

# A Conductivity Method for the Determination of Soap in Refined Vegetable Oil

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ONE OF THE IMPURITIES found in refined vegetable oil is soap. The alkalis in refining reagents react with the fatty acids present in the crude oil to produce sodium soaps. The soap concentration in the oil will vary throughout the refining process and is dependent upon the crude stock, the stage of the refining, the efficiency of the soap separation, and the washing of the refined oil. These soaps are detrimental to the final product and must not be present in excess of the minimum requirements as set forth by the individual manufacturer of vegetable oil products. It is essential therefore that the analytical chemist have access to a method for determining soap in vegetable oil which is reliable, reproducible, and practicable.

Several methods are mentioned in the literature; most of them are basically extractions of soap with hydrochloric acid, followed by a quantitative analysis of the sodium ion by various means. Probably the latest to be developed is the conductivity method, first proposed by H. D. Royce, which consists of a water extraction and analysis for sodium by measuring the conductance of the water extract. We shall discuss this method in detail after a review of other analytical methods.

According to Rodeghier (1) and Bailey (2), the analysis of refined oil for soap in the lower concentrations is uncertain. Richard Durst (3) proposed an extraction with 200 ml. of hot, dilute, hydrochloric acid, ashing and titration with silver nitrate, using 10% potassium chromate as an indicator. The author points out that the considerable time consumed in making a determination is one of the defects of the method. Spielman (4), in a report of the American Oil Chemists' Society committee on the determination of soap in oil, obtained fair accuracy by shaking 50 g. of oil with 50 ml. of hot water for two minutes and with 5 ml. of 0.5N hydrochloric acid for five minutes, washing free of hydrochloric acid with hot water, filtering, and determining the free fatty acid formed by titration with .02N sodium hydroxide. A blank on untreated oil gives a correction for the free fatty acid present. Another article (5) by the same committee recommends as tentative an alcohol-extraction process in which 100 g. of oil is extracted with five 50-ml. portions of hot alcohol. The combined extracts are evaporated and ignited; the residue is dissolved in 50 ml. of hot water and titrated with .02N hydrochloric acid to a methyl orange end-point. They noted that great care was required to obtain concordant results.

E. H. Harvey (6) and a committee of the A.O.C.S. on the determination of soap in oil review five methods: FFA method of Spielman and the A.O.C.S. committee; Durst ashing method; Durst HCl-extraction method in which a hot HCl extract of oil is evaporated and analyzed for sodium; a modification of 3 by Stillman; and ethyl alcohol extraction proposed by Spielman and A.O.C.S. committee.

From the results of collaborative studies the committee made the following observations: the first is rejected as unreliable, the second is unsatisfactorily

troublesome, three and four, which are less laborious, give the most satisfactory results and are recommended for further study with the fifth, in which lower results were obtained.

Kaminskaya (7) suggests dissolving the sample in a mixture of ethyl ether and ethyl alcohol in the ratio of 5:1 up to 8:1, extracting with hydrochloric acid, filtering, and determining the soap by argentometric titration. The analysis requires 40–50 min. It was found that, in oils containing 64 to 1,540 p.p.m. of soap, the largest difference between parallel determinations was 80 p.p.m. Schuette (8) and Hine, in making observations on the determination of soap in oil, note that recovery methods by two different procedures indicate the best method is based upon the assumption that the chloride formed when hydrochloric acid is added is an index of the quantity present. When the concentration of soap is 100 p.p.m. or less, the Durst method, as modified by Stillman, was found to be quantitative and requires one-half of the time consumed by the Durst or alcohol-extraction methods.

Highly purified cottonseed oil was impregnated with 50, 100, and 200 p.p.m. of sodium oleate. Blank determinations on the oil were as follows: Durst 9 p.p.m.; Durst-Stillman 12 p.p.m.; alcohol extraction 12 p.p.m. The results of all methods were low by 2–46 p.p.m. Harvey (9) again reports that the Durst-Stillman (6) method gave high results. It is of interest to note that Schuette and Hine (8) obtained low results by this same method. As a result, a modified method is proposed in which 125 g. of oil are shaken with 25 ml. of conc. hydrochloric acid. Then 100 ml. of hot water are added, shaken, allowed to settle, and cool. Next 100 ml. of the water-acid solution are evaporated to dryness and cooled, and 50 ml. of water are added and again evaporated. This is repeated a third time, after which the residue is taken up in 10 ml. of water and cooled to room temperature; 1 ml. of 10% potassium chromate is added and titrated with .01N silver nitrate. A blank determination is made. Crapple (10), in a report of the A.O.C.S. committee, shows that the modified Durst-Stillman method (9) was studied in two laboratories. The method was considered most satisfactory for accuracy and the time required. It usually gives high results at 25 p.p.m. or less. The end-point is only accurate to about 10 p.p.m., which would account for difficulty in the lower concentrations.

