Does the American fat consumption increase and absorb this additional lard? No. This additional consumption replaces lard substitutes or shortenings, which are made principally from cottonseed oil.

What will happen to cottonseed oil? It will go to the soap kettle, unless those interested in the fat and oil industry of America develop new outlets; the most promising one at the present time being the Margarine Industry. If it is forced to the soap kettle, it means a lower value for the southern farmer, and will replace imported oils; such as cocoanut, palm, and palm kernel.

What will happen to these imported oils? They will be forced upon the world market to compete with whale oil and other vegetable oils that enter the edible channels as described at the beginning. There you have the completed circle.

From the information presented, the balance of 1935 should be one of restricted to somewhat decreased production of edible fats and oils. When one or two complete new crops have been harvested, an entirely different situation may exist.

In conclusion—the factors influencing the world oil and fat situation in their order of importance are as follows:

1. The consumers' ability to buy.
2. Supply of raw materials.
3. Tariffs and quotas.
4. Nationalistic policies.

THE DETERMINATION OF SOAP IN REFINED OILS*

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VARIOUS laboratories have developed methods of soap determination in the refined oils coming under their inspection. However, there is no standard method of conducting the test, and, like any other non-standard operation it wouldn't be surprising to find that the results of analysis obtained by the different analysts would not agree very closely.

The quantitative test for small percentages of soap which is being presented in this paper appeals to me as being more reliable than some of the other methods. It has its apparent weaknesses and there are one or two points that have been called to my attention wherein inaccuracies might be introduced. Perhaps by bringing the details of the test to you so that it may receive the benefits of your criticisms and suggestions it may become a tool increasing the range of our control over our charge, the vegetable oils.

In the refining process, wherein there is a reaction of the free fatty acids of the oil, and the albuminoid and proteins with caustic soda, the soap formed by this reaction is separated from the oil by the differences in their specific gravities either by the batch process or continuously by centrifugal separation. By either method the efficiency of the process is measured by the sharpness of the separation of the soap or foots from the oil, and likewise by the freedom of the foots of entrained oil. In the continuous process, the conditions may be varied to such a degree as to give an oil free of measurable amounts of soap, but in carrying the separation so far in this direction, oil is lost in the foots. Going the other direction the foots can be discharged free from oil, but in so doing more soap is discharged into the oil than the refiner will tolerate. The economics of good refining specify the minimum of oil in the foots with also the minimum of soap in the oil.

Just what limits of impurities as soap are allowed in the oil is partially dependent upon the flow sheet of operations in the individual refineries. When the refining process is followed by a washing operation the soap content of the refined oil need not be of grave concern unless it throws too great a burden upon the washing equipment. The refiner who stores his neutralized oil without further treatment than the initial removal of foots must concern himself with the most thorough separation possible, with good economics, in order that his stored oils will not be so polluted with foots and moisture as to cause the oils to deteriorate, due to the action of the moisture and the fermentation of the foots. It is the determination of the small percentages of foots about which we are now most concerned.

We are familiar with the floc which appears in soapy oil when a beaker of it is placed on a steam bath for 24 to 48 hours, and it is possible to say that one sample has more soap than another when the difference is rather great, but it is impossible to give any estimate quantitatively of the soap simply by such inspection.

Soap determinations have been made by ashing a quantity of the oil and weighing the ash. Assuming all the alkali has been converted to the carbonate and that nothing remains of the ash but this carbonate then quite easily may the corresponding soap weight be obtained. Recognizing the error of assuming the ash to be only alkali carbonate, the determination of soap is made more accurate by titrating the ash with a weak acid, thereby determining its alkalinity, making an assumption that this alkalinity is all in the form of the carbonate. Quite obviously, any free alkali which may be in the oil examined will be determined along with that which is combined with the fatty acids.

Another method of soap determination which has been practiced consists of extracting the soap from an ethereal solution of the oil with

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*A paper presented at 26th annual meeting of American Oil Chemists' Society, Memphis, May 23-24, 1935.

alcohol, decomposing the soap in the alcohol with acid, then extracting the liberated fatty acids with ether. After evaporating the ether the fatty acids are weighed and calculated as soap.

Rather than ash the large quantity of oil to obtain the alkali carbonate, at least one laboratory extracts the soap with alcohol, evaporates the alcoholic solution and ashes the residue. The alkalinity of this residue is determined by titration. Its soap equivalent is then calculated as in the first method.

