A Method of Calculating Fatty Acid Composition from Ester Fractionation Analysis

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ESTER fractionation analysis according to the usual procedure by Hilditch (1) involves first a separation of the acids into solids and liquids by using the Twitchell method, or by means of low temperature crystallization. These two groups of acids are converted to methyl esters and distilled in an efficient fractionating column to separate into fractions that contain not more than two adjacent series of homologous saturated and unsaturated acids.

From the saponification equivalents and iodine values of the fractions it is possible to calculate the proportions of each saturated acid and of each of the homologous groups of unsaturated fatty acids in the mixture.

In connection with the unsaturated acids, the method does not give the proportions of each type of unsaturation, *i.e.*, the proportions of monoene, diene, etc. For the purposes of calculation the unsaturated acids of the same carbon number are given a mean unsaturation expressed in terms of the number of H atoms required to convert to the fully saturated acid, *e.g.*, methyl oleate would be represented by (−2H), methyl linoleate (−4H) and mixtures by intermediate values. These are determined by plotting saponification equivalents against iodine values.

Two Saturated and Two Unsaturated Esters Present

Assuming that in any given fraction the saponification equivalent of the saturated acids is the same as that of the whole fraction, the proportions of the three components are given as w_1, w_2, and w_3 in the solution of three simultaneous equations as follows:

$$\begin{aligned} w_1/s + w_2/s_2 + w_3/s_3 &= 1/s \\ w_2I_2 + w_3I_3 &= I \\ w_1 + w_2 + w_3 &= 1 \end{aligned}$$

w_1 is the proportion of saturated C_n plus C_{n+2} components, w_2 the proportion of the unsaturated component whose saponification equivalent is S_2 and iodine value I_2, and w_3 the proportion of the unsaturated component whose saponification equivalent is S_3 and iodine value I_3.

The solution of this set of equations is:

$$\begin{aligned} w_1 &= 1 - w'_1I \\ w_2 &= w'_2I \\ w_3 &= w'_3I \end{aligned}$$

where

$$\begin{aligned} w'_1 &= -S\,(S_3 - S_2)\,[I_2S_2\,(S - S_3) - I_3S_3\,(S - S_2)]^{-1} \\ w'_2 &= +S_2\,(S - S_3)\,[I_2S_2\,(S - S_3) - I_3S_3\,(S - S_2)]^{-1} \\ w'_3 &= -S_3\,(S - S_2)\,[I_2S_2\,(S - S_3) - I_3S_3\,(S - S_2)]^{-1}. \end{aligned}$$

Insertion of the numerical values in the expressions will yield the proportions of the components, but the chemist having a large number of analyses with the same components may have tables prepared beforehand, by substituting the appropriate constants in the expressions. w'_1, w'_2, and w'_3 involve only S and the constants S_2, S_3, I_2 and I_3 and therefore can be determined for values of S ranging from S_2 to S_3 by unit intervals; the results may be recorded in the form of a table. The values of w'_1, w'_2, and w'_3, corresponding to a value of S found in an analysis, are multiplied by the value of I, and the result subtracted from 1 in the case of w'_1, to give the proportions w_1, w_2, and w_3 of the three components. As an example for $C_{14}-C_{16}$ (tetradecenoic and hexadecenoic acids) we have the constants $I_2 = 105.8$, $I_3 = 94.8$, $S_2 = 240$, $S_3 = 268$.

The analysis gives $S = 251.4$ and $I = 73.6$. Corresponding to $S = 251.4$ in the table of w'_1, w'_2, and w'_3 computed from the above constants we find

$$\begin{aligned} w'_1 &= 0.009899 \\ w'_2 &= 0.005602 \\ w'_3 &= 0.004296 \end{aligned}$$

Multiplying w'_1 by $I = 73.6$ and subtracting from 1, $w_1 = 0.27$
w'_2 by I $w_2 = 0.41$
w'_3 by I $w_3 = 0.32$

Slide Rules and Nomograms

From the solution $w_2 = w'_2\,I$ it is deduced that $\log w_2 = \log w'_2 + \log I$, and therefore it is possible to construct a simple slide rule if the values of I and w'_2 are marked off along separate logarithmic scales, the values of w'_2 being labelled with the corresponding values of S. Figure 1 shows a slide rule

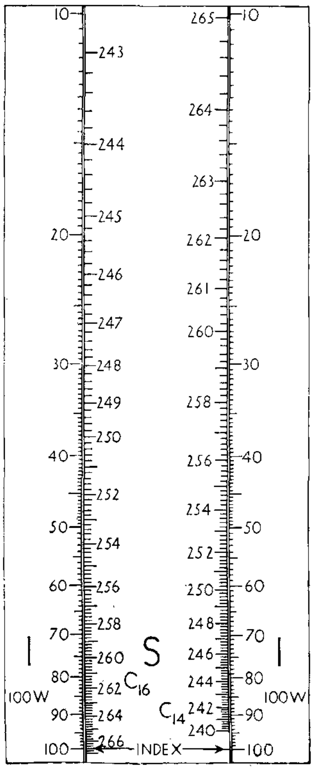

FIG. 1. Slide rule for the calculation of w_2, (C_{14}) and w_3, (C_{16}).