Boekenoogen's (11) method uses a 115-g. sample of the oil. It is vigorously shaken in a separatory funnel with 10 ml. of 0.05N ammonium hydroxide for 1 min., 25 ml. of concentrated hydrochloric acid are added and shaken for an additional minute. After standing for 15 min., 100 ml. of hot distilled water at 70°C. are added and thoroughly shaken. The mixture is allowed to settle for 1 hr., the water layer is drawn off into a quartz evaporating dish, a drop of concentrated sulfuric acid is added and evaporated to dryness. The residue is dried for a short time to drive off the ammonium salts, and the organic matter is

ashed in a muffle furnace. The dish is washed with a small amount of water, the solution is transferred to a small beaker and concentrated to approximately 1 ml. After cooling to 20°C., 10 ml. of Kahane's reagent are added. It is allowed to stand for 2 hrs., filtered through a tared asbestos-covered micro Buchner funnel and washed with 2 ml. of acetone. It is then dried for 10 min. at 105°C., cooled, and weighed. A reagent blank is also required.

$$\% \text{ Soap as sodium oleate} = \frac{\text{wt. p.p.t.} \times 0.2015 \times 100}{115}$$

Kahane's Reagent contains magnesium acetate, uranyl acetate, glacial acetic acid, and formula No. 30 alcohol. The precipitate formed in the reaction is a sodium magnesium uranyl acetate complex  $(\text{UO}_2)_3 \text{Mg Na} (\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\frac{1}{2} \text{H}_2\text{O}$ .

In work on the Modified Durst method it was found that action of the acid on glass introduced error. Blanks run in Pyrex and Jena beakers were high but decreased in quartz. Oil of 100 p.p.m. soap with the modified Durst method and a quartz crucible gave results of 50 to 90 p.p.m. Using the Durst-Stillman method on the same oil, the results were  $40 \pm 10$  p.p.m. It was concluded that hydrochloric acid failed to convert all the soap to sodium chloride. Further shaking did not improve the results. These methods have been modified by Boekennoogen so that the oil is first emulsified with ammonium hydroxide and then shaken with hydrochloric acid and warm water. Results of this modification are given in Table I.

TABLE I  
Results of Boekennoogen's Modification

Known Soap	Determined Soap
100 p.p.m.	$100 \pm 20$
50 p.p.m.	$40 \pm 10$
10 p.p.m.	10
0 p.p.m.	0

In concentration of 200 p.p.m., the deviation was only 20 p.p.m.

Another report of the A.O.C.S. committee by Crapple (12) stated that it was difficult to prepare a stable sample of oil containing soap. Upon standing, the soap flocculates out and thus makes it difficult to obtain a representative sample.

R. G. Zehnpfennig suggested a colorimetric determination of the chloride ion as found in the Durst and Stillman-Durst methods. It was adapted from Snell (13) and involves shaking a chloride solution with silver chromate, then determining the chromate ion colorimetrically. A higher degree of accuracy is obtained than by the titration of chlorides with silver nitrate, using a chromate indicator. Desnuelle (14) investigated the reliability of the sodium ion methods for soap in oil by incorporating known quantities of sodium oleate in an oil and analyzing it. The method of Boekennoogen was found to give the best results. A proposed method consisted of shaking 5 to 10 g. of oil dissolved in petroleum ether with two 100-ml. portions of 4N sulfuric acid and measuring the increase in acidity. However it is not reliable for oils containing less than 1,000 p.p.m.

Jamieson (15) gives a method for soap which is a slight modification of the Durst method, using a hydrochloric acid extraction and titration with silver nitrate employing potassium chromate indicator.

