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Simplified Methods for Determining Composition of Commercial Stearic and Palmitic Acids[1]

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THE need for a simple and rapid method for determining the composition of commercial stearic and palmitic acids has assumed increasing importance in recent years. This is due largely to the emphasis being placed by both consumers and producers on the use of fatty acids of given composition. The so-called Double and Triple Press Stearic acids are commercial grades which have been made and sold for more than 100 years. Each is a crystalline mix of saturated acids which has been separated from animal fatty acids either by pressing or solvent crystallization. The normal compositions of these crystalline "Stearic" acids are as follows:

	Double Press	Triple Press
% Stearic	41.00	46.5
% Palmitic	51.0	50.0
% Myristic	2.0	0.5
% Oleic	6.0	3.0
Stearic/palmitic ratio	45/55	48/52

New manufacturing methods have enabled producers of fatty acids to supply special fractions covering a much wider range of composition than were previously available. Also research and development on the utilization of fatty acids have shown the advantages and need for special fatty acid compositions. To produce and sell these new products with a given composition requires the control of composition during production.

The most generally acceptable method of determining composition of commercial stearic and palmitic acids is the fractional distillation of their methyl esters in efficient fractionating columns. Since this method requires a relatively long time, expensive equipment, and a technically trained operator, it is unsuited for production control.

The purpose of this paper is to present rapid, simple, and reliable methods of determining the composition of commercial stearic and palmitic acids. It is presented for general use to enable both the producer and the consumer to analyze the composition of fatty acids without the inherent disadvantage of the fractional distillation method used at present.

Data are presented to show the accuracy and limits of the methods when compared to composition determined by the fractional distillation of methyl esters.

Experimental Work

To check the accuracy of the fractional distillation method, used for comparison test in most of this work, samples of "high" stearic and "high" palmitic acids were prepared and analyzed. Then a mix was prepared and analyzed, using 50% of each of the "high" acids. Methyl esters were prepared for distillation in all cases. The results were obtained using a 4-ft. column with modified Stedman packing (1). They are shown in Table I.

TABLE I

Accuracy of Methyl Ester Fractionation

	High Palmitic	High Stearic	50/50 Mix	
			Calculated	Found
Palmitic	71.7	4.2	37.95	37.1
Stearic	27.4	92.3	59.85	60.3
Myristic	trace	1.3	0.65	1.0
Oleic	0.9	2.2	1.55	1.6

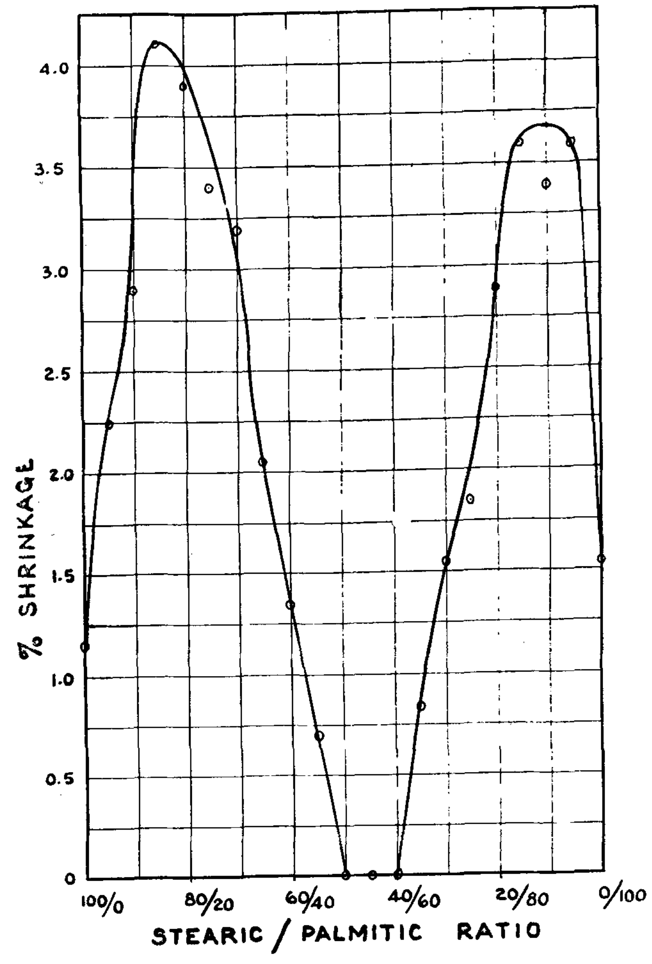

FIG. 1. Shrinkage.

