Titrimetric Determination of Soap in Refined Vegetable Oils

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ABSTRACT

The low levels of soap encountered in well refined vegetable oils can be determined quickly and accurately in an isopropyl alcohol solution of the oil by a direct titration with .01 N hydrochloric acid in isopropyl alcohol using bromophenol blue as the indicator. Fifty parts per million soap calculated as sodium oleate can be determined with good accuracy and as little as 2 ppm can be detected in refined and bleached soybean oil. Soap in palm oil can be determined using the same solvent and titrant and titrating the sample to pH 5.0.

INTRODUCTION

Until recently methods for determining .01% or less soap in vegetable oils were too slow and time consuming for control of refining operations. Ashing methods, while they give acceptable results, require 2-4 hr lapsed time. In fact the tentative AOCS conductivity method is standardized by ashing oil samples and titrating the bases formed (1).

A variety of other methods have also been proposed for soap determinations. Atomic absorption (2), neutron activation (3) and flame photometric (4) methods have been used successfully, but require equipment that is still not available in many control laboratories. Furthermore these instruments are most efficient when applied to large batches of samples. Most process control situations require the rapid analysis of small numbers of samples submitted periodically throughout the work day. The above mentioned instruments are inefficiently utilized under this condition. Also instrumental methods which determine total sodium in alkali refined oil will most certainly be affected by the presence of sodium salts of phosphatides which remain in refined oils in amounts up to three times the soap content.

Wolff proposed direct titration procedures for soaps in both light and dark oils (5). Sensitivity and accuracy are good, but the titrant, hydrochloric acid in acetone is unstable and requires frequent restandardization.

Neither the above mentioned procedures nor the one described below distinguish between soaps and free alkalinity. In each case, total alkalinity is measured and calculated as soap.

The procedures proposed in this paper are sensitive enough to assure the production of high quality oil and rapid enough for process control.

EXPERIMENTAL PROCEDURES

Materials and Equipment Used

ACS reagent grade isopropyl alcohol and HCl were used to make the titrant. 1.000 N aqueous HCl was prepared and standardized against NaOH solution freshly standardized against potassium acid phthalate. .0100 N HCl was prepared by diluting the 1.000 N acid with isopropyl alcohol.

Bromophenol blue in isopropyl alcohol (.05%) was prepared from ACS reagent grade isopropyl alcohol and water soluble bromophenol blue. This solution was adjusted to an apparent pH of 5.0 ± 0.1.

ACS reagent grade isopropyl alcohol was neutralized to a pH of 5.0 ± 0.5 by adding 5 ml indicator per liter and

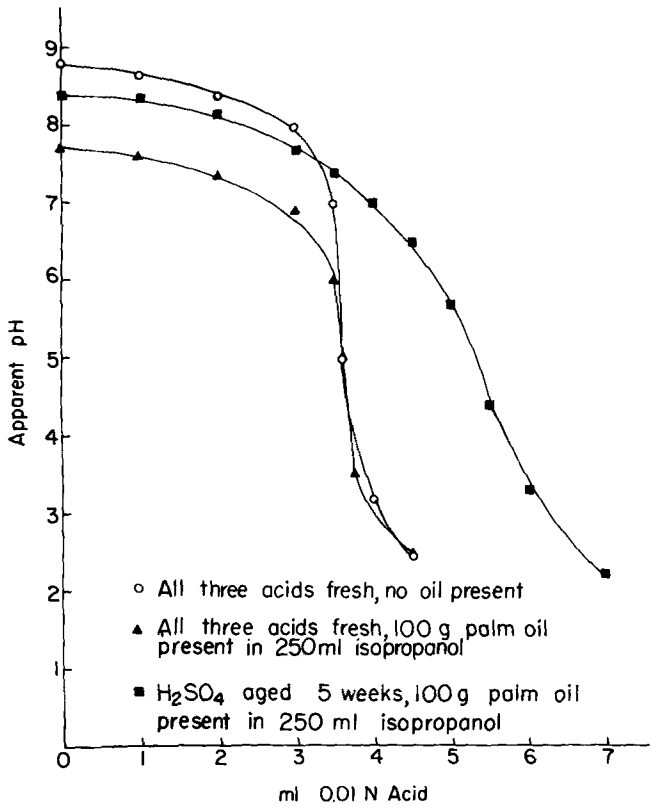

FIG. 1. Titration curves obtained with hydrochloric, sulfuric and perchloric acid solutions.