One of the last articles on the subject to be found in the literature is by Newby (16). He points out three things which are significant. The determination of soap in oil is important as attested by the numerous articles discussing analytical methods. The analytical methods available are unreliable. Regardless of the reliability of the method, the refinery chemist is asked to make determinations of soap in refined oil.

Wolff (17) published a technique in which oil is dissolved in acetone containing 2% water. It is then titrated with 0.01N hydrochloric acid, using bromphenol blue as an indicator. The color change is blue to yellow and takes place in the acetone layer.

There are several methods, although not listed in the literature as such, that are used by various people throughout the vegetable oil industry. The first of these places 100 g. of oil in a liter flask, to which is added 50 ml. of alcohol neutral to bromphenol blue, 200 ml. of distilled water, and 2 ml. of bromphenol blue. This mixture is titrated with 0.1N sulfuric acid to a green end-point.

$$\% \text{ Soap as sodium oleate} = \text{ml. } 0.1\text{N H}_2\text{SO}_4 \times .0304$$

We have analyzed several samples in our laboratory by this method, but the end-point was not definite and hence difficult to reproduce. A modification of the above method is a potentiometric titration, in which 100 g. of oil and 50 ml. of 2B alcohol neutral to bromphenol blue were extracted with three 50-ml. portions of distilled  $\text{H}_2\text{O}$ . The combined extracts were titrated with 0.1N sulfuric acid, using a Beckman pH meter and magnetic stirring apparatus. The end-point is indicated by the largest change in pH per unit volume. The results obtained on several samples of cottonseed oil by this method failed to check with those obtained by the conductometric method, as described later.

A method employing a conductometric titration is also used. Depending on the expected soap concentration, a sample of 5 to 50 g. is extracted with five 25-ml. portions of a 1 to 1 isopropyl alcohol-distilled water solvent. An excess of .02N hydrochloric acid is added to the combined extracts, and the resistance of the solution is measured. Sodium hydroxide, 0.1N, is added in small increments; the resistance of the solution is measured after each addition. The end-point is determined graphically by plotting resistance *versus* milliliters of sodium hydroxide added. A blank determination is also made. The calculation is given in the following equation:

$$\text{P.P.M. sodium oleate} = \frac{(B-A) \times N \times 304 \times 1000}{\text{wt. of sample}}$$

when

B = ml. NaOH used titrating blank

A = ml. NaOH used titrating sample

N = normality of sodium hydroxide

304 = molecular weight of sodium oleate

One of the newer methods for determining soap in refined vegetable oil is the conductivity method. The apparatus consists of a tetra-ethyl lead extractor, conductivity bridge, and conductivity cell. The water used in the analysis should have a minimum resistance of 40,000 ohms at 30°C. Some 50 ml. of conductivity water are introduced into the tetra-ethyl lead extractor, followed by 100 g. of the sample and an additional 50 ml. of conductivity water. The mixture is refluxed for 4 min. and allowed to separate

2 min.; approximately 80 ml. of the water extract are drawn off into a 100-ml. beaker. The extract is cooled to 30°C., and the resistance is read by means of the conductivity bridge.

Standard curves have been prepared with known amounts of sodium oleate. The resistance of the unknown is easily found on these curves and the p.p.m. of soap as sodium oleate read directly. These curves were developed by measuring the resistance at 30°C. of numerous solutions of sodium oleate of known concentrations. The distilled water used to prepare these solutions had a resistance of 46,000 ohms. In order more accurately to cover the range of 0 to 5,000 p.p.m. of soap, these values were plotted as three separate graphs, as shown in Figures 1, 2, and 3. Be-

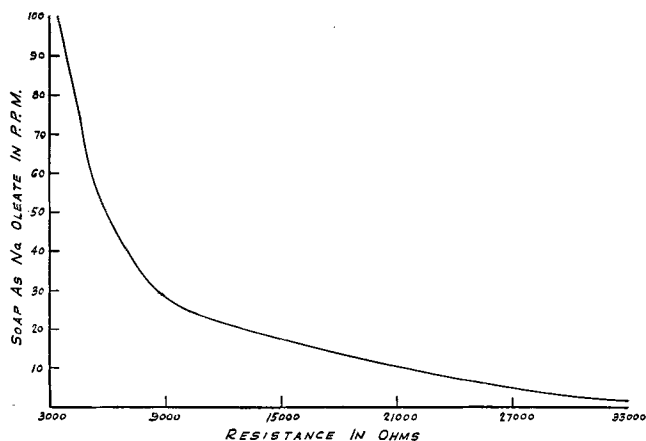


FIG. 1. Determination of soap in refined vegetable oil Standard 0-100 p.p.m.