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[1] Presented at the fall meeting, American Oil Chemists' Society, Chicago, Oct. 31-Nov. 2, 1949.

TABLE II

Pure Acids

	Myristic		Palmitic		Stearic	
	Literature	Found	Literature	Found	Literature	Found
Acid value	245.4	243.0	218.7	218.0	197.5	198.0
Titer	....	51.6°C.	....	60.8°C.	....	68.7°C.
I.V.	0.0	.19	0.0	.20	0.0	1.0
R.I. at 70°C.	1.4273	1.4268	1.4309	1.4310	1.4337	1.4340
M.P.	53.9°C.	52.5°C.	62.3-63.5°C.	61.8°C.	69.2-70.5°C.	69.5°C.
Estimated purity	....	95%	....	96%	....	98%

The accuracy of the column analysis may be considered to be within 1.0%, which is sufficient for most purposes. The precision can be increased by distilling larger samples, which would have taken a considerably longer time.

To obtain curves showing stearic/palmitic composition versus physical characteristics, pure acids were prepared and mixes were made at 5.0% intervals to cover the complete range from 100% stearic to 100% palmitic. These pure acids were made by fractional distillation of methyl esters prepared from relatively pure commercial fatty acids. The purified esters were hydrogenated to a low iodine value, and the fatty acids were recovered by splitting with glycerol KOH. The fatty acids were then re-distilled and the middle fraction retained. The fatty acids had the characteristics shown in Table II (2, 3).

The oleic acid used in some of the mixes was obtained by solvent crystallization of commercial oleic to a saturated acid content of less than 3.0%. It should be noted that these "pure" fatty acids were not considered to be 100% pure but were estimated by use of I.V. and constants reported in the literature.

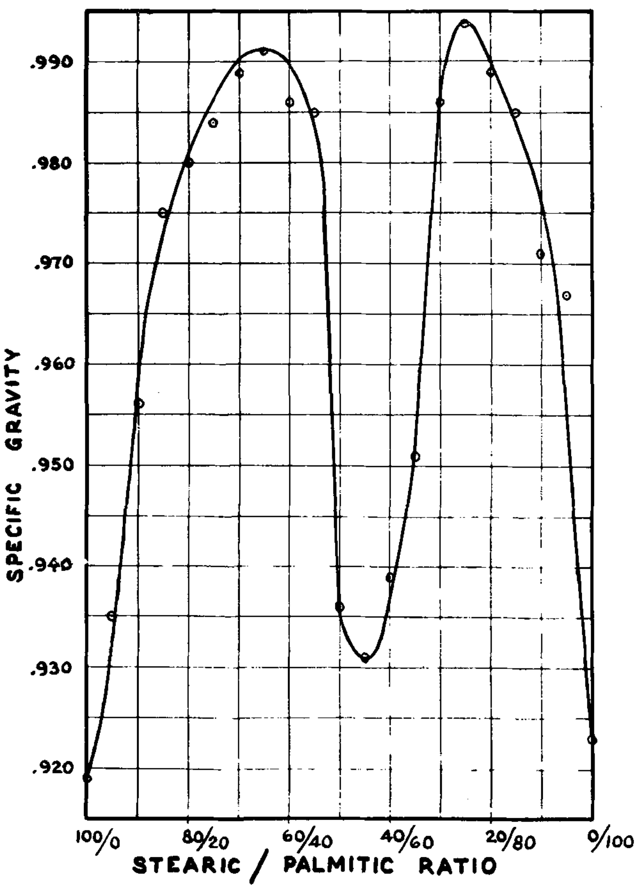

Fig. 2. Specific gravity of soild acids.

