

# The Determination of Soap in Refined Vegetable Oil Using the Flame Photometer

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IN MODERN fatty-oil refining practice a water-washing step follows the initial or subsequent treatment of the crude oil with alkali solution, usually solutions of caustic soda or soda ash. The most common and obvious index of the effectiveness of the water washing is the soap content of the washed refined oil. The soap content of the oil is also a measure of the quality of the oil. A refined oil high in soap content is an oil of poor quality. Assuming an effective refining for the removal of free fatty acids, phosphatides, and other impurities, a water-washed refined oil low in soap content is an oil of good quality. Difficulties in subsequent processing, such as in hydrogenation, are often traceable directly to the high soap content in the washed refined oil. On the other hand, some refiners set standards for the soap content of the washed refined oil. The values vary considerably, downwards from about 50 p.p.m. of soap. A method that gives accurate values for soap in refined oil in this lower range would serve the refiner in an area in which the results should be very useful to him.

The importance of a knowledge of the soap content in refined vegetable oil is well recognized. Goff and Blachly (1) have recently reviewed the extensive literature in the field and have presented a critical evaluation of the published methods. They stress the general unreliability of most, if not all, of these methods and offer for further study a conductivity determination of their own. This method depends upon refluxing the refined oil with conductivity water, followed by the determination of the conductivity of the aqueous layer. Three empirical calibration charts are prepared, covering the ranges 0-100, 100-1000, and 1000-5000 p.p.m. soap and using standards prepared from sodium oleate. They found that the apparent values for soap in a given oil may be greatly increased if the mixture is refluxed for a longer period or if the rate of refluxing, as determined by the voltage applied to the heater, is changed. The oil-water ratio in the extraction and the temperature of the water during the measurement of the conductivity also seriously affected the results. Variations of 900 to 1700% were obtained by changes in the conditions. The extreme sensitivity of the method to these variables and its essentially empirical and indirect nature may limit its scope.

This paper describes a new method of determining soap in refined oil. The oil is extracted with hydrochloric acid, which is recognized as efficient in converting sodium soap to sodium chloride. The sodium is then determined directly in the acid extract by using the flame photometer. The Waring Blender is used in the acid extraction and subsequent water extraction. Petroleum ether is added to dilute the oil after acid treatment to hasten phase separation. The method is rapid, precise, and highly accurate. It is specific for sodium and hence sodium soap.

## Procedure

A blank and a series of standards are prepared by treating varying volumes of standard sodium hydrox-

ide solution each with 1 ml. of concentrated HCl and dilution to 50 ml. They are kept in polyethylene bottles and can be stored indefinitely. A few ml. of those standards in the range of the unknowns are run each working day in order to standardize the flame photometer. Data for a convenient series of standards are given in Table I. The calculated p.p.m. sodium soap (sodium oleate) apply only when the solutions are used in accordance with our procedure. The stock solutions are therefore labeled accordingly.

TABLE I

ml. 0.01 M NaOH (add 1 ml. HCl, dilute to 50 ml.)	p.p.m. Na oleate (100 g. oil, 50 ml. ext.)
0	Blank
0.5	15
1.0	30
2.0	60
4.0	120

The higher range can be prepared more conveniently from 0.1 M NaOH, using corresponding volumes.

## Method of Analysis

A 100-g. sample of refined oil is transferred to a Waring Blender. One ml. of concentrated HCl is pipetted in, and the mixture is blended for about 1 min. Next 50 ml. of petroleum ether are added and blended a minute; 50 ml. of water are added and blended again for 1 min. The mixture is transferred to a 250-ml. separatory funnel. After the phases separate (about one-half hour), the water layer is reserved for the photometric determination. About 10 ml. are required for duplicate determination so that there is no need to wait for complete separation.

The flame photometer should be turned on and adjusted at least one hour before readings are begun, and its stability should be verified. A few ml. of the water extract are aspirated in the flame, and the instrument reading is noted. (In this work the Process and Instruments Flame Photometer was used although any other adjusted to read the intensity of the sodium D lines would suffice.) A blank and two standards selected to bracket the unknown are then run. If a series of samples is to be analyzed, it would probably be more convenient to run all the standards. The unknown is calculated by simple linear interpolation. Because of instrument drift a new calibration is required each day, but this should require no more than about 15 min. A sample calculation is as follows:

$$\begin{array}{rcl} 150 \text{ p.p.m.} & \text{Standard} & 15.5 \\ 300 \text{ p.p.m.} & \text{Standard} & 30.0 \\ \text{Unknown} & & 25.5 \end{array}$$
$$\text{p.p.m.} = 150 + \frac{10.0}{14.5} \times 150 = 253 \text{ p.p.m.}$$

When several samples are to be run at a time, it is convenient to plot p.p.m. soap of the standards *vs.* galvanometer readings. The p.p.m. soap of a given sample is then read directly from the graph.

