in Figure 8 indicate the times at which changes in slope occur. These changes correspond to the melting-point changes shown in Figure 3.

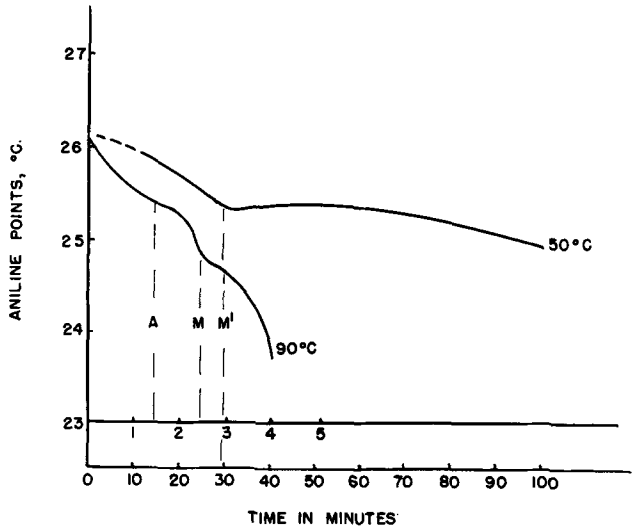

FIG. 8. Plot of aniline points *versus* time for reaction of destearinated lard with sodium methoxide at 90 and 50°C.

It is apparent that the exact times involved to reach specific points in lard treatment are different from the times required to reach equivalent points in the destearinated lard reactions. A change in catalyst activity because of such things as variation in the particle size of the catalyst could easily shift the entire curve on the time scale. In this work all of the lard and the catalyst used for the lard reactions at all temperatures were taken from the same lot. The same is true of the destearinated lard. However a different lot of catalyst was used for each fat, and obviously lard and destearinated lard differ in glyceride composition. Nevertheless similar reaction patterns result from the treatment of each with sodium methoxide.

REFERENCES

1. Weidermann, L. H., Weiss, T. J., Jacobson, G. A., and Mattil, K. F., presented at the 34th Fall Meeting, American Oil Chemists' Society, New York, October 17–19, 1960.

2. Bailey, A. E., Proceedings of the Fifth Research Conference, American Meat Institute, 1953, pp. 11–17.

3. Jacobson, G. A., J. Am. Oil Chemists' Soc., in press.

4. Summerbell, R. K., Franko, B. R., Wiedermann, L. H., and Pollaczek, E., presented at the Minneapolis meeting, American Chemical Society, September, 1955.

5. Eckey, E. W., Ind. Chem., 40, 1183–1190 (1958).

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The Differential Cooling Curve. A Technique for Measuring Certain Fat Characteristics

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The differential cooling-curve technique consists of a measurement of the difference in the cooling rate of a crystallizing and noncrystallizing fat or oil under specific conditions. The temperature differential between the two samples is measured by thermocouples and is plotted as fractions of a millivolt by a recording potentiometer. The significance of the various peaks encountered in the curves is discussed, and a rapid means of determining trisaturated triglyceride content in modified lard and related fats is presented.

The technique is a highly sensitive measurement of the thermal properties of a crystallizing fat, and as such offers an absolute measurement of various degrees of modification of lard.

Curves of other fats representing different types of glyceride mixtures are presented.

THE COOLING CURVE has long been recognized as a valuable tool for studying crystallization phenomena of various substances. Among those who have applied this technique to fats were Quimby and coworkers, who noted differences in the cooling curves of tallow, lard, and other triglyceride mixtures (1). More recently Luddy and coworkers used the cooling-curve technique to illustrate changes in cooling characteristics brought about by treatment of lard and tallow by sodium methylate (2). The method described in their paper is based upon the considerable evolution of heat encountered when lard congeals and is of value in the laboratory for determining the end-point of lard crystal modification. Hannewijk, Haighton, and Lavery have demonstrated the usefulness of the differential type of melting and cooling curves in following the melting characteristics and polymorphism of glycerides and glyceride mixtures (3, 4, 5). In this paper are presented some results obtained by using a rapid and sensitive method of measuring the cooling characteristics of fats, the differential cooling curve.