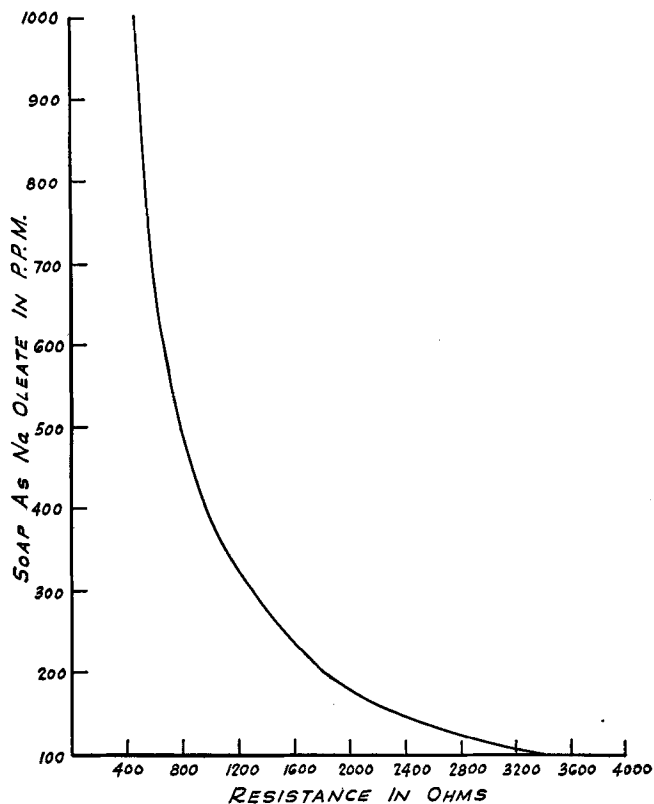


FIG. 2. Determination of soap in refined vegetable oil Standard 100-1,000 p.p.m.

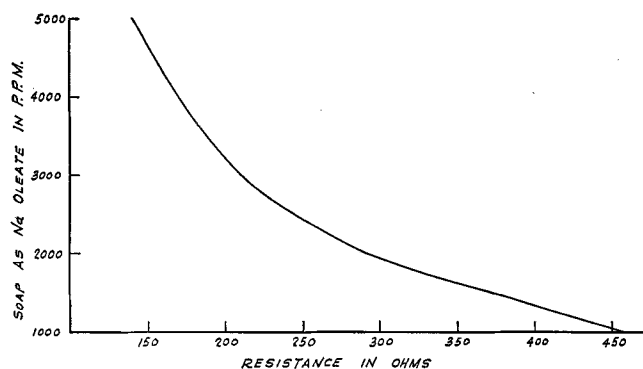


FIG. 3. Determination of soap in refined vegetable oil Standard 1,000-5,000 p.p.m.

fore each analysis the tetra-ethyl lead extractor is cleaned by boiling out with acetone and then with conductivity water. In the routine analysis of a large number of samples containing different amounts of soap, for example refined, re-refined, water-washed, and dried oil, the samples may be lined up in the order of increasing soap content and all the samples extracted without washing out the extractor between each one. This enables one operator to complete a large number of analyses in one day.

We have found that this conductivity method affords a simple, rapid means of determining soap in refined vegetable oil.

There are several variables in the conductivity method. Various modifications of the method are used in several laboratories throughout the industry which have produced discordant results. Unless the procedure is standardized through further research to a technique giving reproducible results which agree closely with the absolute values, there can be no comparison of the data obtained.

The first variable is refluxing time. A composite sample of soapy oil was prepared and analyzed for soap by varying the refluxing period from 4 to 25 min. The results are given in Table II.

TABLE II  
Effect of Time of Reflux on Values for Soap in Oil

Time refluxed (min.)	Resist	Soap in p.p.m.
4.....	820	475
8.....	560	716
10.....	420	1200
15.....	375	1475
20.....	410	1260
25.....	410	1260

It is obvious from the data given in Table II that the apparent values for soap in oil may be greatly increased if the mixture is refluxed for a longer period. Extraction equilibrium occurs around 10 min.