### Test Analyses

Standard oils were prepared, covering the range from 15–1200 p.p.m. soap calculated as sodium oleate by adding calculated quantities of sodium hydroxide solution (0.001, 0.01, or 0.1 M) to separate 100-g. samples of Wesson oil and blending in the Waring Blender. Fairly stable emulsions were thus obtained. The 100-g. treated sample was immediately analyzed, avoiding such sampling problems as settling and inhomogeneity. An additional series of test analyses were made on Wesson oil which had been treated with sufficient oleic acid to bring the FFA to 1%. This assured complete conversion of sodium hydroxide to sodium oleate.

Excellent agreement was obtained with soap concentrations below 150 p.p.m. From 150 to 1200 p.p.m. the results tended to be somewhat low, probably because of the single extraction. Tests showed that further extraction did wash out more sodium. However it was felt that the saving in time warranted the simplified procedure. Refined oils will generally contain well under 150 p.p.m. soap, and the higher samples are so obviously contaminated that analysis is probably unnecessary. Certainly in this range the accuracy is adequate. Representative data, obtained on a Wesson oil containing 1% added oleic acid, are given in Table II.

The applicability of the method to refined oils with soap contents below 15 p.p.m. was tested in the following way. Wesson Oil was extracted three times by our procedure outlined above, *i.e.*, concentrated HCl and petroleum ether, then water added and mixed in the Waring Blender in the manner described. The water layers were discarded. The third water layer gave the same reading on the instrument

TABLE II

p.p.m. Na taken (calc. as Na oleate)	p.p.m. Na oleate found
15	15
30	31
45	47
60	60
150	130
300	250
600	490
1,200	1,060

as the reagent blank. Sodium hydroxide solution, the equivalent of 6 p.p.m. of soap, was added to the "soap-free" oil, and the resulting oil was analyzed for soap by our method. The soap found was 5 p.p.m. In the range of 5 p.p.m. of soap in refined oil the method gives values reliable to  $\pm 1$  to 2 p.p.m. Sensitivity can be increased by decreasing the volume of water for extraction or increasing the size of sample, but the latter would tend to make the procedure somewhat cumbersome.

We are making preliminary studies on direct aspiration of a petroleum ether solution of the oil sample into the flame photometer.

### Summary

A method has been developed for the determination of sodium soap as sodium in refined vegetable oil. The oil is extracted with hydrochloric acid, and the sodium is determined in the aqueous extract by using the flame photometer.

### REFERENCE

1. Goff, Howard Jr., and Blachly, F. E., *J. Am. Oil Chemists' Soc.*, **34**, 320 (1957).

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## Selective Hydrolysis of Soybean Oil Phosphatides<sup>1</sup>

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PHOSPHATIDES obtained from degumming soybean oil are used, after suitable treatment, in a variety of food and industrial products where their emulsifying properties are necessary or important. Although the use of soybean phosphatides has increased year by year, a greater quantity than required for existing uses would be available if the entire production of soybean oil were degummed. Conversion of phosphatides to mono- and diglycerides by selective hydrolysis is therefore a potentially practical method to utilize excess phosphatides, which are now disposed of in soapstock.

Hydrolysis of phosphatides occurs at one or more points in the molecule according to the agents employed (9). Such hydrolytic reagents as aqueous acids or bases hydrolyze the glycerol-fatty acid bonds and the phosphoric acid-choline or ethanolamine bonds first, whereas the glycerol-phosphoric acid bond is the most resistant to attack. Enzymatic hydrolysis is generally more selective. For example, lecithin can be hydrolyzed to lysolecithin, glyceryl-phosphorylcholine,

phosphorylcholine, or choline by the selection of appropriate phospholipases and conditions of treatment. Both a glycerophosphatase of takadiastase and a phosphatase derived from certain animal tissues have been reported to liberate phosphoric acid from egg-yolk lecithin. One product of the hydrolysis appears to be a diglyceride. MacFarlane and Knight showed that  $\alpha$ -toxins of *Clostridium welchii* filtrates contain a lecithinase which hydrolyzes lecithin to a diglyceride and phosphorylcholine (4). This enzyme does not attack cephalins and certain other phospholipides. Enzymes are generally slow acting and they require buffering for maximum effectiveness. The present report describes a rapid method for converting soybean oil phosphatides to diglycerides by using ion-exchange resins.

Ion-exchange resins have been shown to catalyze a variety of organic reactions. Sussman reported in 1946 that cation resins may be substituted for acid catalysts in esterification, alcoholysis, hydrolysis, and other reactions (6). A continuous flow reactor employing a cation resin catalyst for converting acetone to mesityl oxide was described by Klein and Banchemo

<sup>1</sup> Presented at the 49th Annual Meeting, American Oil Chemists' Society, Memphis, Tenn., April 21–23, 1958.