00	0.02	0.00
L. F. Hoyt	0.04	0.05	0.04
R. B. Trusler	0.02	0.02	...
High	0.06	0.05	0.05
Low	0.00	0.01	0.00
Average	0.03	0.04	0.03

Sample No. 2—Built Tallow Soap (Powdered)

	A.O.C.S. Method	Modification (A)	Modification (B)
M. L. Sheely	0.02%	0.23%	0.02%
J. E. Doherty	0.01	..*	0.04
C. P. Long	0.01	0.12	0.06
E. R. Luckow	0.01	0.04	0.01
H. C. Bennett	0.01	0.04	0.01
W. A. Peterson	0.04	0.05	0.05
R. C. Newton	0.01	0.25	0.12
H. E. Cutts	0.00	0.08	0.02
L. F. Hoyt	0.01	0.25	0.07
R. B. Trusler	0.02	1.58	0.03
High	0.04	1.58	0.12
Low	0.00	0.02	0.01
Average	0.01	0.29	0.04

Sample No. 3—Built White Laundry Soap

	A.O.C.S. Method	Modification (A)	Modification (B)
M. L. Sheely	0.01%	0.03%	0.01%
J. E. Doherty	0.00	....*	0.02
C. P. Long	0.03	0.08	0.03
E. R. Luckow	0.03	0.05	0.02
H. C. Bennett	0.02	0.04	0.02
W. A. Peterson	0.04	0.05	0.05
R. C. Newton	0.01	0.06	0.05
H. E. Cutts	0.00	0.14	0.08
L. F. Hoyt	0.03	0.12	0.06
R. B. Trusler	0.00	1.78	0.02
High	0.04	1.78	0.08
Low	0.00	0.01	0.01
Average	0.02	0.26	0.04

Sample No. 4—Neutral Powdered Soap

	A.O.C.S. Method	Modification (A)	Modification (B)
M. L. Sheely	0.01%	0.01%	0.00%
J. E. Doherty	0.00	0.04	0.04
C. P. Long	0.01	0.01	0.01
E. R. Luckow	0.00	0.00	0.00
H. C. Bennett	0.01	0.02	0.01
W. A. Peterson	0.01	0.01	0.01
R. C. Newton	0.02	0.02	0.02
H. E. Cutts	0.00	0.02	0.00
L. F. Hoyt	0.00	0.02	0.01
R. B. Trusler	0.00	0.00	....
High	0.02	0.04	0.04
Low	0.00	0.00	0.00
Average	0.01	0.02	0.01

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*Impossible to titrate.

COMMENTS OF COLLABORATORS

M. L. Sheely: "The endpoints obtained by Modification (A) were very indefinite, especially so in the case of samples No. 2 and No. 3, which contained alkaline salts. We still prefer the official A.O.C.S. method. It would be desirable to study both Modification (A) and (B) further if these are to be considered for adoption."

J. E. Doherty: "On samples No. 2 and No. 3 it was impossible to titrate by Modification (A) due to hydrolysis of sodium silicate."

C. P. Long: "Samples No. 2 and No. 3 did not show endpoints which were at all definite and Modification (B) successive alcohol washings continued to remain alkaline. No trouble was encountered with soaps No. 1 and No. 4. Do not feel that the proposed methods are very satisfactory: at least, a considerable amount of work should be done before either may be considered for adoption."

L. F. Hoyt: "Modification (A): Our experience with this method leads us to conclude that it has little if anything to recommend it. On filled soaps particularly it is useless, since the endpoint when titrating in the presence of filler is extremely indefinite and can be chosen to suit the whim of the analyst."

The method appears to be based on the naive idea that 4 to 6 grams of anhydrous sodium sulphate will dehydrate 150 cc. of 95 per cent alcohol (containing about 6 grams of water, exclusive of whatever amount of water may have been contributed by the sample of soap) and do it practically instantaneously.

To show the fallacy of this idea

we added 5 grams of anhydrous sodium sulphate to 150 cc. No. 30 alcohol and boiled vigorously under reflux for 45 minutes. The cooled filtered alcohol was then compared with the untreated alcohol for refractive index in an immersion refractometer at 17.5° C. The original No. 30 alcohol showed a refractive index of 90.2° Zeiss; the sample boiled for 45 minutes with anhydrous sodium sulphate showed a refractive index of 90.4° Zeiss. This difference, amounting to a difference in refractive index of only 0.00007, is equivalent to a change in concentration of the alcohol of less than 0.25%. Part, even, of this small change would be due to the trace (9 milligrams per 100 cc.) of sulphate held in solution by the alcohol.