Methods and Apparatus

The differential cooling-curve technique is based upon the difference in cooling rate between a standard oil, which will not crystallize when cooled to 0°C., and an unknown fat, which will crystallize at that temperature. To measure this small difference in temperature, copper constantan thermocouples were employed. The constantan leads of the two thermocouples were connected together (series opposed), and the copper leads were connected to the recording potentiometer. Connected in this manner the thermocouple assembly measures directly the difference in temperature in the two tubes. In actual practice two 15 x 125-mm. tubes are filled to a depth of 6 cm. with the reference and the sample, respectively. The thermocouples are inserted and placed 30 mm. from the bottom and in the center of the tube. The tubes are placed in a

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boiling water bath until they are at equilibrium (at least 10 min.) and then are put in an ice bath for the cooling phase. The difference in the temperature in the two tubes measured by the thermocouple is recorded by the recording potentiometer. The potentiometer used in this work is the Speedomax Type G, Model S Indicating Recorder, Leeds and Northrup Company.

Obviously the heat of fusion and the solubility characteristics of the unknown fat at the constantly-changing temperatures will greatly affect the cooling rate of the crystallizing fat as compared with that of the winterized cottonseed oil standard. The temperature differential thus set up is recorded as distinctly different types of curves for different types of fats, such as lard and crystal-modified lard. It should be noted that the curves in this paper are shown as they appear on the recorder, hence are drawn from right to left instead of the more conventional form of left to right. Since this method is empirical by nature, it is necessary to standardize the depth and position of the thermocouples in the tubes as well as the type of tubes used. However, if the thermocouple tips are kept at a uniform distance from the sides and bottom of the tube, the reproducibility is excellent.

Discussion

Interpretation of Differential Cooling Curves. Three factors of importance in the interpretation of differential cooling curves are a) the over-all shape of the curve, b) the height of the occurring peaks, and c) the time at which the peaks occur during the cooling phase. For example, the curve for lard is characterized by a large peak at about 4 min. running time whereas in crystal-modified lard this peak is absent (Figure 1). This evolution of heat at 4 min. is a manifestation of the heat of crystallization of the fat and corresponds to the temperature rise for lard found when a standard type of cooling curve is employed. The peak at 4 min. can be related to the disaturated monounsaturated (S_2U) triglyceride fraction of the lard. A comparison of S_2U rich fractions from lard and modified lard is shown by the curves of Figure 2. The marked absence of the peak at 4 min. in the curve of the modified lard S_2U fraction implies a fundamental change in the crystal habit of the fat, resulting from structural changes in the S_2U triglycerides and is reflected in other physical measurements, such as X-ray diffraction pattern and dilatometric behavior (6, 7).

Concurrent with the elimination of the S_2U peak by lard modification is the development of another peak at about 3 min. (Figure 1). This peak is often not discernible in lard but emerges as modification progresses. The 3-min. peak offers an indication of the trisaturated triglyceride (S_3) content of the fat. Differential cooling curves of samples containing increasing amounts of 58-titer hardened cottonseed oil standard showed a proportional increase in the S_3 peak (Figure 3). From the iodine value of the hard fat and the amount added to each sample the percentage of S_3 was calculated and plotted against the peak height. The resulting curve is shown by Figure 4. It was found that the curve could be used as a standard curve for the rapid determination of S_3 content in modified lard and lard which has been subjected to directed rearrangement. Typical experimental S_3 values from the standard curve are shown in Tables I and II, along with theoretical values and values obtained by fractional crystallization from acetone according to the method of Riemenschneider *et al.* The S_3 fraction was precipitated at 25°C., the S_2U at 5°C. No attempt has been made to determine the S_3 content of lard from the vestigial peak at 3 min. since the formation of the much larger adjoining S_2U peak undoubtedly influences the S_3 peak to an unknown degree.

TABLE I

Comparison of % of Trisaturated Triglyceride Value from Standard Curve with Calculated Values

Sample	% S_3 Standard curve	% S_3 Calculated
CML [a]	2.6	2.4
CML + 2% HCSO	4.1	4.1
CML + 4% HCSO	5.8	5.8
CML + 6% HCSO	7.4	7.5
CML + 8% HCSO	9.3	9.2
CML + 12% HCSO	12.3	12.6

[a] Crystal-modified lard.
[b] 58-Titer hydrogenated cottonseed oil.