Mixes were made using the "pure" acids, and they were analyzed by fractional distillation of their methyl esters. Mixes were used instead of the pure acids to obtain proper operation of the fractionating column. By using the estimated analyses of these "pure" acids, the compositions of the mixes were calculated and compared to column analyses. The results given in Table III show that our original estimation of the pure acids were relatively accurate.

The mixes made, using the "pure" stearic and palmitic acids, were investigated for various physical properties: shrinkage during solidification, specific gravity of solidified acids, hardness (shore and penetration), refractive index at 70°C., and melting point and titer.

In order to obtain uniform solidification conditions for analysis of shrinkage, specific gravity, and hardness, the samples were melted in an 80°C. oven in small straight-sided molds and then allowed to cool slowly in the oven.

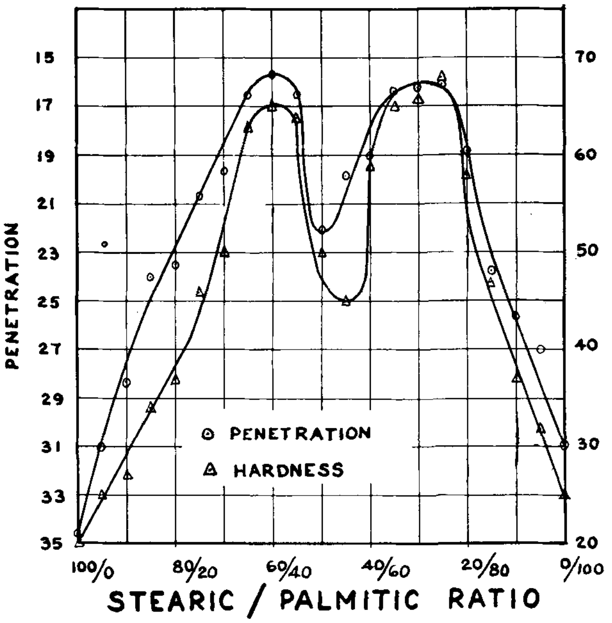

Fig. 3. Hardness

The shrinkage (Figure 1) was determined as follows: % shrinkage =

$$\frac{\text{diameter of mold-diameter of cake}}{\text{diameter of mold}} \times 100$$

The specific gravities (4) of the solidified acids are shown in Figure 2. The hardness of the cakes was obtained by two different methods (Figure 3):

a) Penetration—similar to ASTM D-5-25.
b) Shore hardness (4) (used for waxes).

TABLE III

Fractional Distillation Check on Mixes of the Pure Acids

Acid	Mix A		Mix B	
	Calculated	Found	Calculated	Found
Myristic	2.1	1.9	2.90	3.0
Palmitic	5.6	5.7	86.0	85.6
Stearic	88.4	88.0	7.6	7.9
Oleic	4.0	4.4	3.3	3.5

Crystalline inspection was also made on these samples by fracturing and examining the broken ends.

Figure 4 shows the effect of fatty acid composition on the refractive index. The refractive indices were determined at 70.0°C. within ± .1°C. with an Abbe refractometer.

Figure 5 gives the melting point and titer characteristics of the stearic/palmitic mixes. The melting points were determined by the standard open capillary tube method, using powdered samples, and recording final melting temperature. The titer was determined similar to AOCS method Cc 12-41, except that cooling was at room temperature. Of these properties, refractive index, crystal inspection, and titer seemed to offer the best possibilities for analytical purposes.