Nothing is mentioned in the method about the temperature at which the titration should be made; and in our opinion titrations for free alkali should be on the alcoholic solution, heated practically to boiling, as is done in neutralizing the alcohol prior to use.

Modification (B): This method is scarcely any improvement over Modification (A). In decanting the solution some of the filler, especially if flocculent, is liable to be transferred and cause the same uncertainties in the titration. Since the alcoholic solution is not by any means anhydrous there is no point in using *absolute* alcohol, as specified for rinsing purposes.

In our opinion Modifications (A) and (B), while satisfactory perhaps for unfilled pure soaps, are inherently inaccurate and useless on highly filled soaps and do not merit consideration."

R. B. Trusler: "On samples No. 2 and No. 3, endpoint very indefinite using Modifications (A) and (B). Summarizing, Modification (A) is not at all useful and Modification (B) can be used under some circumstances which would have to be left to the operator's own judgment."

The proposed modifications using calcined Glauber salts for the purpose of dehydrating the alcoholic solution and thus inhibiting hydrolysis are essentially those recommended by Dr. J. Davidson (Melliand Textile Monthly, January and February, 1935). As a matter of record the committee was instructed on these proposed methods as follows:

Modification (A)

Weigh 3 to 5 g. of soap in a 300 cc. Erlemeyer flask and dissolve in about 150 cc. of boiled neutralized 95% ethyl alcohol (Formula No. 30) on a steam bath using a reflux air condenser. Remove from steam bath and when refluxing ceases, add 4 to 6 g. calcined Glauber salt (chemically pure), adding the Glauber salt slowly in small portions. Then titrate with N/10 alcoholic hydrochloric acid using phenolphthelein as indicator.

Modification (B)

Use exactly the same procedure given above under (A) up to the titration. At this point pour off the clear, alcoholic soap solution into a 250 cc. beaker, wash the remaining Glauber salt three times with small portions of neutral absolute alcohol (Formula No. 30), add the washings to the soap solution. Titrate the combined alcoholic solution with N/10 alcoholic hydrochloric acid using phenolphthelein as indicator.

NOTE: Owing to the volatility of the standard N/10 alcoholic hydrochloride, special precaution must be taken to restandardize frequently.

The results reported under the column headed "Official A.O.C.S. Method" were determined by the present A.O.C.S. procedure which for record purposes is as follows:

FREE ALKALI OR FREE ACID

Digest hot a 2 to 10 g. (±0.01 g.) sample with 200 cc. of freshly boiled ethyl alcohol neutral to phenolphthelein (94% or higher). Filter through a counterpoised filter paper neutral to phenolphthelein, or a weighed Gooch crucible with suction, protecting the solution during the operation from carbon dioxide and other acid fumes. Wash the residue on the paper, or in the crucible, with hot neutral alcohol until free from soap. Titrate the filtrate, using phenolphthelein as indicator, with standard acid or alkali solution, and calculate the alkalinity to sodium hydroxide (or potassium hydroxide) or acidity to oleic acid. (Oil & Soap, May, 1934, pp 90-95.)

CONCLUSIONS AND RECOMMENDATIONS

1. In general, results by the official method are more consistent and are appreciably lower than by either of the proposed new modifications.

2. Most collaborators reported difficulty with endpoints by the two new methods, especially with the soaps containing alkaline salts.

3. From a study of the tabulated results, it appears obvious that although the free caustic alkali as determined by the official A.O.C.S. method may not represent the absolute value, nevertheless reasonably consistent results have been obtained by the ten collaborators.

The consensus of opinion of the committee is to the effect that the present official method, while leaving much to be desired, is still to be preferred over either of the proposed modifications, and consequently, the committee recommends that no change be made in the present method, at least until further studies have determined otherwise.

VOLATILE HYDROCARBONS
(P. & G. Method)

The P. and G. method was suggested by C. P. Long. A description of this method will be found in a separate paper entitled "The Determination of Volatile Hydrocarbons in Soaps," found elsewhere in this issue.

