spectra reveal, in addition to the prominent bands assigned to characteristic groupings of the eleostearic acid molecule, the progression bands by means of which carbon chain length can be computed.

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REFERENCES

1. Bickford, W. G., DuPré, E. F., Mack, C. H., and O'Connor, R. T., J. Am. Oil Chemists' Soc., *30*, 376–381 (1953).
2. Hilditch, T. P., "Chemical Constitution of Natural Fats," pp. 132–133, 221–222. John Wiley and Sons, New York, 1941.
3. Holmes, R. L., Pack, F. C., Minor, J. C., and McKinney, R. S., J. Am. Oil Chemists' Soc., *31*, 417–418 (1954).
4. Jackson, J. E., Paschke, R. F., Tolberg, W. E., Boyd, H. M., and Wheeler, D. H., J. Am. Oil Chemists' Soc., *29*, 229–234 (1952).
5. Jones, R. N., McKay, A. F., and Sinclair, R. G., J. Am. Chem. Soc. *74*, 2575–2578 (1952).
6. Meyer, R. J., and Schuette, H. A., presented at the 46th (1955) Annual Meeting of the Am. Oil Chemists' Society, New Orleans, La., April 17–20, 1955; and similar paper, presented before the Division of Paint, Plastics, and Printing Ink Chemistry at the 128th Meeting of the American Chemical Society, University of Minnesota, Minneapolis, Minn., September 11-16, 1955.
7. Mod, R. R., Skau, E. L., and Planck, R. W., J. Am. Oil Chemists' Soc., *30*, 368–371 (1953).
8. Morrell, R. S., J. Chem. Soc., *101*, 2082–2089 (1912).
9. Nicolet, B. H., J. Am. Chem. Soc., *43*, 938–940 (1921).
10. O'Connor, R. T., Heinzelman, D. C., McKinney, R. S., and Pack, F. C., J. Am. Oil Chemists' Soc., *24*, 212–216 (1947).
11. Paschke, R. F., Tolberg, W. E., and Wheeler, D. H., J. Am. Oil Chemists' Soc. *30*, 97–99 (1953).
12. Paschke, R. F., and Wheeler, D. H., J. Am. Oil Chemists' Soc., *32*, 473–478 (1955).
13. Paschke, R. F., and Wheeler, D. H., J. Am. Oil Chemists' Soc., *32*, 469–473 (1955).
14. Planck, R. W., Pack, F. C., and Heinzelman, D. C., Proc. Am. Tung Oil Assoc., *1950*, 37–47.
15. Strain, H. H., J. Am. Chem. Soc., *63*, 3448–3452 (1941).
16. Thomas, A. W., and Thomson, J. C., J. Am. Chem. Soc., *56*, 898 (1934).

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Analysis of Polyethylene Glycol Esters

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FATTY ACID MONOESTERS of polyethylene glycols are widely useful surface-active substances. As prepared industrially, these products usually contain not only the monoester but also appreciable amounts of the diester and unreacted polyethylene glycol as well. This result is unavoidable when one mole of fatty acid is esterified with one mole of polyethylene glycol, and it is also encountered in the base-catalyzed reaction of ethylene oxide with a fatty acid:

$$3RCOH + 3n\ C_2H_4O \rightarrow RCO(CH_2CH_2O)_nH + RCO(CH_2CH_2O)_nCR + HO(CH_2CH_2O)_nH$$

In an investigation of the latter reaction in this laboratory it was of interest to know approximately the relative amounts of the three products obtained under various reaction conditions. The nature of the mixture precludes estimating the composition by means of the hydroxyl and saponification numbers. Attempts to find a colorimetric or a precipitation method specific for the polyethylene glycol were unsuccessful (1, 2, 5). Chromatography as a means of separation also did not appear to be promising.