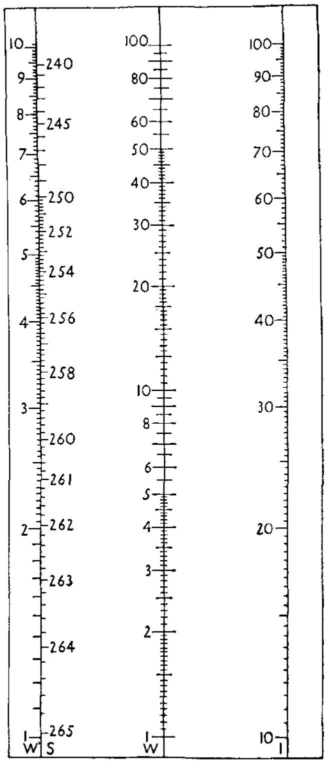

FIG. 2. Nomogram for calculating w_2, (C_{14}) in fractions containing $C_{14} - C_{16}$.

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for determining w_2 and w_3 for the mixture $C_{14}-C_{16}$. The index is set to the required value of I on the outer scales, and 100w is read on the outer scales at the points opposite the required S on the inner scales. A nomogram for determining w_2 can be constructed, using three parallel logarithmic scales similar to those in the slide rule. In the nomogram the scale of w_2, which is drawn parallel to and halfway between the scales of I and w'_2, has an interval equal to half that of I and w'_2. Two strips of one cycle and one strip of two cycle graph paper would be convenient. Figure 2 is a nomogram for finding w_2 for fractions containing $C_{14}-C_{16}$.

The Condition $I_2S_2 = I_3S_3$

This condition can be used to simplify the expressions of the solutions written above. They reduce to

$$\begin{aligned}
w_1 &= 1 - IS/I_2S_2 &&= 1 - IS/I_3S_3 \\
w_2 &= I\,(S - S_3)\,[S_3\,(I_3 - I_2)]^{-1} &&= I\,(S - S_3)\,[I_2\,(S_2 - S_3)]^{-1} \\
w_3 &= I\,(S - S_2)\,[S_2\,(I_2 - I_3)]^{-1} &&= I\,(S - S_2)\,[I_3\,(S_3 - S_2)]^{-1}
\end{aligned}$$

and the quantities w'_1, w'_2, and w'_3 are now in a more suitable form for the computation of the tables and subsequent building of slide rules and nomograms. But these simplified solutions are now in a form which can be quickly evaluated with the aid of a calculating machine or tables. Substituting the appropriate constants, we find the particular solutions in three cases are as follows:

$$\begin{aligned}
&\quad C_{10} - C_{12} \\
w_1 &= 1 - 3938\,I.S.\,10^{-8} && \text{(saturated components)} \\
w_2 &= 2590\,I(212 - S).\,10^{-7} && \text{(unsaturated } C_{10}\text{)} \\
w_3 &= 2981\,I(S - 184).\,10^{-7} && \text{(unsaturated } C_{12}\text{)} \\
&\quad C_{12} - C_{14} \\
w_1 &= 1 - 3938\,I.S.\,10^{-8} && \text{(saturated components)} \\
w_2 &= 2981\,I(240 - S).\,10^{-7} && \text{(unsaturated } C_{12}\text{)} \\
w_3 &= 3376\,I(S - 212).\,10^{-7} && \text{(unsaturated } C_{14}\text{)} \\
&\quad C_{14} - C_{16} \\
w_1 &= 1 - 3938\,I.S.\,10^{-8} && \text{(saturated components)} \\
w_2 &= 3376\,I(268 - S).\,10^{-7} && \text{(unsaturated } C_{14}\text{)} \\
w_3 &= 3767\,I(S - 240).\,10^{-7} && \text{(unsaturated } C_{16}\text{)}
\end{aligned}$$

One Saturated and Two Unsaturated Esters Present

This condition is found in the methyl esters of liquids. In mixtures of methyl esters of C_{16} and C_{18} acids only one saturated acid, palmitic acid, is present. This is because stearic acid (C_{18}) is removed with the "solid" fraction. The fundamental equations for this case are:

$$\begin{aligned}
w_{1/S_1} + w_{2/S_2} + w_{3/S_3} &= 1_{/S} \\
I_2w_2 + I_3w_3 &= I \\
w_1 + w_2 + w_3 &= 1
\end{aligned}$$

where w_1 is the proportion of saturated ester, whose saponification equivalent = S_1, w_2 the proportion of the unsaturated ester whose saponification equivalent = S_2 and iodine value = I_2, w_3 the proportion of the unsaturated ester whose saponification equivalent = S_3 and iodine value = I_3.