The only published material the author found on the determination of soaps in oil was an article by Davidsohn entitled "The Determination of Alkali and Calcium Soaps in Fats."[1]

Following his procedure, the free fatty acid of the fat being examined is first determined in the usual manner. Another portion of the fat is refluxed for thirty minutes with 50 ml. of ether and 2 ml. of concentrated hydrochloric acid. The refluxed sample is washed with water until free of mineral acid. The ether is then evaporated and the oil taken up in 96 per cent neutralized alcohol. The difference between the original free fatty acid content and the free acids in the treated portion is taken as the acids liberated by the decomposition of the soap. The amount and kind of soap is calculated after a qualitative test, to determine the base. The most obvious criticism of this test is the accuracy which must attend the determination of the free fatty acids. Failure to remove thoroughly the mineral acid would destroy the determination completely. In the few determinations which have been made comparing Davidsohn's method with that proposed by the author the agreement has been good. In one case there was a difference of only 2.8 per cent in the amount of soap found. In another case in which just a trifle less care was used in washing the mineral acid from the refluxed material the difference was 72 per cent in the amount of soap found, as shown in the data tabulated in Table IV. The test has much to recommend it in its rapidity of manipulation.

The basis for the development of the proposed test for soap in vegetable oils is that small amounts of soap will be decomposed by large excesses of hydrochloric acid forming the corresponding chloride, which, separated from the oil with the excess acid may be recovered by removing the free acid. The remaining chloride may then be measured by titration in solution, with a standard silver nitrate solution using potassium chromate as the indicator. From the amount of chloride found the per cent of soap in the oil can be easily calculated.

PROCEDURE:

Into a large separator funnel weigh a quantity of the oil to be analyzed. 300 gms. of oil in a liter funnel have been found to work very nicely. This gives enough soap even when present in small amounts to give an appreciable titration with silver nitrate. Add in 50 ml. portions 200 ml. of hot dilute, 1:1 hydrochloric acid, using of course a C. P. acid. Shake the oil and acid together violently. Allow the two liquids to separate, and draw off the acid solution into a clean beaker. Repeat the addition and shaking until the 200 mls. of acid are used. Combine the four acid portions in a 250 ml. beaker and evaporate to dryness, heating carefully to prevent spattering. Take up the residue in distilled water and evaporate again to dryness. A second evaporation to dryness from distilled water will usually remove all the free acid, and a third evaporation will insure freeness from any uncombined chlorine which would be titrated with the silver nitrate.

Take up the final residue in 50 ml. of distilled water and heat nearly to boiling, add 1 ml. 10 per cent potassium chromate solution and titrate with silver nitrate solution to a brick red color. A silver nitrate solution standardized to that 1 ml. is equivalent to 0.01 gm. sodium chloride make a convenient working solution. Twenty nine and sixty-two thousandths grams of silver nitrate made up to 1 liter of solution with distilled water will titrate very closely to 1 ml. for each 0.01 gm. of salt.

From the volume of silver nitrate used in titrating, the weight of soap in the oil is found by using the following factors:

.05195 × ml. $\mathrm{A_g\,20_3}$ used — gms. sodium oleate.

.03794 × ml. $\mathrm{A_g 20_3}$ used — gms. sodium laureate.

.0475 × ml. $\mathrm{A_g 20_3}$ used — gms. sodium palmitate.

OPTIONED PROCEDURE:

The following method of analysis has checked nicely with the above procedure in the cases in which I have compared them.

Ignite carefully in a clean platinum crucible a quantity of the oil. After the ignition is completed place the crucible in a clean beaker and extract the ash with dilute, 1.3 hydrochloric acid. Carefully wash the crucible with a stream of distilled water, catching the wash water in the beaker with the acid. Evaporate to dryness, take up the residue in distilled water, repeating the evaporations as in the first method. The procedure from this point is identical with that given above.

The criticism of this optional method is that in treating oils in which very small percents of soap are present a large amount of oil must be burned to yield a quantity of ash which when converted to the chlorides will give an appreciable titration with silver nitrate. The method is however much more rapid than the first procedure.

That the method of determination might be tried against samples of oil having known percentages of soap, thereby testing its reliability, a quantity of refined cottonseed oil was washed repeatedly with distilled water, dried and stored for use in making up samples of known soap content. To this oil was added various amounts of potassium soap made by saponifying cottonseed oil with C. P. potassium hydroxide.

The data of these tests are tabulated for comparison:

TABLE I

Analyses of Oils of Known Soap Content

Test No.	% soap in oil	% soap found	Difference
1.........	0.1	0.096	0.004
2.........	0.075	0.0726	0.0024
3.........	0.05	0.044	0.006
4.........	0.025	0.0236	0.0014
Average			0.0034

A sample of refined cottonseed oil analyzed by washing with the strong acid, method one, and by the optional method of ashing showed the same amount of soap, as shown in Table II.

TABLE II

Comparison of Methods 1 and 2

Material tested	% soap found, Method No. 1	% soap found, Optional method
Refined cotton oil..	0.1032%	0.1032%

In the optional method 60.5 gms. of the oil were ashed in a platinum crucible.