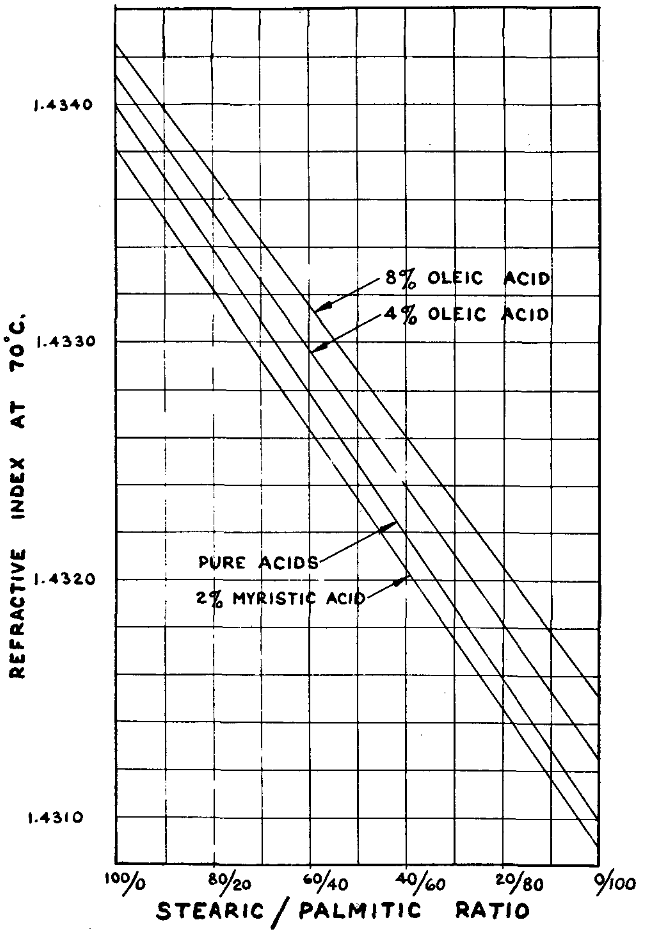

Fig. 4. Refractive index.

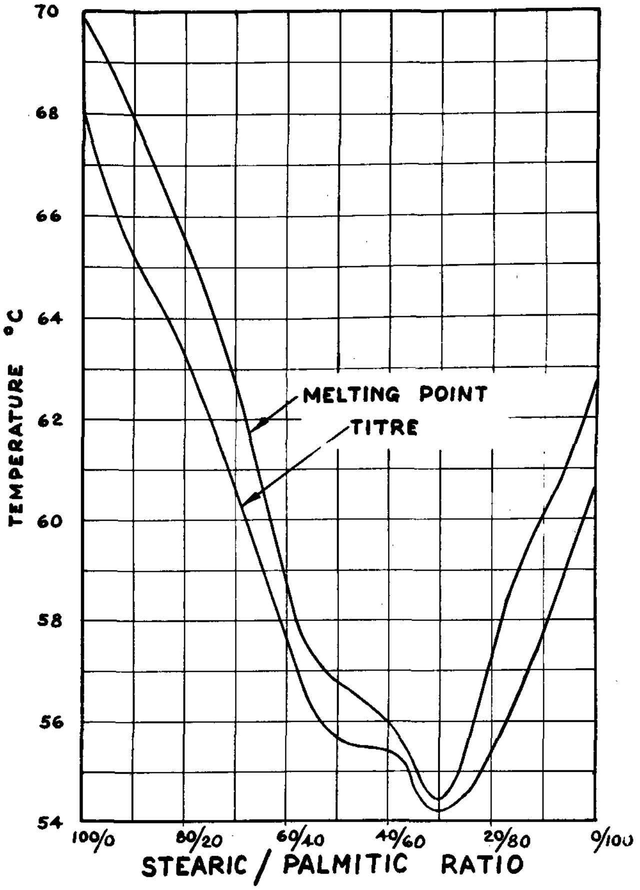

Fig. 5.

Additional curves were made showing the effect of oleic and myristic acids on refractive index and titer, within the usual limits of normal commercial products. The curves were drawn based on our estimated purities of the stearic and palmitic acids, and the 100% pure curves were extrapolated to obtain a workable set of curves for analytical purposes.

These curves were then investigated to determine their accuracy in checking composition of commercial production. The samples checked and reported were obtained from five different manufacturing sources and therefore are representative of more than one company's production. No work was done on applying these methods to mixtures containing other acids (C_{12} and C_{20}), but it is believed that they would affect the titer the same as do myristic and oleic acids. In general, the addition of 1.0% contamination to stearic or palmitic acid will lower the titer by about 0.2°C.