Solving these, it is found that

$$\begin{aligned}
w_1 &= 1 - K\,[S^{-1}S_1S_2S_3\,(I_3 - I_2) - S_2S_3\,(I_3 - I_2) + S_1\,(S_3 - S_2)\,I] \\
w_2 &= K\,[S^{-1}S_1S_2S_3I_3 - S_2S_3I_3 + S_2\,(S_3 - S_1)\,I] \\
w_3 &= -K\,[S^{-1}S_1S_2S_3I_2 - S_2S_3I_2 - S_3\,(S_1 - S_2)\,I] \\
K &= [I_3S_3\,(S_1 - S_2) - I_2S_2\,(S_1 - S_3)]^{-1}
\end{aligned}$$

If the expressions —

$$\begin{aligned}
m_1 &= 1 - K\,[S^{-1}S_1S_2S_3\,(I_3 - I_2) - S_2S_3\,(I_3 - I_2)] \\
m_2 &= K\,[S^{-1}S_1S_2S_3I_3 - S_2S_3I_3] \\
m_3 &= K\,[S^{-1}S_1S_2S_3I_2 - S_2S_3I_2]
\end{aligned}$$

are each evaluated for the 27 values of S ranging from 270 to 296, tables of w_1, w_2, and w_3 can be prepared by adding the quantities —

$$\begin{aligned}
n_1 &= -KS_1\,(S_3 - S_2)\,I \\
n_2 &= +KS_2\,(S_3 - S_1)\,I \\
n_3 &= -KS_3\,(S_1 - S_2)\,I
\end{aligned}$$

to each of the respective 27 values. If punched card machines or other computing facilities are available, m_1, m_2, m_3, and n_1, n_2, n_3 can be evaluated at intervals of 0.1 in S and I. Then to calculate the values of w_1, w_2, and w_3 in an analysis, the entries m_1, m_2, m_3 corresponding to S are respectively added to the entries n_1, n_2, n_3 corresponding to I. Note that $m_3 = 1 - m_1 + m_2$, and $n_3 = n_1 + n_2$. For example if $S_1 = 270$ (palmitic acid), $S_2 = 268$, $I_2 = 94.8$ (hexadecenoic acid), $S_3 = 295.7$, $I_3 = 98.7$ (C_{18} unsaturated acids) the solutions are:

$$\begin{aligned}
w_1 &= m_1 + n_1 = -117.3\,S^{-1} + 1.434 - 0.010514\,I \\
w_2 &= m_2 + n_2 = 2969.0\,S^{-1} - 10.996 + 0.009683\,I \\
w_3 &= m_3 + n_3 = -2851.6\,S^{-1} + 10.562 + 0.000831\,I
\end{aligned}$$

Two Saturated and One Unsaturated Esters Present

In the solid acids it is assumed that hexadecenoic acid is not present in the mixtures of methyl esters containing C_{16} and C_{18} acids. It is present almost exclusively in the liquid fractions on account of its high solubility. Thus in the solids the methyl esters within the saponification equivalent range 270-298 will contain two saturated acids, but only one unsaturated.

In this case the equations to be solved are these:

$$\begin{aligned}
w_{1/S_1} + w_{2/S_2} + w_{3/S_3} &= 1_{/S} \\
w_3I_3 &= I \\
w_1 + w_2 + w_3 &= 1
\end{aligned}$$

where w_1 is the proportion of the saturated ester whose saponification equivalent is S_1, w_2 the proportion of the saturated ester whose saponification equivalent is S_2 and w_3 the proportion of unsaturated ester whose saponification equivalent is S_3 and iodine value I_3. w_3 is simply equal to $I_{/I_3}$.

The solutions w_1 and w_2 reduce to:

$$\begin{aligned}
w_1 &= M\,[S^{-1}S_1S_2S_3I_3 - S_1\,(S_2 - S_3)\,I - S_1S_3I_3] \\
w_2 &= M\,[-S^{-1}S_1S_2S_3I_3 - S_2\,(S_3 - S_1)\,I + S_2S_3I_3] \\
M &= [I_3S_3\,(S_2 - S_1)]^{-1}
\end{aligned}$$

Insertion of numerical values in these expressions will give the proportions, or tables may be prepared by substituting the appropriate constants and evaluating each of the expressions:

$$\begin{aligned}
p_1 &= M\,[S^{-1}S_1S_2S_3I_3 - S_1S_3I_3] \\
p_2 &= M\,[-S^{-1}S_1S_2S_3I_3 + S_2S_3I_3]
\end{aligned}$$

for the 29 values of S from 270 to 298 and adding the values:

$$\begin{aligned}
q_1 &= -MS_1\,(S_2 - S_3)\,I \\
q_2 &= -MS_2\,(S_3 - S_1)\,I
\end{aligned}$$

respectively, for the range of I desired. Or if facilities are available, p_1, p_2, q_1, and q_2 can be determined at intervals of 0.1 in S or I. It is noticed that

$p_2 = 1 - p_1$ so that it is necessary to evaluate either p_1 or p_2 only. Also $w_3 = -(q_1 + q_2)$.

