During the same period we have lost members as follows:

By resignation	14
By non-payment of dues	18
By death	2
	34
Total Membership of the Society May 12, 1938	446
Total Membership of the Society May 13, 1937	409
Net Gain of Members for year ending May 12, 1937	37

Mr. President:

In submitting the foregoing report I ask that an Auditing Committee be appointed to make a thorough audit of the accounts of the Secretary-Treasurer, and report back to the Society before the adjournment of our meeting, May 13, 1938.

J. C. P. HELM, Secretary-Treasurer.

DETERMINATION OF TOTAL SATURATED FATTY ACIDS

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Abstract

This paper discusses the methods of previous investigators and shows variations of results as obtained in studies of corn, sesame, and liquid cotton fatty acids —as well as of artificial blends from oleic and palmitic acids. The Bertram method was found to be most reliable while procedures of other authors gave inconsistent results. A detailed description of the Bertram method, as adopted by the Woburn Laboratories, follows.

TABLE 1.
Saturated Fatty Acid Content of Three Commercial Fatty Acids by Bertram Method and Two Variations.

	Sample A	Sample B	Sample C
Titer ° C.	23.1	27.5	26.2
Iodine Value (Hanus 1 hour)	116.4	122.3	102.5
Unsaponifiable Matter	3.2%	4.5%	2.5%
Saturated Fatty Acids determined by Bertram Method.	17.5	18.9	18.6
(Uncorrected)	16.7	18.7	
(Ditto, corrected*), average	16.9	18.6	18.4
Hilditch-Priestman method	16.5	....	18.5
Gay method	8.4	10.7	7.6

*The corrections have been derived from the iodine values of the separated fatty acids, which varied between 0.5 and 1.2.

DURING the study of the composition of some commercial fatty acids the necessity of determining the saturated fatty acid content arose.

The method by S. H. Bertram (1) is generally said to be more accurate than older methods. It makes use of the oxidation of unsaturated fatty acids in alkaline permanganate solution under conditions which leave the saturated portion unchanged. The temperature during the oxidation according to Bertram must not be allowed to rise above 25°.

Later, however, in working on Linseed Oil, P. J. Gay (2) came to the conclusion that the temperature used by Bertram is not sufficient to insure complete oxidation of the unsaturated portion. He recommended using two subsequent oxidations at 50 to 60° and 70 to 80°, respectively. A third oxidation at 80°, according to Gay, is sometimes advisable but not always necessary.

Hilditch and Priestmann (3), on the other hand, employed a single oxidation at 35 to 50°. The latter procedure omits the extraction of the unsaponifiable matter.

We applied the above three modifications to the following materials. Sample A represented an average of the liquid portion of cotton fatty acids obtained by pressing. Samples B and C represented averages of a number of commercially distilled fatty acids from corn and sesame soapstocks respectively.

The results obtained by the three modifications are shown in table 1.

The actual oxidation temperature in the Bertram procedure was between 5 and 15° C. It will be noted that duplicate determination employing this method agreed fairly closely; the Hilditch-Priestmann procedure in the two cases where it was used led to results identical with those obtained by the Bertram method. The Gay procedure, on the other hand, in which we oxidized twice at the specified temperatures, gave entirely different results, all of them lower than those above. In order to evaluate these methods a blend was made from c. p. palmitic acid (I.V. = 0.6) and supposedly c.p. oleic acid (I.V. = 92.45). Unfortunately, however, most "c.p. oleic acids" contain appreciable amounts of saturated as well as higher unsaturated fatty acids. Although the actual composition of this "c.p. oleic acid" was not known, a comparison of the results obtained by the Bertram method and the Gay procedure shows beyond doubt that the latter method actually gave a decidedly low value. As shown in table 2, only 8.6% of saturated acids were found by the latter method in the sample which contained at least 15.76% of saturated fatty acids. The figures in the last column represent the saturated constituents of the blended sample calculated by adding the quantity of palmitic acid used (15.76% corrected) to the saturated acid contained in the oleic acid, as determined by the method in question (see first column).