The second variable is agitation. It has been found that 120 volts will supply enough heat to produce good boiling of the oil-water mixture. However, in the range of 60 volts, the boiling is considerably less, and much lower values are obtained. They are listed in Table III.

The increase in soap determined at 120V over that at 60V represents a factor of 8.6, or nearly 900%.

The oil-water ratio is also a variable. The method as described employs a 1:1 ratio, but the same two samples were analyzed, using a 5:1 ratio. Table IV contains the data obtained on this phase of the work.

TABLE III  
Effect of Amount of Heat on Values for Soap in Oil

Volts	Soap in p.p.m.	
	No. 1	No. 2
120.....	29	33
100.....	23	25
80.....	11	13
60.....	3.4	3.8

TABLE IV  
Effect of Oil-H<sub>2</sub>O Ratio on Values for Soap in Oil

Sample	Oil-H <sub>2</sub> O ratio	Soap p.p.m.
1.....	1:1	50
1.....	5:1	29
2.....	1:1	51
2.....	5:1	33

The values obtained with a 5:1 ratio are approximately 60% of those found at a 1:1 ratio.

The fourth variable is the temperature at which the resistance of the water extract is measured. The original method measures resistance at 30°C. Three samples were measured at both 30°C. and 25°C.; the values are recorded in Table V.

TABLE V  
Effect of Water-Extract Temperature on Values for Soap in Oil

Sample	Oil-H <sub>2</sub> O ratio	Volts	Soap p.p.m.	
			30°C.	25°C.
1.....	1:1	120	50	48
2.....	1:1	120	51	45
3.....	1:1	120	74	61
1.....	5:1	60	3.4	2.8
2.....	5:1	60	3.8	3.6
1.....	5:1	120	29	27
2.....	5:1	120	33	29

Measurements at the two temperatures produced values which differed by 4-18% on the same sample; all other conditions remained constant.

Of all the variables mentioned, the amount of heat or voltage applied to reflux the oil-water mixture seems to have the greatest effect. The difference here is 880%. Of all the combinations which might be encountered by two laboratories using different variables, the greatest spread in values are condensed in Table VI.

TABLE VI

Oil-H <sub>2</sub> O ratio	Volts	Temp.	Soap p.p.m.
1:1.....	120	30°C.	50
5:1.....	60	25°C.	2.8

From these data of Table VI it is entirely possible that one laboratory could report 50 p.p.m. of soap while the other laboratory would find only 2.8 p.p.m. of soap on the very same oil. This creates an error of 1700%.

One other thing might be pointed out, which has been mentioned in the literature reviewed, that soap concentrations in vegetable oil are not stable and analyses on the same oil vary after the oil has stood for a day or more.

In summation, we have in the course of this paper observed several things regarding the determination of soap in refined vegetable oil. First of all, we have realized that soap in oil is a necessary and important analysis for the oil chemist. Secondly, there is a wide variation of analytical methods suggested, most of which are time-consuming and, to varying degrees, unreliable. Thirdly, a rapid, easy method has been described, and observations have been made on the variables of this method.

In view of these facts it seems imperative that the vegetable-oil industry have an official method for the determination of soap in refined vegetable oil. Therefore we would like to propose that the Conductivity Method for the Determination of Soap in Refined Vegetable Oil, as set forth in this article, be given further study by a committee of the American Oil Chemists' Society in order to ascertain a standardized form and the feasibility of its adoption as the official method of the Society.

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## The Chemistry of Lauric Acid-Diethanolamine Condensation Products

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THE CONDENSATION PRODUCTS of higher molecular weight carboxylic acids and diethanolamine have been of primary commercial interest as surface-active agents for the past quarter of a century. The most important class of alkanolamides are those obtained from the coconut fatty acids and, in recent years, from lauric acid. These products have been

incorporated into formulations which find their greatest use in the textile and cosmetic fields.

The reaction of a carboxylic acid with diethanolamine is not a simple process primarily because of the presence of three functional groups on the alkanolamine and the inter-related reactivity of these groups both in the presence and absence of the reacting carboxylic acid. The complexity of this reaction was recognized by the U. S. Patent Office in 1937

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