The characteristic high solubility of the polyethylene glycols in water suggested that this component of the mixture might be selectively extracted. This would permit analysis by means of hydroxyl and saponification numbers. However, when the ester is derived from a fatty acid having 9–20 carbon atoms and a polyethylene glycol having 9–20 oxyethylene units, the monoester will also be appreciably, if not completely, soluble in water at room temperature. If water is added to a mixture containing such a monoester, a solution or an emulsion is generally obtained. Advantage must be taken of the knowledge that the monoester will follow an inverse solubility-temperature relationship in water and will also be less soluble in salt solutions. This behavior is typical of the nonionic surfactants. Accordingly the fatty acid monoester is found to be substantially insoluble in hot salt solution while the polyethylene glycol dissolves and consequently can be separated.

Several tests were carried out to determine the effectiveness of extraction of polyethylene glycol in the manner contemplated. Sodium chloride was used to prepare a saturated salt solution at room temperature. Typically 25 g. of sample were extracted with 50 ml. of salt solution at 95–100°C. The procedure used in carrying out the extraction and in recovering the extracted sample is described in detail in the following section. Typical lauric acid-ethylene oxide condensation products, known to contain free polyethylene glycol along with monoester and diester, were extracted successively three times, and the change in hydroxyl and saponification numbers was noted after each extraction. From the data obtained (Table I) it was concluded that three extractions would insure complete removal of the polyethylene glycol.

TABLE I
Effect of Successive Extractions on Polyglycol Removal

	Hydroxyl number [a]		Saponification number [a]	
	Sample 1	Sample 2	Sample 1	Sample 2
Original material	100.9	80.0	95.3	75.7
After one extraction	61.9	53.2	108.3	85.3
After two extractions	56.5	47.3	107.8	85.8
After three extractions	56.3	46.7	109.8	87.5

[a] mgKOH/g.

As a further check on the removal of polyethylene glycol, relatively pure polyethylene glycol-600 monolaurate and dilaurate were used to prepare a blend which contained about 30% monoester, 35% diester, and 35% free polyethylene glycol-600. A sample of this blend was extracted, using the standard procedure, and the hydroxyl and saponification numbers were determined after extraction. Polyethylene gly-

TABLE II
Completeness of Removal of Polyglycol by Extraction

	Original material	After extraction	With 10% polyglycol added	After re-extraction
Hydroxyl No.[a]	81.7	32.2	49.0	32.1
Saponification No.[a]	58.1	91.3	83.8	93.5

[a] mgKOH/g.

TABLE III

Analysis of Typical Polyethylene Glycol "Monoesters"

Material	Saponification number [a]		Hydroxyl number after extraction [a] (B)	Calculated composition			
	Before extraction (A)	After extraction (C)		Polyglycol %	Monoester %	Diester %	Total %
Polyethylene glycol 600 "monolaurate"	69.0	86.2	44.6	20.0	49.8	28.6	98.4
Polyethylene glycol 400 "monooleate"	82.7	97.3	50.2	15.0	50.5	33.1	98.6
Polyethylene glycol 600 "monooleate"	62.6	75.0	42.4	16.5	59.7	26.8	103.0
Polyethylene glycol 400 "monostearate"	84.6	102.5	40.6	17.5	38.9	41.1	97.5
Oleic acid-12 mol ethylene oxide adduct	69.1	87.0	45.9	20.6	51.5	30.7	102.8
Stearic acid-10 mol ethylene oxide adduct	77.2	100.8	32.9	23.4	31.9	44.6	99.9

[a] mgKOH/g.

col, in amounts approximately 10% of the weight of the extracted sample, was then added and the extraction was repeated. The results obtained (Table II) show that both the originally present and the added polyethylene glycol were removed in the extractions. This is seen from the close agreement of the hydroxyl and saponification numbers obtained after the two sets of extractions.

The effect of pH on the rate of phase separation during extraction was found to be not critical. With the salt solution at pH 10 separation was slow, but in the range 2 to 8.5 satisfactory results were obtained.

Considerable importance attaches to the steps described in the procedure for removing dissolved water and salt from the extracted sample. These contaminants are present in amount sufficient to introduce considerable error in the determinations. In the present investigation hydroxyl numbers were obtained by a procedure essentially as described by Ogg, Porter, and Willits (3). A 2-g. sample was mixed with 10 ml. of acetylating reagent, and the mixture was heated for 1 hr. on a steam bath. Saponification numbers were determined by refluxing a sample with alcoholic potassium hydroxide, as described by Scott (4).

