abietic type acid. It has been shown that iron contaminated gum can be treated with oxalic acid without isomerizing the primary acids to forms that give color to soap.

Aging tests showed that, after the first month the rosin soap cakes changed color slowly. The change that took place in the following months involves an appreciable darkening of the lighter samples, except in the case of the white rosin soap made with pyroabietic acid.

Acknowledgement

The authors are indebted to Dr. B. A. Brice for help and suggesting the method of measuring the color of rosin soap, and to W. C. Smith for his helpful suggestions throughout the investigation.

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A Crystallization Method for the Determination of Saturated Fatty Acids in Soybean Oil

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THE American Oil Chemists' Society has adopted two official methods (6) for the determination of the amount of saturated acids in vegetable and animal oils and fats, namely, the thiocyanogen and the modified Twitchell lead salt-alcohol methods. The thiocyanogen method is applicable only to those oils which do not contain linolenic acid and therefore cannot be used with the drying oils and a few of the semi-drying oils. The modified Twitchell method is probably the most generally used procedure for determining saturated acids, although the data presented at the time of its adoption as a tentative method (3) showed that the results obtained with it were from 0.9 to 2.0 percent lower than those calculated by the thiocyanogen method. This discrepancy had been noted previously by Martin and Stillman (5) who suggested that the results of the thiocyanogen method were probably more nearly correct. Aside from the question of the accuracy of the results, the manipulation involved in a lead salt separation is so tedious and time consuming that the method is not well adapted to routine determinations.

In addition to these official methods, there are a number of procedures involving oxidation of the unsaturated compounds with potassium permanganate and isolation of the unaltered saturated acids. Probably the best known of these methods is that devised by Bertram (1) which is said to be more accurate (4) than the Twitchell method, but it is also more tedious.

In preparing linoleic acid by crystallization at low temperatures, Brown (2) observed that the saturated acids could be separated from the unsaturated acids in acetone at -20° C. with an efficiency at least equal to that of the Twitchell method. This observation led the present authors to the development of a crystallization method for determining the saturated acids present in soybean oil. The determination can be made in a short time with simple equipment. During the developmental stages, the apparatus used consisted of a number of 38 by 200 mm test tubes, a 30-mm glass filter stick of G3 porosity, and a two-quart vacuum food jar to contain the low temperature acetone bath. The temperature was controlled by the addition of dry ice as required. A larger bath with automatic temperature control would be highly desirable for any long series of determinations.

Method

The mixed fatty acids are prepared from the oil according to the present official method of the American Oil Chemists' Society (6).

A sample of about 5 g of mixed acids is placed in a test tube, and 50 ml of acetone is added. The tube and its contents are suspended in a cold bath consisting of acetone and dry ice at about -41° C., and the sample is stirred occasionally with a thermometer until the temperature reaches -40° C. The soluble acids are then removed by filtering through a glass filter stick which has been previously cooled to the temperature of the bath. The solid materials clinging to the thermometer and filter stick are washed back into the test tube with 50 ml of acetone and permitted to dissolve. After two more crystallizations the solid acids are dissolved in acetone and transferred to a small tared flask. The solvent is removed on a steam bath, and the residue is dried in an oven at 105° C. for one-half hour. The flask and contents are cooled and weighed, and the amount of "solid" acids is calculated. The iodine number of the "solid" acids is determined and used to calculate the amount of unsaturated acid in the "solid" acid fraction, assuming that the only unsaturated acid present is oleic. Subtraction of the "oleic" acid from the "solid" acids gives the amount of saturated acids present in the original sample of mixed fatty acids.

Discussion

In the study of soybean oils, it was found that working at a temperature of -40° C. permitted a sharp separation of the unsaturated acids from the saturated acids and at the same time gave excellent recovery of the saturated acids. The solubilities of stearic, palmitic, and myristic acids in acetone at -40° C. were found to be approximately 1, 8, and 75 mg per 100 ml, respectively. Losses of this magnitude were not considered to be serious in the case of stearic and palmitic acids, and, in the case of myristic acid, the loss is probably no more serious than those which occur in the Twitchell and oxidation methods. The solubility of the saturated acids in acetone solutions of the unsaturated acids was not studied. The work on soy-

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[1] A cooperative organization participated in by the Bureaus of Agricultural Chemistry and Engineering and Plant Industry of the U. S. Department of Agriculture, and the Agricultural Experiment Stations of the North Central States of Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin.

bean oil did not indicate that the solubility of the saturated acids was altered under those conditions, but a few determinations on perilla oil seemed to indicate that the presence of larger amounts of the more unsaturated acids increased the solubility of saturated acids enough to cause serious losses. Sharp separations of the unsaturated acids of perilla oil were made at -50° C., and the recovery of saturated acids was much better than at -40° C. On the other hand, when the analysis of the acids from soybean oil was attempted at temperatures below -40° C., the separation was poor and the correction for unsaturated acids in the "solid" acids was found to be in serious error as a result of the presence of significant amounts of linoleic acid. The correction for linoleic acid could have been calculated by means of the iodine and thiocyanogen numbers but it was believed preferable to work at -40° C., at which temperature such a correction is unnecessary.

