Some Observations on the Determination of Soap in Refined Oil

By H. A. SCHUETTE and CHARLES H. HINE
UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

Abstract

Recovery experiments which were made by two quite different procedures indicate that the most satisfactory approach to a solution of the problem of determining the soap content of a refined oil probably rests upon the assumption that the chloride which is formed upon the addition of hydrochloric acid is an index of the quantity present. At soap concentrations of 100 pts/M² and less, the Durst method, as modified by Stillman, was found to be quantitative for all practical purposes.

TABLE I.
EFFECT OF INTRODUCING CERTAIN VARIABLES ON THE DETERMINATION OF SOAP IN REFINED OIL

Oil	Method Used	Volume of solution titrated ml.	Strength of $AgNO_3$ solution N	Soap Content found pts./M²	Soap Content deviation from ave. pts./M²
1.	Durst-Stillman	10^{4}*	0.01	56	±4
		20^{2}	0.01	77	±8
		10^{1}**	0.01	73	—
		10^{2}**	0.005	69	±20
	Durst	10^{3}	0.005	75	±10
2.	Durst-Stillman	10^{1}	0.01	100	—
		10^{2}	0.005	111	±3
	Durst	50^{2}	0.10	103	0
		10^{1}	0.01	93	—
		10^{2}	0.005	110	±5
		10^{2}**	0.005	96	±11
		20^{1}	0.01	103	—
		20^{1}**	0.01	128	—

* Superscripts show the number of determinations made.
** Acid extract of soap was washed with ethyl ether before evaporation to dryness.

TABLE 2
RELATIVE EFFICIENCIES OF SEVERAL METHODS FOR THE DETERMINATION OF THE SOAP CONTENT OF A REFINED OIL

Method	Soap added pts./M²	Soap Content blank pts./M²	Soap Content total pts./M²	Soap recovered pts./M²	Deviation pts./M²
Durst	50	9	59	43	—16
	100		109	92	—17
	200		209	190	—19
Durst-Stillman	50	12	62	59	—3
	100		112	110	—2
	200		212	193	—19
Alcohol-extraction	50	12	62	42	—20
	100		112	96	—16
	200		212	166	—46

Of some half-dozen proposed procedures for the determination of soap in a fatty oil, three have to date survived the scrutiny of the Society's present committee on Soap in Refined Oil. The methods in question reach a common objective from somewhat different approaches. Two — one of them is a modification of the other — rest upon the assumption that the chloride formed upon the addition of dilute hydrochloric acid to the oil is a measure of the soap content of that oil; the other was developed from the premise that soap is the only alcohol-soluble material in the mixture which will yield a basic substance upon incineration. In the order referred to above, the procedures are the Durst[1], the Durst-Stillman[2] and the alcohol-extraction[3] methods. Since all have been only recently described[2] again, it seems hardly necessary now to go over the same ground except, perhaps, to recall that in our experience the Stillman-modified Durst method requires about one-half as much time for completion as either of the other two.

The nature of the results obtained by a number of analysts working in this Laboratory and in others with samples sent out by the Committee in 1937 made it plainly evident that a critical examination of the more promising, if not all, of the methods is desirable. To that end, all unused samples were combined into two lots — the whole in no wise, however, now representing the originals — which were then analyzed by the Durst and the modified Durst procedure. Variations were made in the volume of solution titrated and the strength of silver nitrate solution used. In several instances, also, the acid chloride solution was washed with ether before concentration. The results of this short study (Table 1) need little comment beyond the fact that, except in the first instance, there was obtained fairly satisfactory agreement in data when considered as *averages*; but that from the standpoint of deviation from them (column 4), the introduction of another step in the analysis (purification of extract) would probably lead to no useful ends.

Inasmuch as the soap content of these samples was unknown, the foregoing data take on only a qualitative significance in the sense that the yardstick, or measure of accuracy, was missing. It was apparent that not much progress would result until studies could be made on samples containing known amounts of soap. To that end a highly purified cottonseed oil was impregnated with varying amounts of a laboratory preparation of sodium oleate. Samples containing added soap in the amounts of 50, 100 and 200 parts per million, respectively, were prepared. Blank determinations were made on the cottonseed oil itself by the three methods under investigation and the soap content so indicated was corrected for in evaluating results eventually obtained in recovery experiments. By all methods an average of approximately 11 parts per million of soap was indicated. Specifically the findings, based upon triplicate analyses, were: Durst 9.4 pts./M²; Durst-Stillman 12.4 pts./M²; alcohol extraction 11.7 pts./M².

Contrary to the conditions set down by Durst[1], titrations of the chloride solution were not made in 50-ml. but in 10-ml. volumes, and a 0.01 *N*-silver nitrate solution was used rather than one ten times as strong. Preliminary trials had indicated that better and reproducible results would be obtained under these conditions. Because of quantitative solubility product considerations involving the formation of the insoluble silver chromate, it was deemed desirable to have the concentration of the latter in the final solution five per cent. Titrations were carried out against a black background in yellow light. A semi-micro burette was used and comparisons at the end-point were made with controls.