Results for typical polyethylene glycol monoesters obtained by the method described are given in Table III. The small free-acid content of the samples has been neglected in the totals.

Experimental Procedure

A 125-ml. separatory funnel is needed for the extraction. Then 25 g. of sample and 50 ml. of sodium chloride solution, saturated at room temperature, are added to the separatory funnel, which is then immersed to the neck in a boiling-water bath. Sufficient time is allowed for the contents to reach about 95–100° C., and then the funnel is removed and vigorously shaken. It is returned to the bath and allowed to stand until the separation of phases is visibly complete. This usually requires 10-15 min. The lower brine layer is then separated and discarded. Using the same amount of fresh brine, the extraction is repeated two more times in the same manner.

After the third extraction the organic layer is transferred to a 100-ml. round-bottom, distillation flask, equipped with a short column, condenser, receiver, and trap. The apparatus is connected to a vacuum, and the flask is heated with a water bath. The usual care must be taken to control the heating and regulate the vacuum so as to avoid bumping and foaming. When the pressure is reduced to about 2 mm. and the water bath is brought to boiling, the stripping operation is continued for 15 min. The organic layer is then removed and filtered through a medium-porosity, sintered glass filter. An infrared lamp is useful for keeping the material hot and speeding the filtration. The recovered sample should be clear. Saponification and hydroxyl numbers are obtained and recorded in terms of milligrams of potassium hydroxide per gram. A retained sample of original material is used to obtain the additional necessary saponification number.

Calculation of Results

The accuracy of the method of analysis described depends upon the substantially complete removal of polyethylene glycol by extraction, which must be presumed in calculating the results. It is also necessary to know the molecular weights of the fatty acid and the polyethylene glycol used, from which the hydroxyl number of the monoester and the saponification numbers of the monoester and the diester, are calculated. Commercial grades of polyethylene glycol are designated according to average molecular weight, and, in the case of fatty acid-ethylene oxide condensation products, the polyethylene glycol molecular weight can be calculated from the quantity of ethylene oxide known to have been consumed in the condensation reaction. The same average molecular weight is presumed to apply to the polyethylene glycol present in both the esters as well as in the free state. When the ester mixture contains residual free acid, corrections must be made to the hydroxyl and saponification numbers as these are determined.

The following formulae can be developed for the content in weight percentage of polyglycol, monoester, and diester.

Where:

p = weight percentage of polyglycol
m = weight percentage of monoester
d = weight percentage of diester
e = weight percentage of total ester
A = saponification number of original sample as mgKOH/g.
B = hydroxyl number of extracted sample as mgKOH/g.
C = saponification number of extracted sample as mgKOH/g.
y = calculated hydroxyl or saponification number of the monoester as mgKOH/g.
z = calculated saponification number of the diester as mgKOH/g.

it can be shown that,

$$p = 100(C - A)/C$$
$$m = 100\,BA/Cy$$
$$d = 100\,A(C - B/Cz$$
$$e = 100\,A/C$$

The above formulae were derived from the following material balance equations:

$$A = \frac{m}{100}y + \frac{d}{100}z$$

$$B = \left(\frac{100}{100-p}\right)\left(\frac{m}{100}v\right)$$

$$C = \left(\frac{100}{100-p}\right)\left(\frac{m}{100}y\right) + \left(\frac{100}{100-p}\right)\left(\frac{d}{100}z\right)$$

Alternatively the hydroxyl number of the original sample can be determined and used with A, B, and C in several possible combinations of three to obtain additional solutions for p, m, and d. When the acid number of the sample is small and there is reason to believe that inert substances are not present to any appreciable extent, the sum of p, m, d should approach 100%. Further, when this is the case, p = 100-e, d = e-m, and m = e-d.