CONCLUSIONS AND RECOMMENDATIONS

It is quite obvious from the data presented that the P. and G. method gives by far the greater recovery of naphtha, the averages showing from 97 to 98% yields with known naphtha contents ranging from 1 to 5%. Most members reported little or no difficulty with the method and further stated that they prefer it over the method now in use. The committee gives its approval to the proposed method and recommends same for tentative adoption

NAPHTHA DETERMINATIONS

	Present A.O.C.S. Method Percent Recovery			P. and G. Method Percent Recovery		
	1% added	3% added	5% added	1% added	3% added	5% added
M. L. Sheely*	70.0%	85.7%	82.0%	102.0%	93.7%	96.0%
J. E. Doherty**	79.0	82.0	78.8	98.0	98.0	98.0
C. P. Long**	52.0	53.6	57.7	100.0	98.7	97.6
E. R. Luckow	93.7	91.6	93.8	96.0	98.7	94.6
H. C. Bennett	....	88.3	....	95.6	97.7	99.3
R. C. Newton	96.0	92.0	96.0	98.0	100.0	97.0
High	96.0	92.0	96.0	102.0	100.0	99.3
Low	52.0	53.6	57.7	95.6	93.7	94.6
Average	78.1	82.2	81.7	98.3	97.8	97.1

*Blank determinations by A.O.C.S. method showed 0.05 cc. and 0.05 cc., by P. and G. method, 0.05 and 0.10 cc.; results not corrected for blanks.

**Blank determinations showed none found.

The methods used in the naphtha determinations were:
1. Present tentative A.O.C.S. method (Oil and Soap, May, 1934).
2. Procter and Gamble method (unpublished).

superseding the present tentative method. The method includes a sketch of the apparatus used.

SCREEN DETERMINATIONS

The methods outlined to the committee for study were as follows:

Method A

Bureau of Standards proposed specification for "Soap, Toilet, Powdered, for use in Dispensers," dated November 13, 1934. The sieves used in these tests shall conform to Federal Specification RR-S-366 for "Sieves; Standard, Testing." Section 1-3.

"Transfer 100 g. (±0.1 g.) of the well-mixed sample, without previous drying, to a dry No. 12 sieve and sift, tapping the sieve frame from time to time and catching all of the material passing through the No. 12 on a dry No. 40* sieve. The sifting on the No. 12 sieve is continued until the weight of the residue retained on the No. 12 sieve is not reduced by more than 0.1 g. on further sifting for one minute, tapping the sieve frame as before. Calculate the final weight of residue to percentage retained on the No. 12 sieve. Sift the material on the No. 40 sieve, tapping the sieve frame from time to time and catching all of the material passing through the No. 40 sieve on a dry No. 100 sieve. The sifting on the No. 40 sieve is continued until the weight of the residue retained on the No. 40 sieve is not reduced by more than 0.1 g. on further sifting for one minute, tapping the frame as before. Add the final weight of the residue retained on the No. 12 sieve to the final weight of the residue retained on the No. 40 sieve and calculate the sum to percentage of residue retained on the No. 40 sieve. Sift the material on the No. 100 sieve, tapping the sieve from time to time, until the weight of the residue retained on the No. 100 sieve is not reduced by more than 0.1 g. on further sifting for one minute, tapping the frame as before. Add the final weight of the residue retained on the No. 40 sieve (sum of weight retained on No. 12 and No. 40 sieves) to the final weight of the residue retained on the No. 100 sieve and calculate the sum to percentage of residue retained on the No. 100 sieve."

SCREEN DETERMINATIONS

		On U. S. Standard Sieve No. 12	On U. S. Standard Sieve No. 40	On U. S. Standard Sieve No. 100
M. L. Sheely	Method A	0.2%	48.6%	95.0%
	Method B	0.3	49.4	96.1
	Method C	0.3	54.0	97.7
J. E. Doherty	Method A	0.6	54.2	93.4
	Method B	0.5	56.4	97.0
	Method C	0.4	56.9	97.0
C. P. Long*	Method A	0.2	....	97.4
	Method B	0.2	....	97.2
	Method C	0.2	52.7	96.6
E. R. Luckow	Method A	0.3	52.9	95.5
	Method B	0.3	51.8	96.0
	Method C	...	....	....
H. C. Bennett	Method A	0.7	49.1	94.5
	Method B	0.4	47.3	94.5
	Method C	...	....	....
W. A. Peterson**	Method A	0.3	59.9	96.3
	Method B	0.3	61.5	97.2
	Method C	0.4	60.8	96.9
R. C. Newton	Method A	1.3	57.5	93.0
	Method B	1.3	59.1	95.8
	Method C	2.9	59.9	95.4
High	Method A	1.3	59.9	97.4
	Method B	1.3	61.5	97.2
	Method C	2.9	60.8	97.7
Low	Method A	0.2	48.6	93.0
	Method B	0.2	47.3	94.5
	Method C	0.2	52.7	95.4
Average	Method A	0.5	53.7	95.0
	Method B	0.5	54.3	96.3
	Method C	0.8	56.9	96.7