TABLE 2.
Saturated Fatty Acid Content of (1) "C. P. Oleic Acid" and (2) of a Blend Containing 84.14% "C. P. Oleic Acid" and 15.86% (corrected 15.76%) Palmitic Acid.

Saturated F. A. determined by	"C. P. Oleic Acid"	Blend	Blend (calculated)
Bertram Method (corrected)	5.2	19.5	20.2
Gay Method	1.6	8.6 (!)	17.1

Through the courtesy of Professor H. P. Kaufmann of Muenster, Germany, we later obtained a small sample of c.p. oleic acid [analysis as given, I. V. (Kaufmann method) = 89.6; Thiocyanogen V. = 89.3]. To 4.000 grams of this oleic acid we added 0.772 gram of palmitic acid (I. V. = 0.6). This blend therefore contained 16.07% (corrected) of saturated fatty acids.

This mixed sample was then analyzed according to the Bertram procedure, the petrolether extraction of the unsaponifiables being omitted. The result is shown in table 3.

TABLE 3.
Higher Saturated Fatty Acid Content Determined on Sample of Known Composition.

Palmitic Acid (I. V. = 0.6)	=	16.18%
Palmitic Acid, corrected	=	16.07%
Oleic Acid	=	83.93%
Higher Saturated Fat Acids found	=	15.6%
Error		0.47

Conclusions:

Identical results were obtained by the Bertram method and its variation by Hilditch-Priestmann for the saturated fatty acid content of three commercial fatty acids.

The Bertram method gave an almost theoretical result on a sample of known composition.

The two-fold oxidation at higher temperatures as recommended by Gay in the cases studied led to low results, a large part of the *saturated* fatty acids obviously being oxidized under these conditions.

Since the same results were obtained by the original Bertram method, i.e., upon oxidation below 25° (5°-15°) as well as by the Hilditch-Priestmann variation at 35° to 50°, it seems justifiable to eliminate both heating or cooling and to work simply at room temperature. The necessity of removing the unsaponifiables should depend on their percentage present and upon their unsaturation. In the above cases all unsaponifiables had iodine values above 100. No appreciable difference was observed with or without removal, although the percentage of unsaponifiables was 2.5 and 3.2, respectively.

The possibility of checking the results obtained independently by the calculation of the composition from the iodine and thiocyanogen values depends on the certainty with which linolenic acid can be proven to be absent. Unfortunately a small percentage of the latter can usually not be detected by the hexabromide precipitation. Results with this method will be reported at a later date.

Suggested Method: As a result of the foregoing study this laboratory has adopted the following slightly modified form of the Bertram method.

(a) Determination of the higher saturated fatty acid content of oils and fatty acids containing less than 2% of unsaponifiable matter.

Weigh out 5 grams of the dry sample in a 250 ml. Erlenmeyer flask. Add 75 ml. of appr. 0.5 n. alcoholic KOH and reflux under an open air or water condenser for ½ hour. Wash into a 300 ml. porcelain dish with 50 ml. of water. Evaporate the soap solution until it begins to solidify. Add 100 ml. of water and boil again until the odor of alcohol has entirely disappeared. Wash into a 2 liter Florence flask with 100 ml. of water and add 5 ml. of KOH solution (50%). Warm while swirling until the solution is clear. Cool thoroughly with cold water and slowly with swirling add a solution of 35 g. of $KMnO_4$ in about ¾ liter of water, then allow to stand over night.

After 12 hours or more add dilute sulfuric acid (50%) and concentrated $KHSO_3$ solution until all manganese is reduced and dissolved. Heat to just below the boiling point. Cool and extract 3 times with 50 ml. of petroleum ether. Collect the extractions in a 250 ml. separatory funnel and wash 3 times by running 50 ml. of water down along the inside of the funnel and swirling gently. Filter the solution into a 500 ml. extraction flask, following it up with enough fresh petroleum ether to insure quantitative transference.