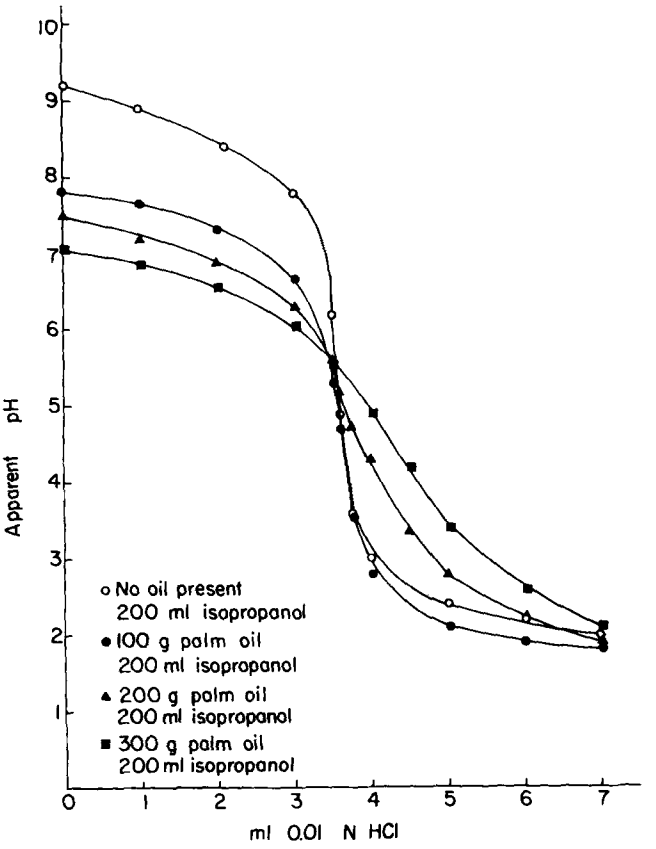

FIG. 2. Change in titration curve vs. per cent oil in oil-isopropanol mixture.

TABLE I

Sample Weight and Volume of Solvent Required

Soap, %	Sample wt, g	Neutral isopropanol, ml
.003 or less	200	200
.003-.03	100	200
0.03-0.10	25	100
0.10 or more	10	100

TABLE II

Accuracy of Bromophenol Blue Titration Based on Recovery of Known Amounts of Soap

Sample	Recovery, %	
	Palit's method (6)	Proposed method
Sodium oleate (technical grade), 0.0100 g	104.0, 105.3	104.9, 105.5
Sodium palmitate (Eastman 9035), 0.0100 g	100.6, 99.0	99.4, 99.4, 100.2, 100.2

titrating to the yellow end point or by titrating to an apparent pH of 5.0 with a pH meter. Less pure grades of isopropanol can be used as solvent if carefully neutralized.

A .00100 g/ml solution of sodium palmitate was prepared by dissolving sodium palmitate (Eastman 9035) in a small amount of water and diluting to volume with ACS reagent grade isopropyl alcohol.

A .00100 g/ml solution of technical grade sodium oleate was prepared in the same manner as the sodium palmitate.

USP Oleic Acid was purchased from Matheson, Coleman and Bell and was used as received.

A 10 ml buret graduated to 0.05 ml was used for the titrations.

Titration (Visual End Point)

A sample of oil (Table I) was weighed into an appropriate flask or beaker and hot neutral isopropyl alcohol added. The solution was warmed on a steam bath for 10-15 min to dissolve the oil and soap. Next 3-5 ml of indicator was added and the solution titrated rapidly to a yellow end point. The color change was from blue (if high levels of soap were encountered) to green to yellow. The correct end point was attained when all the green color just disappeared. Although a green color may reappear within a few seconds, the titration should not be carried beyond the first yellow end point. The end point is best detected against a white background. The sample should be agitated vigorously during the titration. Any good magnetic stirrer is suitable.