TABLE II

Comparison of Trisaturated Triglyceride Values from Standard Curve with Fractional Crystallization Values

Sample	% S_3 Standard curve	% S_3 Fractionations
A	3.9	3.6
B	6.4	6.6
C	7.2	7.4
D	8.6	8.7
E	8.2	9.0
F	9.5	9.7
G	12.4	12.8
H	16.2	16.9

Much of the variability of lard seen in commerce can be traced to the geographical origin of the lard as well as the proportion of fat from different parts of the animal body. The difference between the "killing" or internal fat and the "cutting" or more external fat is shown by the comparison of fat extracted from the ruffle depot fat and the external back fat of the pig (Figure 5). The known variation in S_3 content is quite evident by the height of the curve in the 3-min. region. An examination of the untreated lard by differential cooling curve thus provides insight into the melting characteristics of the ultimate crystal-modified lard product to be made from the lard.

Differential Cooling Curves of Fat Containing Other Types of Glyceride Mixtures

The differential cooling curve may be used to identify other types of fat since many show curves of a shape peculiar to their own glyceride mixture. For example, the S_2U and SU_2 glycerides of hydrogenated vegetable oils of the C_{16-18} class produce a curve found to be characteristic of selectively hydrogenated vegetable oil (Curve A, Figure 6). Curves for a non-selective type of hydrogenation where more trisaturated triglycerides are formed during the reaction show development of the expected 3-min. S_3 peak in addition to the broad peak at 4 min. (Curve B, Figure 6).

Monoglyceride and diglyceride preparations produce a curve marked by a high initial peak after about 1 min. of cooling (Figure 7). This peak however appears to be in part the result of insulation effects

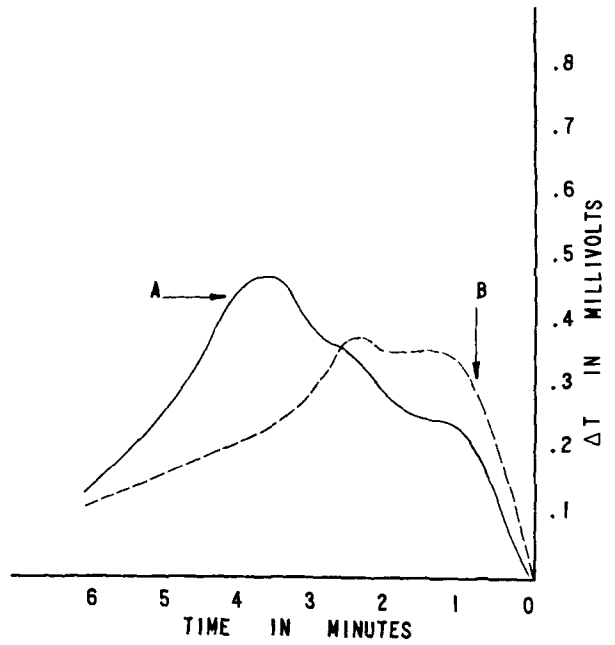

FIG. 1. Differential cooling curves of lard (Curve A) and crystal-modified lard (Curve B).

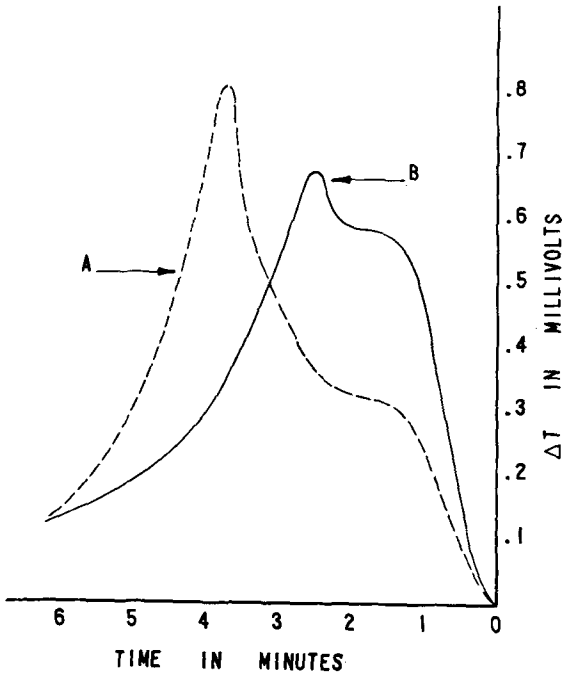

FIG. 2. Differential cooling curves: Curve A—40% of ($S_3 + S_2U$) portion of lard in cottonseed oil; Curve B—40% of ($S_3 + S_2U$) portion of crystal-modified lard in cottonseed oil.