Distill off the petroleum ether and warm the remaining fatty acids with a few ml. of ammonia. Add 200 ml. of hot distilled water and when all fatty acids have gone into solution add 30 ml. of 10% NH_4Cl solution. Heat to boiling and add 20 ml. of a 15% $MgSO_4$ solution. Heat again to boiling, cool and filter with suction through a layer of absorbent cotton, which is placed inside a Buchner funnel so as to cover the perforated plate as well as the walls. Wash flask and filter, neglecting any precipitate adhering to the inside of the flask. Transfer the cotton with the precipitate into the flask and add a few ml. of sulfuric acid (50%). Heat, avoiding boiling, and swirl until the cotton wad is disintegrated and the fatty acids form a clear layer. Cool, add an excess of ammonia and warm until all the fatty acid is dissolved. Repeat the precipitation and filtration as above. Transfer back to flask and decompose as before with sulfuric acid. After cooling transfer to a separatory funnel with outlet wide enough to allow the cotton fibres to pass, using petroleum ether to wash the flask. Extract twice with petroleum ether and wash the petroleum ether solution three times with water by rinsing and swirling as above. Filter into a weighed 250 ml. extraction flask washing funnel and filter with petroleum ether. Take care that all water droplets are retained by the filter paper as their presence in the filtrate is undesirable. Distill off the solvent on a steam bath and dry the flask containing the saturated fatty acids in the oven at 105° for 10 minutes.* Cool, weigh and repeat the drying in the oven until constant weights are obtained or the loss of weight does not exceed 2 mg.

The isolated fatty acids will in many cases contain several tenths of a per cent of unsaturated fatty acid. These may be assumed to consist mostly of oleic acid because the ease of oxidation increases with the degree of unsaturation. To obtain the actual saturated content it is advisable to determine the approximate iodine value of the product.** This is done directly in the flask after dissolving in 10 ml. of chloroform. Add 10 ml. of Hanus or Wijs solution from the burette or pipette, swirl for 2 minutes, then add 10 ml. of KI solution and proceed to titrate as usual. A blank run in similar fashion is required to calculate the iodine value.

The "corrected" higher saturated fatty acid content is then calculated from the following equation:

$$G = \frac{100}{S}\left[W - \frac{IW}{90}\right]$$

where G = Higher saturated fatty acids content in %

W = Weight of isolated fatty acids

I = Iodine value of the isolated f.a.

S = Weight of sample used.

(b) Determination of higher saturated fatty acid content of oils and fatty acids containing more than 2% of unsaponifiable matter.

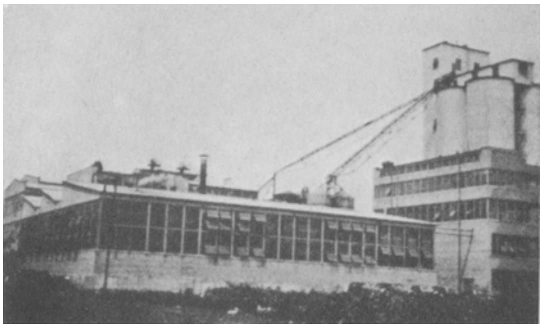
Weigh out 5 grams of the dry sample in a 250 ml Erlenmeyer. Add 75 ml of approx. 0.5 n alcoholic KOH and reflux for 1 hour. Wash into a 250 ml separatory funnel with 75 ml of water. Shake out with 50 ml of petrolether. Evaporate the soap solution in a 300 ml porcelain dish until it begins to solidify and proceed as under (a).

LITERATURE

1. S. H. Bertram, Zeitschr. f. Unters. Lebensmittel 1928, 180.

2. P. J. Gay, J. Soc. Chem. Ind. No. 51, p. 126 T (1932).

3. Hilditch & Priestmann, Analyst 56, 354 (1931).



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*This is permissible for the higher sat. fatty acids. It has been pointed out by Hilditch-Priestmann (2) that the method is not exact for lauric and lower acids, because the solubility of their magnesium salts is considerable. Myristic Acid according to the same authors should not be present to the extent of more than 5% of the total mixed fatty acids.

**The appr. iod. val. if determined as described above on a mostly saturated compound is so close to that determined by the standard methods that no noticeable error is introduced for this purpose.