In order to use these curves accurately for composition determinations it was found necessary to determine the myristic acid plus oleic acid content. The oleic acid content is easily obtained from the iodine value, but the myristic acid content must be estimated. As an aid for estimating the myristic acid content of normal commercial stearic and palmitic acids, the following values were assembled, based on the average of numerous column analyses:

Double press stearic	1.5% myristic
Triple press stearic	.5% myristic
High stearic	1.0% myristic
High palmitic	1.0% myristic

All calculated compositions were made using these estimated myristic acid contents, and all the results reported include any errors made in these estimations.

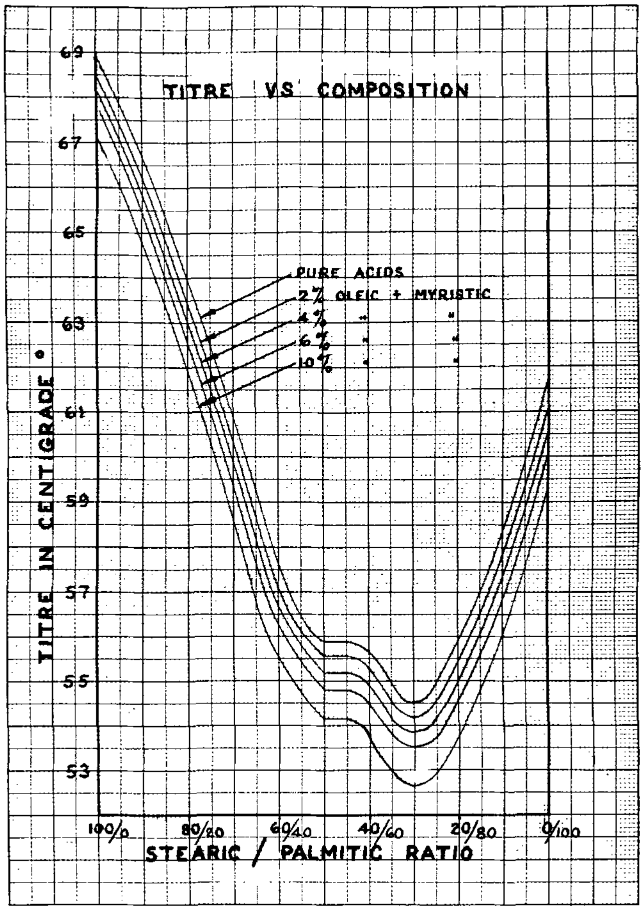

FIG. 6.

Refractive Index

Refractive index measurements (Figure 4) were made on several samples of commercial stearic and palmitic acids of known compositions. Care was taken to obtain constant temperature (within 0.1°C.) and accurate iodine values in order to make proper adjustment for oleic acid content, but the results obtained were about 5.0% in error and hence not satisfactory.

The following refractive index values measured at 70°C. are presented to show that a small error made in estimating minor constituent acids has a relatively large effect on the refractive index of the stearic-palmitic acid mix: myristic, 1.4268; palmitic, 1.4310; stearic, 1.4340; oleic, 1.4411. Due to this inherent disadvantage the method was not investigated further.

Crystal Inspection

Inspection of the crystals on the stearic-palmitic mixes showed that there was a definite visual crystal range between 40/60 and 50/50 stearic/palmitic ratio. This crystalline range had sharp limits since mixes of 39/61 and 51/49 stearic/palmitic ratio showed marked decrease in crystal structure. The presence of oleic acid and myristic acid within the scope of this investigation did not affect this crystalline range.

It was also noted that the relatively pure acids had a large soft flaky crystal. There was no definite limit of crystal pattern useful for analytical purposes, but it may be reported that 90% or better purity would give a product which is very soft and has large crystals.