The highest sensitivity is obtained by adding a hot neutral isopropanol-indicator solution to a sample of warm oil. Five milliliters of indicator was added to 300 ml isopropanol and carefully titrated to the end point from the alkaline side using .01 N hydrochloric acid. This neutral solution was added to 200 g oil. The presence of 1-2 ppm soap will give a definite pale green tint to the mixture which should be titrated carefully until the green tint just disappears.

pH End Point

For best accuracy, palm oil should be titrated on a pH meter, using a glass electrode and calomel electrode with a ground glass collar. The collar should be loose enough to give a rather rapid seepage of electrolyte; otherwise, it will quickly become clogged. Preferably the pH meter should have an automatic temperature compensator, since the sample should be warm to keep the oil dissolved. Oils containing phosphatides cannot be titrated in this manner since they react slowly with the titrant near the pH of the end point.

TABLE III

Per Cent Soap by Titrimetry and Ashing[a]

Sample		Soap by titration, %		Soap by ashing, %	
1.	Soybean oil	.017	.018	.018	.016
2.	Soybean oil	.016	.019	.017	.016
3.	Soybean oil	.017	.018	.019	.016
4.	Soybean oil	.024	.029	.023	.022
5.	Soybean oil	.18	.18	.16	.17
6.	Palm oil	.13	.13	.12	.13
7.	Palm oil	.098	.096	.10	.10
8.	Palm oil	.015	.015	.016	.016
9.	Palm oil	.10	.11	.12	.12
10.	Palm oil	.0052	.0052	.004	.006
Standard deviation		.003		.003	

[a]Palm oils were titrated to pH 5.0. Soybean oils were titrated visually.

The titration curve can be plotted, or for more rapid determinations, pH 5.0 can be taken as the end point. From pH 6 to the end point ca. 2 min should lapse between additions of titrant to allow the system to come to equilibrium. Table I provides a convenient range of sample sizes and dilutions.

Calculation

The following formula is used to calculate total alkalinity as per cent soap: Per cent soap = (N x T x 31.0)/g sample, where N = normality of titrant, T = ml titrant and 31.0 = molecular weight factor, (in this case the molecular weight of sodium oleate ÷ 10). If the result is to be calculated in terms of the soap of a different fatty acid, the appropriate factor should be used in the place of 31.0.

RESULTS AND DISCUSSION

Experiments were run using sulfuric, hydrochloric and perchloric acid to determine which is the most appropriate titrant. The 0.0100 N solutions of each in isopropanol were prepared in a similar manner. When fresh, all three titrants behaved alike (Fig. 1). After aging for 5 weeks, hydrochloric acid did not change but the normality of sulfuric acid solutions decreased appreciably. The shape of the titration curve also changed (Fig. 1). Perchloric acid solutions were not aged. Hydrochloric acid was judged to be the most suitable of the three titrants tested.

The addition of 1% of USP oleic acid reduced the titration of a standard sample containing .01% soap by 8 ppm. Since this is a much larger amount of free fatty acid than will normally be encountered, it should have a negligible effect on most titrations.

It is possible that the mixture of oil and isopropyl alcohol behaves much as Palit's G-H solvent (6). The addition of ethylene glycol to samples before or after addition of isopropanol did not appear to have any effect on the titration.

A series of experiments was run to determine the effect of different oil-isopropanol ratios on the pH end point. The break in the pH curve shifts as the proportion of oil increases. Up to 50% oil, the shift is negligible for all practical purposes (Fig. 2).

Accuracy was determined by preparing standards of known quantities of sodium oleate and sodium palmitate and adding these to mixtures of isopropanol and oils known to contain less than 2 ppm soap. Similar samples were prepared without oil and titrated according to the method of Palit (6). Recoveries were essentially 100% and are shown in Table II. The results obtained using technical grade sodium oleate containing free alkalinity underscore the fact that not only soap but free alkalinity is determined

by the proposed method.

A series of refined soybean and palm oils was analyzed by the titrimetric methods described and by an ashing procedure which consisted of ashing the samples then titrating the bases formed. The data are presented in Table III. Statistical analysis of the results shows that for these samples the titrimetric and ashing methods are equivalent.

In addition to the above samples, a sample of palm oil gave different results when analyzed by the two methods. Per cent soap by titrimetry was .028 ± .001 (three results) and by ashing, .022 ± .002 (five results). These results, although statistically different, agree well enough for most purposes.

ACKNOWLEDGMENTS

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