For example, if $S_1 = 270$ (palmitic acid), $S_2 = 298$ (stearic acid), $S_3 = 296$, $I_3 = 85.8$ (oleic acid), we find

$$w_1 = p_1 + q_1 = 2873.6\,S^{-1} - 9.643 - 0.00076\,I$$
$$w_2 = p_2 + q_2 = -2873.6\,S^{-1} + 10.643 - 0.01090\,I$$
$$w_3 = -(q_1 + q_2) = 0.01166\,I$$

Summary

The calculations involved in ester fractionation analysis require the solution of sets of three simultaneous equations. Repeated solution of these equations is avoided by obtaining expressions for the proportions of the components. Frequent analysis of similar fractions is further simplified by the preparation of tables, slide rules, or nomograms.

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Solvent Extraction of Granular Cottonseed Cake

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DURING the past several years a process for extracting granular presscake which has many novel features has been developed and put into successful commercial operation in several plants. Although some of these features have been described piece-meal in the past, an integrated picture of this solvent extraction plant has not before been presented.

Considerable experience in the extraction of cottonseed and cottonseed cake has been gained in recent years. In some plants cottonseed meats are flaked and then extracted in equipment essentially similar to that used for soybeans. A more popular approach has been to extract presscake. In the 1951-52 period 14 solvent plants were put into operation. Eleven of these were designed to operate on prepressed cottonseed meats or presscake, and three employ direct extraction of meats. The popularity of extraction of prepressed meats is due in part to lower residual oil in finished meal, simpler operation, and ease of conversion from an existing screw-press to a prepress extraction operation.

All cottonseed solvent extraction processes must overcome certain fundamental hurdles. First, the economics of the cottonseed industry do not justify a large investment for solvent-extraction equipment, especially where there is an existing screw-press plant. Second, solvent-extracted cottonseed is dusty and difficult to pelletize. Third, cottonseed is difficult to handle mechanically through a solvent-extraction plant. In devising this process, the designer took all of these factors into account.

This new process takes presscake prepared by conventional screw-pressing, except that it may contain 10% oil, prepares it for extraction by simple granulation to a coarse size, and extracts it with the Rotocel system which will be described. This method results in an improved granular meal prepared in compact, easily operated equipment that can be installed at an economical price.

Preparation of Presscake

Presscake for extraction is prepared in essentially the same fashion as regular low-oil cake. The solvent extraction process is surprisingly flexible, and it will accept a wide variety of presscake including hydraulic cake. Generally speaking, the only change in the pressing process that is required is new shafts for the screw-presses, by which their capacity is about doubled for prepressing compared with low-oil meal operation. The oil content of the cake may be between 6.5 and 11%, and the moisture content may be as low as 6%.

The rate of feed to the plant is controlled by the feeder under the presscake surge bin as shown on the flow diagram. Cake directly from the screw presses, normally in the form of pieces ¼ to ½ in. thick and 1 to 3 in. in length and width, is first broken in a double roll sawtooth horizontal crusher to make particles ¼ to ½ in. in size with a minimum amount of fines. Broken hydraulic presscake may be mixed with or substituted for the screw press cake fed to the crusher. The broken cake is granulated in a three-high corrugated rolling mill.

This is the entire preparation system. It may be housed in a small building immediately adjacent to the solvent extraction plant. The operator need only make occasional inspection visits to this building. The total connected horse power in this area is 40 h.p. for 100 tons per day of cake; the actual power requirement is about 21 h.p.

Rotocel Extraction System

The cake extraction system consists of a Rotocel extractor, a vapor-type meal desolventizer, and miscella desolventizing system combined in an unconventional manner. A description of construction and operation of the Rotocel is necessary to understand this system.

In the extractor a rotor approximately 6 ft. high and 13 ft. in diameter, divided into 18 sector-shaped cells, rotates slowly about a vertical axis inside a vapor-tight tank. Only a ¼ h.p. motor is required to turn the rotor at about one revolution per hour.

Cake granules are fed continuously through a seal conveyor, where they are slurried with miscella, into each cell. There the granules form beds which rest on hinged, screened doors, supported by rollers on a track. As the cells move around the circular path,

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[1] Presented at the 45th annual spring meeting, San Antonio, Tex., April 12-14, 1954.