Summary

The products obtained by esterification of polyethylene glycols with fatty acid, or by means of the reaction of ethylene oxide with fatty acids, can be analyzed for their content of monoester, diester, and unreacted polyethylene glycol by taking advantage of the extractability of the polyethylene glycol with water. A hot salt solution is used to insure selective extraction. Saponification and hydroxyl numbers are used to calculate the composition of the mixture; the molecular weights of the acid and glycol are presumed to be known.

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REFERENCES

1. Dal Nogare, Stephen, and Mitchell, John Jr., Anal. Chem., *25*, 1376 (1953).
2. Hill, Uno T., Ind. and Eng. Chem., Anal. Ed., *18*, 317 (1946).
3. Ogg, C. L., Porter, W. L., and Willits, C. O., Ind. and Eng. Chem., Anal. Ed., *17*, 394 (1945).
4. Scott, W. W., "Standard Methods of Chemical Analysis." vol. II, p. 2043, D. Van Nostrand Co. Inc., New York, 1939.
5. Shaffer, C. B., and Critchfield, F. H., Ind. and Eng. Chem., Anal. Ed., *19*, 32 (1947).

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Report of the F.A.C. Subcommittee on Dilatometry, 1956-1957

THE DILATOMETRIC METHODS SUBCOMMITTEE of the Fat Analysis Committee was established in 1953 to select a standard dilatometric method. Dilatometry is used extensively to compare the solid-liquid phase relationships of fats, based on the specific volume change that occurs when fat goes from a solid to a liquid state. A standardized procedure is needed because the dilation values depend not only on the composition of the fat but also on the manner in which the fat is solidified and conditioned.

The following is a summary of the collaborative work which led to the method that is being recommended by the subcommittee. The results are reported as solid fat index values, which are equivalent to the melting dilation in milliliters per 1,000 g. of fat. The melting dilation is the total dilation minus the dilation caused by the thermal expansion of the fat and indicator fluid.

First Series of Collaborative Samples

Because dilation values are to some extent empirical, it was decided to determine first how well the different laboratories agreed with each other. Therefore each of the eight laboratories represented on the subcommittee was asked to analyze three check samples by its own laboratory method. The results fell into two general groups.

SOLID FAT INDEX

	Sample	10°C.		21.1°C.		33.3°C.	
		Av.	Range	Av.	Range	Av.	Range
Group 1 (3 labs.)	1	29.1	28.6–29.6	22.2	21.6–22.7	7.1	7.0– 7.3
	2	28.5	27.8–29.5	18.3	17.6–19.1	10.4	9.9–11.0
	3	42.8	42.1–43.0	25.7	25.3–26.3	4.4	4.3– 4.5
Group 2 (5 labs.)	1	33.0	32.5–33.5	24.6	23.8–25.3	7.6	7.2– 8.0
	2	36.3	35.0–36.9	24.2	23.4–24.8	10.9	10.6–11.6
	3	50.0	49.0–51.0	32.3	31.7–33.5	4.9	4.2– 6.7

Sample 1: Prime steam lard.
Sample 2: Soybean oil shortening.
Sample 3: Soybean margarine oil.

The laboratories whose results were in group 1 included a tempering step in the conditioning of the fat. Those whose results were in group 2 did not. There were variations in the fat conditioning procedure in each group however.

Group 1

10 or 15 min. at either 0°C. or −5.3°C.
30 min. at 26.7°C.
15 min. at either 0°C. or −5.3°C.

Group 2

Either 70, 90, or 120 min. at 0°C.

There were also differences in the dilatometers that were used.

Number	Sample size	Confining fluid
5	9 g.	Water
1	6 g.	Water
1	3 g.	Mercury
1	4 g.	Alcohol-water

Second Series of Collaborative Samples

The following variations in the conditioning of the fat were studied with the second series of samples.

Procedure A

15 min. at 0°C.
30 min. at 26.7°C.
15 min. at 0°C.

Procedure B

15 min. at −5°C.
30 min. at 26.7°C.
15 min. at −5°C.

Procedure C

90 min. at 0°C.
(3 laboratories studied the effect of 30, 60, 90, and 120 min. at 0°C.)

Dilation readings were taken at 10°C., 21.1°C., and 33.3°C. when they were considered constant. The