To use the crystalline range between 40/60 and 50/50 stearic/palmitic ratio for a method of analysis of an unknown requires the addition of a relatively pure "known" to determine one or both of the limits of this crystalline range. When one of the crystal composition limits has been obtained, the stearic/palmitic ratio of the mix can be determined. Composition of the unknown may then be calculated by determining I.V. and estimating myristic acid. This calculation is made, using method similar to Calculation Example, Table V.

A comparison of crystal method with fractional distillation method is shown in Table IV.

TABLE IV

Composition by Crystal

Per Cent Palmitic Acid	
Crystal Method	Column Method
74.3	74.7
68.5	67.4
78.0	78.4
73.0	71.7

The accuracy of the crystal method was surprisingly good, but it had the disadvantage of usually requiring several mixes, and the accuracy of the results depended on a visual inspection of the crystal structure, thus introducing a human error dependent upon the experience and training of the operator.

Titer Method

The titer method (Figure 6) proved to be the most reliable method because results are accurate and are reproducible even with relatively untrained operators. The usefulness of the titer curve for analytical work is confined to the steep part of the curve where there is a decided difference in titer for a small change in stearic/palmitic ratio. The novelty of this titer method lies in the deliberate shifting of the composition from the flat part of the curve by the addition of a "known" high stearic or palmitic acid.

To test a product for stearic/palmitic ratio which is completely unknown, it is first necessary to obtain a titer and I.V. Then it is necessary to add a small amount (about 10%) of "high stearic" content fatty acid and determine titer on the mix. If second titer is higher than the original, the unknown is on the stearic side of the eutectic, and, if lower, it is on the palmitic side of the eutectic. Normally, the approxi-

TABLE V

Calculation Example

A sample of double pressed stearic acid having an I.V. of 5.9 and titer of 54.5°C. is used as an example. The myristic acid content is 1.5% as previously mentioned. To shift composition onto the steep part of the titer curve, 33% of a relatively pure stearic acid "known" is added.

	% Oleic	% Myristic	% Stearic	% Palmitic
Known..................................	3.5	0.0	95.0	1.7
Unknown..............................	6.5	1.5	A	B

Two-thirds of "unknown" and one-third "known" gave titer = 57.3°C. Mix has 5.5 oleic, 1.0 myristic, 64/36 stearic/palmitic ratio as read from the titer curve.

Stearic Acid Balance Equation

$$.666A + .333 \times 95 = 64 \times .935^{a}$$

A = 42.3% stearic
6.5% oleic
1.5% myristic
B = 49.7% palmitic

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[a] Per cent of stearic plus palmitic acids in the mix.

mate composition during production is known and it is not necessary to run the above tests.

When the sample to be tested has a titer on the steep part of the titer curve, all that is needed to determine composition is iodine value and titer. Samples with titers within the eutectic or flat part of the titer curve require the addition of either stearic or palmitic acid to obtain a titer on the steep part of the curve. The composition of the unknown can then be calculated from the composition determined on the mix.

A calculation example is given in Table V, showing the necessary adjustments which must be made on a material balance equation in order to obtain good results.

Table VI shows the composition of commercial stearic and palmitic acid determined directly from titer and iodine value in comparison with the composition determined by fractional distillation of the methyl ester. Note that his method is accurate in ranges of fairly high stearic or palmitic content, that is, when the titer falls on the steep part of the curve.

TABLE VI

Composition Determination
Comparison of Direct Titer Method With Column Analysis

	Titer Method		Column Analysis % Stearic	Diff.
	Titer	% Stearic		
	°C.			%
A	67.3	92.4	91.6	+0.8
B	64.0	80.0	81.2	—1.2
C	63.2	77.5	78.0	—0.5
D	58.5	63.0	65.1	—2.1
E	59.4	65.5	64.4	+1.1
F	56.0	51.5	53.1	—1.6
G	65.7	86.0	85.3	+0.7
H	63.4	78.0	79.0	—1.0
I	64.3	81.0	81.2	—0.2
J	56.2	55.0	57.6	—2.6
K	66.3	87.8	86.8	+1.0
L	66.7	89.8	90.6	—0.8
M	60.0	67.7	67.1	+0.6
N	58.3	63.4	62.7	+0.7
O	67.6	93.0	92.3	+0.7
P	57.8	60.6	60.7	—0.1
Q	66.6	89.4	89.7	—0.3
	Titer Method		**Column Analysis % Palmitic**	**Diff.**
	Titer	**% Palmitic**		
	°C.			%
R	54.7	75.0	72.8	+2.2
S	55.7	79.5	78.4	+1.1
T	54.7	75.0	74.4	+0.6