The iodine number of the "solid" acids obtained from soybean mixed acids by crystallization at -40° C. was found to depend on the composition of the oil, particularly on the proportion of oleic acid present. For those oils containing less than about 27 percent oleic acid, the iodine number of the "solid" acids was ordinarily below 2. As the proportion of oleic acid increased above 27 percent, the iodine number of the "solid" acids increased rapidly and, in the extreme case of a sample of mixed acids containing 55 percent oleic acid, reached a maximum of 63. These higher figures resulted from the limited solubility of oleic acid, the volume of solvent which was used being sufficient to remove only about 1.35 g of oleic acid, equivalent to 27 percent of a 5-g sample. The more unsaturated acids, however, were removed satisfactorily, and the correction for the amount of "oleic" acid in the "solid" acids could still be calculated. By increasing the amount of solvent to about 2-1/2 times the quantity recommended, the iodine number of the "solid" acids of even the extreme case could be brought quite low, although there seemed to be no particular advantage in doing so.

A single determination of the saturated acids in cottonseed oil indicated that the crystallization method is applicable to this oil. Application of the method to olive oil, however, led to unexpected results. The saturated acid content was found to be 12.5 percent, which was higher than the result 11.5 percent, obtained by use of the oxidation method. No attempt was made to explain this difference between the results obtained by the two methods.

The saturated acid content of the mixed fatty acids from several soybean oils was determined by three methods, and the results are presented in Table I. The methods used were the official modified Twitchell method, the Bertram oxidation method as modified by Pelikan and Von Mikusch (7), and the crystallization procedure reported in this paper.

TABLE I.
THE SATURATED ACIDS IN MIXED ACIDS FROM SOYBEAN OIL

Sample	Source	Iodine number of mixed acids	Saturated acid content of mixed acids: Modified Twitchell method	Crystallization method	Oxidation method
			Percent	Percent	Percent
E-123	Commercial press	134.8	12.6	14.1[1]	15.0
0-73	Laboratory expeller	135.2	13.1	15.2	15.2
0-88	Laboratory extracted	157.7	13.5[2]	15.2	16.1
0-88-1	Laboratory extracted	157.4	—	15.5[2]	15.3
E-125	Laboratory extracted	138.8	12.3	14.6	14.7
E-125-1	Laboratory extracted	138.5	12.4	14.4	14.5
1063	Laboratory extracted	129.2	14.6	16.3	—
66	Laboratory extracted	106.2	12.2	14.4	14.9

[1] Crystallized at -30° C. The value would be higher if obtained at -40° C.
[2] Single determination. The other figures represent the average of duplicate determinations.

The results of the crystallization and oxidation methods, with the exception of one sample, agreed very well. The Twitchell method, on the other hand, gave results which were about 2 percent below those of the other methods.

The single discrepancy between the crystallization and oxidation methods, sample 0-88, apparently resulted from the presence of an unusually large amount of unsaponifiable matter. Pelikan and Von Mikusch recommended the removal of the unsaponifiable matter from oils which contain more than 2 percent, before proceeding with the determination of saturated acids by the oxidation method. The abnormal oil referred to above contained 2.20 percent of unsaponifiable matter and some portion of it, or some oxidation product derived from it, was weighed as saturated acid, thus making the result obtained by the oxidation method too high. When the unsaponifiable matter was removed before analysis, as in the case of sample 0-88-1, the value obtained by oxidation was found to agree very well with the value obtained by the crystallization method. As further proof that the unsaponifiable matter does not normally interfere with the crystallization method, the liquid acids obtained by crystallization of sample E-125 were examined. These liquid acids contained unsaponifiable matter equivalent to 0.61 percent of the original sample of mixed acids, while the determination made directly on the mixed acids gave a value of 0.59 percent. Obviously, the saturated acids isolated from soybean acids by crystallization could not, therefore, have contained any appreciable amount of unsaponifiable matter.

The difference between the results of the Twitchell and Bertram methods has been previously reported (4). In investigating this difference, the liquid acids from the Twitchell separation were analyzed for saturated acids by the crystallization and oxidation methods. The results obtained are recorded in Table II. The material recovered from the Twitchell liquid acids by crystallization was examined further to establish its identity. The iodine number of the material obtained from several samples ranged from 1 to 6. The equivalent weights of two portions were determined by alkali titration and found to be 272 and 282, theory for palmitic acid 256, stearic acid 284. A composite from several samples, after treatment with decolorizing carbon, melted at 60.0°—60.8° C., and it was found to contain 75.45 percent carbon and 12.52 percent hydrogen, theory for palmitic acid, 74.90 percent carbon, 12.59 percent hydrogen; stearic acid 75.96 percent carbon, 12.76 percent hydrogen. From these data it is evident that the material recovered by crystallization from the liquid acids of the Twitchell separation was, for the most part, a mixture of long-chain saturated fatty acids.