*Used No. 45 sieve in Method A and B, therefore, results omitted on this screen; on Ro-Tap Method used No. 40 screen as called for, but only 50 gram sample instead of eight ounces.

**Used 200 gram sample instead of eight ounces as called for.

Method B

Screens Used: U. S. Standard, as given in Federal Specifications RR-S-366, "Sieves, Standard, Testing"—8 in. screens being employed.

Procedure: Nest the No. 12, No. 40 and No. 100 sieves (U. S. Standard or corresponding Tyler sieves) making sure that they are dry, and transfer 100 g. (±0.1 g.) of the well-mixed sample, without previous drying, to the top sieve, (No. 12). Shake the sieves simultaneously, occasionally tapping the edge of the bottom sieve on a large rubber stopper or a flat, thick piece of rubber. When the portion of soap passing through the bottom sieve appears to be negligible (this can be well judged by sifting into a large, dark colored pan), remove the top sieve (No. 12) and shake this sieve separately over a clean, dark pan, to be certain that no more of the residue will pass through. Place any material, passing through the No. 12 sieve, on the No. 40 sieve, using a small camel's hair brush to remove the material from the catch-pan. Follow the same procedure of sifting for the No. 40 and No. 100 sieves as used for the No. 12 sieve.

Calculations:

1. Calculate the weight of the residue on the No. 12 sieve to percentage retained.
2. Add the weight of the residue retained on the No. 12 sieve to the weight of the residue retained on the No. 40 sieve and calculate the sum to percentage retained on the No. 40 sieve.
3. Add the weight of the residues retained on the No. 12 and No. 40 sieves to the weight retained on the No. 100 sieve and calculate the sum to percentage retained on the No. 100 sieve.

Method C (Ro-Tap Method)

Screens Used: "U. S. Standard, as given in Federal Specifications RR-S-366 — "Sieves, Standard, Testing"—8 in. screens being employed.

Procedure: Nest the No. 12, No. 40 and No. 100 sieves, (U. S. Standard or corresponding Tyler Sieves) making sure that they are dry, and transfer eight ounces of the well-mixed sample, without previous drying, to the top sieve, No. 12. Place the nest of sieves in the Ro-Tap machine and run for ten minutes. Carefully weigh the portion held on the No. 12, No. 40 and No. 100 sieves; also, the portion passing through the No. 100 sieves.

Calculations:

1. Calculate the weight of the residue on the No. 12 sieve to percentage retained.
2. Add the weight of the residue retained on the No. 12 sieve to the weight of the residue on the No. 40 sieve and calcu-

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*The Bureau of Standards method calls for a No. 45 sieve. However, in order to be consistent with Method B and also to conform to general practice in screen tests, we have changed this sieve to No. 40.

late the sum to percentage retained on the No. 40 sieve.

3. Add the weight of the residue retained on the No. 12 and No. 40 sieves to the weight retained on the No. 100 sieve and calculate the sum to percentage of residue retained on the No. 100 sieve.

CONCLUSIONS AND RECOMMENDATIONS

Considering the difficulties of sampling and the friable characteristics in general of all soap powder products, it is believed that the screen tests as reported are in fairly good agreement. Most collaborators seemed to favor method B, or as an alternative method, the Ro-Tap procedure. Inasmuch as the present official methods do not include a method for screen tests, it is felt desirable to recommend B as a tentative hand screening method and method C as an alternative method for use where a large number of samples are to be examined.

GENERAL RECOMMENDATIONS

The present set of methods of soap analysis has been tentative for a period of two years. It is now recommended that all methods, with the exception of the screen and naphtha determinations above recommended for tentative adoption, be made official methods of the Society.