Table VII shows the composition of stearic and palmitic acids where the titer of the "unknown" is in the flat or eutectic part of the titer curve in comparison with the composition determined by fractional distillation of the methyl esters.

TABLE VII

Composition Determination
Comparison of Indirect Titer Method With Column Analysis

Per Cent Palmitic Acid
Double and Triple Press Stearic Acid

	Titer Method	Column Analysis	Diff.
	%	%	%
A	49.9	50.9	—1.0
B	49.3	49.9	—0.6
C	50.2	52.7	—2.5
D	51.1	52.3	—1.2
E	51.6	53.4	—1.8
F	49.2	51.6	—2.4
G	52.2	52.9	—0.7
H	47.6	48.0	—0.4
I	47.7	50.5	—2.8
J	48.6	50.2	—1.6
Higher Palmitic Content Acids			
K	68.9	68.2	+0.7
L	68.9	67.4	+1.5
M	70.2	71.6	—1.4
N	74.8	74.4	+0.4

The composition of Double and Triple Press Stearic acids required the addition of 33⅓% of 95% stearic content "known" to obtain a titer in the steep part of the curve. The "unknown" composition was calculated as shown in Calculation Example, Table V.

The higher palmitic content unknowns were determined by the addition of 30% "known" high palmitic acid.

The data given show that the composition as determined by titer and titer curve is normally within about 1.5% error. With accuracy of column analysis being 1.0%, the 1.5% error of the titer method when compared to column analysis is very good and gives a sufficiently reliable composition determination for production control. The method is very rapid, and satisfactory results can be obtained with relatively untrained operators.

The titer curve presented may also be used to determine the total per cent of oleic acid and myristic acid of a sample if the approximate stearic/palmitic ratio is known. This is useful in checking Double and Triple Press Stearic acids since their stearic/palmitic ratio is normally between 50/50 and 45/55, which is in the flat part of the titer curve. As an example, Triple Press Stearic has a titer of about 55.4°C. which from the chart would indicate 3.0% oleic acid plus myristic acid. An iodine value of 2.5 would show 2.8% oleic acid content, thus indicating myristic acid content of only 0.2%.

Another feature of this titer curve is that high stearic or palmitic acids may be tested for percentage of the main constituent by the use of titer alone. The results in Table VIII indicate that stearic and myristic acids are equivalent in effect on the titer of a high palmitic content fatty acid. Analogous results are also obtained on high stearic content fatty acids.

TABLE VIII

Composition of High Palmitic Acid
Titer = 56°C.

Composition	Column Analysis		Calculated from Titer Curve	or
	Sample 1	Sample 2		
Palmitic	81.0	81.0	81.0	81.0
Stearic	15.0	9.0	15	19
Myristic	1.0	7.0	1.0	
Oleic	3.0	3.0	3.0	

It is evident from these results that the composition of the main constituent of a high palmitic or stearic acid can be determined by titer alone, without reference to other fatty acids. The steep slopes of the curves are such that the oleic and myristic acids have about the same effect on the titer as the change in stearic/palmitic ratio.

Summary

The most reliable method for determining composition of commercial stearic and palmitic acids has been fractional distillation of their methyl esters. Because of the long time required for this determination it was desired to devise a more simple and rapid method which could be used for plant production control.

Pure acids were prepared and mixes of myristic, palmitic, stearic, and oleic acids were made to cover the usual composition range of commercial stearic and palmitic acids. Physical properties of these mixes were determined, resulting in data showing composition versus titer, melting point, refractive index, hardness, shrinkage, and crystallinity.