It was suggested that a weaker acid than that called for in the description be used. To determine the advisability of using a weaker acid a quantity of the oil which tested above showing 0.1032 per cent soap

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[1] Sefin-Sieder-Ztg. 60, 219 (1933) C. C. 27, 3098 (1933).

was analyzed using a 1:3 dilution of hydrochloric acid. The oil was repeatedly washed with 100 ml. of hot 1:3 hydrochloric acid and the amount of soap decomposed by each wash was determined, as shown in Table III.

TABLE III

Results obtained using 1:3 HCl

Soap found using 1:1 HCl	.1032%
Soap found using 1st wash 1:3 HCl	.0546%
Soap found using 2nd wash 1:3 HCl	.0251%
Soap found using 3rd wash 1:3 HCl	.0191%
	.0788%

Even with three washes of the weaker acid the amount of soap decomposed was not equal to that found using the stronger acid; also the separation of the aqueous phase from the oil was slower than with the more concentrated acid.

The most apparent defects of the test are; the time consumed in making a determination. Considerable time is required to extract with the acid, and carry out the evaporations. The second criticism is that any free alkali in the oil will be measured as soap unless the free alkali be determined separately This defect is of course common to any method of ashing or extracting and determining the alkalinity of the ash. In testing oils which have been given a brine wash, any brine remaining will also be included as soap.

In Table IV are tabulated the data showing the results obtained by the proposed method and by the method as given by Davidsohn. The second determination by Davidsohn's procedure illustrates the effect of insufficient washing to remove the mineral acid.

TABLE IV

Comparison of Davidsohn and Durst Method of Soap Determination

Material: Refined unwashed cottonseed oil	% soap found
Durst method	0.0709%
Davidsohn method	0.0689%
Davidsohn method*	0.119%

*Improperly washed to remove mineral acid.

CONCLUSIONS:

1. A review of methods of soap determination is given, outlining the procedures followed for the analysis of soap in refined oils.

2. A new test has been described for the determination of soap in refined oils. The test depends upon the formation of the alkali chloride by the decomposition of the soap with hydrochloric acid. The chloride being determined by titration with a standard silver nitrate solution.

3. An optional method is given substituting for the acid washing of the oil, ashing in a platinum crucible followed by conversion to the chloride and titration with silver nitrate.

4. Factors are given for converting the silver nitrate titration into its equivalent of soap.

5. Data are given showing the analyses of prepared samples of known composition. The average deviation of the analyses from the actual soap content being 0.0034%.

6. The proposed method is compared with the published method of Davidsohn.

Analysis of removal of soap by standard washing, using 1:1 HCl.
Material, Shoeflis refined Soya Bean Oil, unwashed.

No. 1.	Soap found, 4 washes combined			0.05368%
No. 2.	Soap found, 1st wash	0.03636%	53.86%	
	2nd wash	0.01730	25.62	
	3rd wash	0.00866	12.83	
	4th wash	0.00519	7.69	
		0.06751%	100.00%	0.06751%
	Difference between two determinations			0.01383%

REPORT OF CRUDE MILL OPERATIONS COMMITTEE

PRESENTED AT 26TH ANNUAL MEETING, AMERICAN OIL CHEMISTS' SOCIETY, MAY 23-24, 1935

THE activity of the Committee on Crude Mill Operations this season has been of the same general character as in recent years; that is to say, rather more on individual than on cooperative lines. At the beginning of the season the chairman suggested to the membership certain problems which it appeared might be of interest to study. Some of these were relatively unimportant; others were in the nature of "long-shots." The members were invited to suggest any others and were asked to make some contribution relating to oil milling, even if not of outstanding significance.

The result has been the assemblage of four papers contributed by three members, as follows:

"A Study of the Possible Catalytic Effect of Some Metals and Alloys on the Changes Occurring in Crude Cottonseed Oil During Storage," by F. R. Robertson and J. C. Campbell, Houston Laboratories, Houston, Texas. (Published in the October issue of OIL & SOAP.)

"Effect of Different Methods of Disintegration of Cottonseed Meats on Some Properties of the Crude Oil," by J. M. Newbold, Eastern Cotton Oil Company, Hertford. N. C. (Published in August issue OIL & SOAP.)

"A Modified Procedure for Determining the Amount of Lint on Cottonseed, the Development of a More Rapid and More Accurate Technique," by Egbert Freyer, South Texas Cotton Oil Company, Houston, Texas. (Published in September issue OIL & SOAP.)

"A Rapid Visual Method for Estimating the Amount of Lint on Cottonseed, the Relation of Its Moisture and Lint Content to Some Properties of the Seed," by Egbert Freyer, South Texas Cotton Oil Company, Houston, Texas. (Published in November issue.)

Respectfully submitted,
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