DETERMINATION OF VOLATILE HYDROCARBONS IN SOAPS

A CONTRIBUTION FROM THE LABORATORIES OF PROCTER AND GAMBLE

THE method for determining volatile hydrocarbons in soaps which is given in detail below is one that has been in use in the laboratories of Procter and Gamble for the last 15 years. In its development a considerable number of men have participated, so it cannot be credited to any one or two chemists, but can only be designated as a company method.

The method is not only applicable to volatile hydrocarbons which are lighter than water, but can be applied with simple modifications to any constituent in soaps and other materials, such as paints, that is volatile with steam, immiscible with water, and liquid at temperatures of condensing water. The volatile constituent may be heavier than water and collected in a measuring tube of the Bidwell Stirling type.

Method for Volatile Hydrocarbons

(Developed in the Laboratories of the Procter & Gamble Co.)

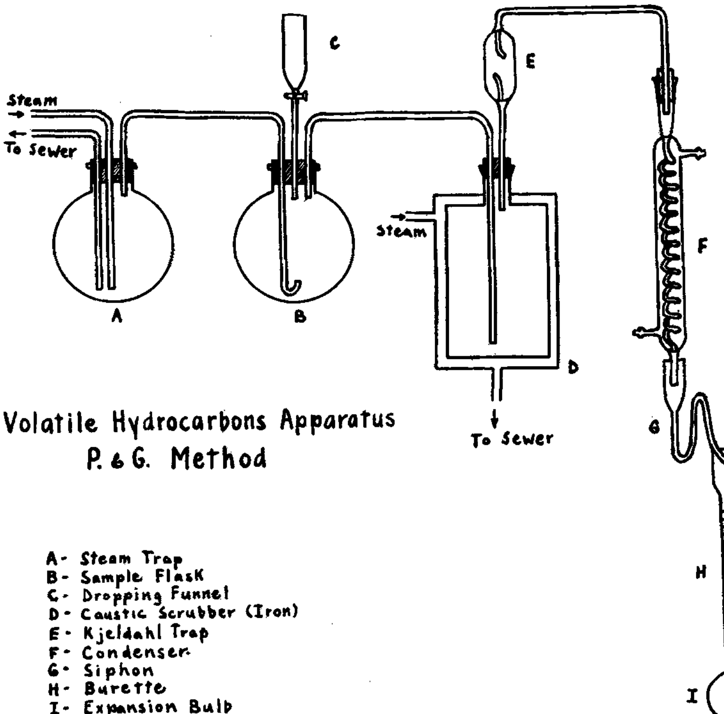
This method requires a source of dry, oil-free steam which is passed through the sample treated with acid, sufficient to liberate the fatty acids from the soap. The steam is next passed through strong caustic solution to scrub out any volatile fatty acids while the volatile hydrocarbons are condensed with the steam in a suitable arrangement which allows the excess water to flow away leaving the volatile hydrocarbon in the measuring burette. The method may be applied to samples containing substances immiscible with water and volatile with steam. For solvents heavier than water a Bidwell Stirling tube should be used.

Apparatus

The apparatus and its arrangement are shown in the sketch. The following are the important items, lettered to correspond to the lettering of the sketch:

Steam Trap, A, a litre round bottom ring neck flask equipped with a siphon tube to the drain from the bottom of the flask and provided with a means of regulating the steam flow from the flask.

Evolution or sample flask, B, a litre round bottom ring neck flask. In case large samples are desirable the size of this flask may be increased.



Volatile Hydrocarbons Apparatus
P. & G. Method

A- Steam Trap
B- Sample Flask
C- Dropping Funnel
D- Caustic Scrubber (Iron)
E- Kjeldahl Trap
F- Condenser
G- Siphon
H- Burette
I- Expansion Bulb
J- Automatic Overflow

Caustic scrubber flask, D, a steam jacketed metal flask is preferred, but a liter Florence flask provided with a steam coil of ⅛-in. copper tubing around the upper half may be used. If the glass flask is used it should be provided with a safety bucket below it and should be renewed frequently since the strong caustic dissolves the glass rather rapidly. This flask should be connected to the condenser by a Kjeldahl connecting tube, E, or similar safety device.

The inlet tubes for the steam into