Refractive index measurements did not give desired accuracy when applied to commercial products although they appeared to be accurate when using pure acids.

A definite, easily perceptible crystalline range is between 50/50 and 60/40 palmitic/stearic ratio. The addition of palmitic or stearic as necessary to determine limits of the crystalline range permits calculation of the unknown with a fair degree of accuracy.

The composition versus titer curves were found to be reproducible and accurate. Composition of a sample may be determined directly when the titer falls on the steep part of the curves. Samples with titer on the eutectic or on the flat part of the titer curve require the addition of stearic or palmitic acids to obtain a titer on the steep part of the curve. The composition of the unknown is then calculated from the composition determined on the mix. The myristic acid content is estimated from the source of the sample, and oleic acid is calculated from iodine value determination.

Of the three methods presented in this report, the titer method proved to be the most versatile and reliable. The use of crystal inspection was surprisingly accurate but had the disadvantages of requiring several mixes, and accuracy relied on visual inspection of crystals. The use of refractive index for composition determination, although rapid in nature, only had an accuracy of about 5.0%.

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Nomographs for Calculating the Fatty Acid Composition of Oils and Fats From Iodine and Thiocyanogen Values

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NOMOGRAPHY is a rapid and relatively accurate means of graphic analysis. In a nomographic or alignment chart an index line intersects three scales of values which satisfy an equation involving three variables. When more than three variables are present, auxiliary lines are also constructed to read the value of a variable when the other variables are known. The precision of these charts depends on the selection of scale and the design and accuracy of the graduations on the axes.

Nomography has been frequently employed in chemical engineering to avoid multiplicity of routine calculations in operating a process or designing equipment and also in industrial laboratories for analytical control purposes. Few nomographs are found in the literature which are applicable to oils and fats. Wan and Ho (1) constructed a nomograph for correction and consequent calculation of the iodine value of tung oil at standard conditions from the iodine value determined at different temperatures, times of contact, and excess of reagent. Osburn, Wood, and Werkman (2) published an alignment chart for the partition determination of volatile fatty acids in a ternary mixture of acids. Using the half distillation value, Suomalainen and Archimo (3) prepared a nomograph for the calculation of the quantitative relations of the lower molecular weight fatty acids in a binary mixture of acids. Illarionov and Torchinskii (4) described a nomograph for determining the iodine values of oils from their refractive indices at different temperatures. However no nomographs have been published for the calculation of glyceride composition of oils and fats from their physical or chemical constants.

The present report describes the construction of nomographic charts for the calculation of glyceride composition of oils and fats. Equations published in the Official Methods of the American Oil Chemists' Society (5) relating the glyceride composition and the iodine and thiocyanogen values were used in constructing the nomographs by the application of the technique described in detail by Davis (6).

Construction of the Nomographs

Equations (5) for the calculation of the glyceride composition when the iodine and thiocyanogen values are determined on the triglycerides, and (A) *when no linolenin is present, are:*

(1) % Linolein, $Y = 1.246\ \mathrm{IV} - 1.253\ \mathrm{TV}$
(2) % Olein, $Z = 2.525\ \mathrm{TV} - 1.348\ \mathrm{IV}$
(3) % Saturated + Unsaponifiable, $S = 100 - (Y + Z)$

a) For the equation

(1) % Linolein, $Y = 1.246\ \mathrm{IV} - 1.253\ \mathrm{TV}$

$$\mathrm{IV} = \frac{Y}{1.246} + \frac{1.253}{1.246}\mathrm{TV} \qquad (4)$$

$$\mathrm{IV} = 0.8025\ Y + 1.0056\ \mathrm{TV} \qquad (5)$$

If the desired length of the scale for the Y- and TV-axes is 20 inches, and the range of change of Y, TV, and IV is between 0 to 100 units, and if m_Y, m_{TV}, and m_{IV} are the moduli[2] for Y, TV, and IV, respectively, then

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] The modulus is defined as the length of line that represents a change of one unit in the function of a variable.