TABLE II.—The rocovery of saturated acids[1] from the liquid acids obtained by the Twitchell method

Sample	Saturated acids determined by the modified Twitchell Method	Saturated acids recovered from the liquid acids of the Twitchell determination: By crystallization	By oxidation
	Percent	Percent	Percent
E-123	12.7	—	1.9
E-123	12.7	—	1.8
E-123	12.5	—	2.2
E-123	12.7	—	1.6
O-73	13.0	—	1.8
O-73	13.1	—	1.9
E-125	12.2	1.5	—
E-125	12.3	1.7	—
E-125	12.4	1.7	—
E-125-1	12.4	1.5	—
O-88	13.5	1.2	—

[1] Expressed as percent of mixed acids.

Summary

A crystallization method has been developed for the determination of saturated fatty acids in soybean oil. The method is simple and rapid. The results obtained by this method agree quite well with those obtained by the use of the Bertram oxidation method and are about 2 percent higher than those obtained by the use of the modified Twitchell method. The procedure recommended seems to give satisfactory results on soybean and cottonseed oils, but it will probably have to be modified for use with highly unsaturated oils such as perilla, or with oils such as olive which contain large amounts of oleic acid.

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pH Meter Control of Spent Soap-Lye Purification

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Introduction:

In the usual method of clarification of spent soap-lyes for glycerine recovery, alkaline salts are neutralized with a strong acid, insoluble fatty acids are precipitated by a strong acid from the soap dissolved in the spent lye, and fibrous semi-colloidal impurities are adsorbed to the flocculent precipitate of aluminum or iron salts. After the addition of a diatomaceous filter-aid, the treated lye is filtered. The clear liquor is then neutralized with caustic soda to a value of pH 8-9 which is least corrosive to the evaporator. The flocculent precipitate which is a product of the caustic soda and the portion of the aluminum or iron salt soluble at the acid pH value of the treatment is allowed to settle out or is filtered off. The weak liquor after the second treatment is evaporated to 80% crude glycerine and the dropped salt is recovered.

It has been the experience of this plant that the use of colorimetric pH control in the recovery of glycerine from spent soap-lye did not give consistently good results. A review of the literature offered nothing except colorimetric pH control. Consequently, closer control was attempted with the electric pH meter. This led to the problem of ascertaining the optimum pH range for the treatment prior to filtration.

Theoretical:

Four factors had to be considered in the ideal method of treatment:

1. The pH value at which soap is completely broken down into insoluble fatty acid.
2. The proportion of strong acid necessary to accomplish this.
3. The optimum pH range of coagulation of the aluminum or iron salt allowable under the conditions of treatment.
4. The amount of aluminum or iron salt to completely adsorb the unfilterable fibrous impurities.

Soap as the salt of a weak acid exerts a buffer action against the addition of strong acid and consequently tends to hold up the pH value of its solution until it is completely broken down into insoluble fatty acids. Since these insoluble fatty acid constituents of the soaps found in spent lye are of practically the same nature in every spent lye, then the hydrogen ion concentration of the completely precipitated fatty acids is a constant value fixed by their ionic dissociation. This hydrogen ion value can be determined by plotting the electrometric titration of spent lye with strong acid and noting the characteristic point of inflection which marks the end of the buffer action of the soap in the lye.

The proportion of acid for each treatment of spent lye can be determined by the proportion of acid needed to lower the pH value of a sample to the point of inflection.

The optimum pH range of coagulation of the iron or aluminum salt can be obtained by observing the appearance of the floc at and below the pH value of the point of inflection.

The amount of coagulating salt necessary for complete adsorption should differ for lyes from varying sources. This can be found by direct tests on each individual batch of spent lye.

Experimental:

This paper will deal with sulfuric acid and aluminum sulfate as the chemicals used in treating spent lye. However, the methods used in this paper are also applicable to the hydrochloric acid-ferric chloride method of treatment.

A number of 100 ml. samples were titrated, using a glass-electrode pH meter, and .25 normal sulfuric acid. The curves represting pH values vs. ml. of acid all had a marked break in continuity near the value pH 3.0. Filtered samples of lyes which were titrated to a value higher than pH 3.0 showed a further precipitation of fatty acid on adding more strong acid. Conversely, filtered lyes of a value lower than pH 3.0 showed no precipitate with the addition of strong acid. Hence, it was concluded that this break represented the pH value at which precipitation of insoluble fatty acid was completed.

For a more accurate determination of the "break," the section of the titration curve between the pH values 3.5 and 2.3 was then plotted on graph paper substituting hydrogen-ion concentrations for pH values. This gave a broken line which consisted of two curves, one of which was evaluated to the formula $Y = 784X + 38.5$ and the other to the formula $Y = 39.8\ (1 + \Sigma^{-7.45 \text{ x } 10-3X})$ where X is the hydrogen-ion concentration, and Y is the volume of quarter-normal sulfuric acid used. The common point of these curves is $X = 0.00167$, and $Y = 39.8$, which corresponds to a pH of 2.8. (See illustration) At this value the buffering action of the soap is entirely spent, and the remainder of the titration conforms to the nearly-straight line of an unbuffered solution titration.