An examination of the results obtained in sextuplicate with the Durst method (Table 2) shows that it consistently yielded low results of from 16 to 19 pts./M². Even though four extractions were made, apparently all the alkali metal is not recovered from the mixture as its chloride. The method was found to be somewhat more consistent than the others, however, in that it appears no less effective at higher concentrations of soap than at lower levels. The alcohol extraction method gave results comparable with those obtained by the Durst procedure at soap concentrations up to 100 pts./M^2, but it fails completely when approaching the 200-parts-per-million range. Even when eight extractions were made the alcohol failed to remove 20 per cent of the soap. The modified Durst method proved to be most satisfactory of the three. At low and medium soap concentration, the recovery was, for all practical purposes, quantitative. That it proved to be less efficient at the 200-part level is probably due to an insufficiency of acid used in the decomposition of the soap. Further study, and perhaps some modification, is probably necessary here.

Literature Cited

1. Durst, Oil & Soap, 12, 271 (1935).
2. Harvey et al, Oil & Soap, 15, 209 (1938).
3. Spielman et al, Oil & Soap, 14, 153 (1937).

INTERNATIONAL DEVELOPMENTS IN OILS & FATS*

By J. H. REDDING
17 BATTERY PLACE, NEW YORK

IN placing this paper before you, it is done more to give you an impression of the great importance of the world's industry in oil, fats and oil-bearing seeds. Very few people realize the magnitude of this industry and its far flung interests throughout the world, — from whale oil produced in the Antarctic in the South, to oils produced from various marine animals in the far North.

During the past year the demand for vegetable oils, both for edible and industrial purposes, indicated a decided increase over previous years. The United States, particularly, has continued to exert a powerful influence on the world markets for oil-bearing seeds and vegetable oils. The influence of bumper crops in the United States is of most importance and to a very great extent is a decided factor in regulating price levels of foreign oils.

The group of fixed or fatty oils, composed mainly of glyceride and fatty acids, is to be distinguished on one hand from the hydrocarbon oils of mineral origin, and on the other hand from the volatile or essential oils of vegetable origin.

Many of the fatty oils are of vegetable origin, being obtained from the seeds and nuts of a number of seeds and plants. At least 30 different trees and plants have been used for the production of oil on a commercial scale and a much larger number of varieties are known to contain oils which up to the present are not produced commercially.

Falling within the fatty oil group are several marine oils, notably whale oil. Animal products, namely butter, lard and tallow, remain the principal animal fats in commerce, but with the increasing demand for fats, the consumption of vegetable fatty oils has increased enormously.

The demand for fatty oils comes from many sources, of which the most important are the food and soap industries. There are no fatty oils equally suitable for all purposes, but by such processes as hydrogenation certain oils can be now adapted to uses for which they were not previously suitable. The effect has been to make the various oils more readily interchangeable in response to price fluctuations.

At the same time, some oils are more generally used than others for certain purposes. Thus, for the manufacturer of margarine, the most important vegetable oils are cocoanut, palm kernel, cottonseed, soya bean and peanut oil. For soap making, cocoanut, palm, and palm kernel are widely used, and also to a lesser extent, cottonseed and olive oils. For compound lards, cottonseed oil predominates while olive oil is important for salads and cooking. A drying oil is required in the manufacture of paint, varnish, and linoleum, and for these, linseed and tung oils are most generally employed, with soya bean and perilla oil as substitutes. Castor oil and rapeseed oil have special qualities rendering them suitable as lubricants.

In the same way, for the numerous other uses in which vegetable oils are employed in the producing and importing countries, there are generally certain oils which are preferred to others.

By far the greater part of the vegetable oils available in the United States and Europe are consumed, together with fatty oils and fats of animal and marine origin, in the production of soap, margarine, and edible fats.

With the principal oilseeds produced, after the vegetable fatty oils have been extracted either by crushing or with solvents, the residue, namely oil cake or meal, is available either as food for livestock or as a fertilizer.

Butter and lard although they are used at times as constituents of margarine and compound lard, compete with these finished products rather than with the alternative raw materials. On the other hand, tallow (which is a byproduct of the meat industry) is used extensively in soap, and also in the manufacture of candles.

Whale oil, the most important of the marine animal oils, through the great development which has taken place especially in the Antarctic, is now a very serious competitor of vegetable oils. Last year's production of whale oil in the Antarctic was approximately 600,000 tons. To give an impression of the magnitude of this industry, the new floating factory ships which proceed to the Antarctic each year for the production of whale oil are vessels running anywhere from 15,000 to 25,000 tons each. Last year there were 30 of these factory whaling ships used, attached to which ships were 176 killer boats. The number of men employed in these various ships totalled 9,321. The actual number of whales killed in the Antarctic was approximately 36,000.

A special international agreement, to which most of the principal countries are now parties, restricts the vessels to a specific period of fishing and each factory vessel to a maximum capacity of oil produced. The main idea of this international agreement is to eliminate the indiscriminate killing of whales which, if continued without cessation, would undoubtedly have resulted in the quick extermination of the whale. The regulations also stipulate that no whales under a specified length may be killed, the stringent enforcement of which under the international agreement is giving the industry a new lease on life.

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