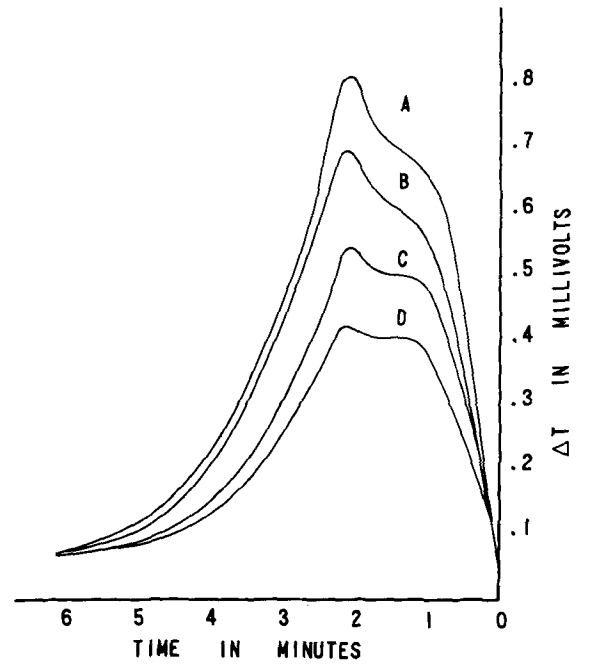

FIG. 3. Differential cooling curves of 58-titer hydrogenated cottonseed oil in winterized cottonseed oil.
Curve A, 20% Curve C, 10%
Curve B, 16% Curve D, 6%

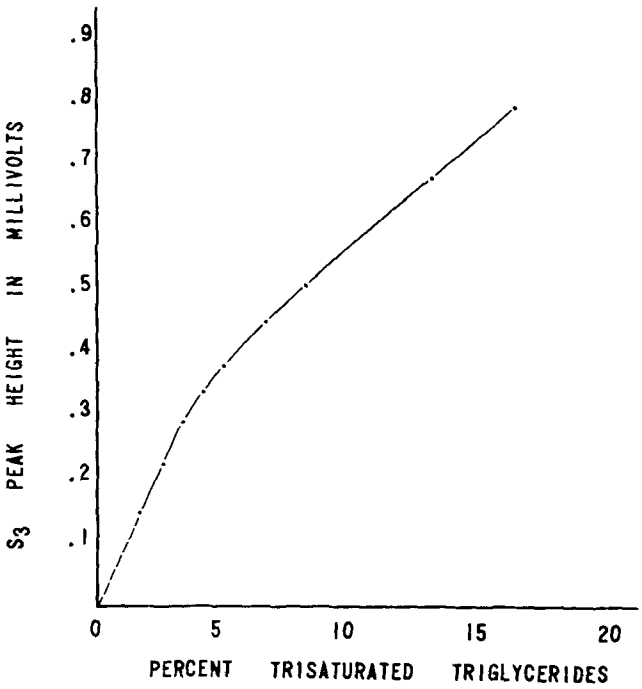

FIG. 4. Standard curve: % S_3 *vs.* peak height.

from fat crystal deposition on the wall of the sample tube rather than a release of the heat of fusion alone. The slight peak occurring at 2½ to 4 min. can be related to the saturated fatty acid content of the fat used in the monoglyceride reaction.

Fats composed of glycerides containing shorter-chain fatty acids exhibit cooling curves similar to those observed for S_2U and SU_2 rich fats (Figure 8). Even though coconut oil contains approximately 80% trisaturated triglycerides, the effect of the shorter-chain lengths upon the curve was to eliminate any S_3 peak in the 3-min. area and to displace the curve beyond the area where the C_{16-18} acids normally appear.

Blends of different fats produce curves which may or may not reflect the characteristics of the fats comprising the blend, depending on the proportion of the components and the diversity of the glyceride composition of each fat used. A curve for a 50:50 blend of tallow with coconut oil reveals each component of

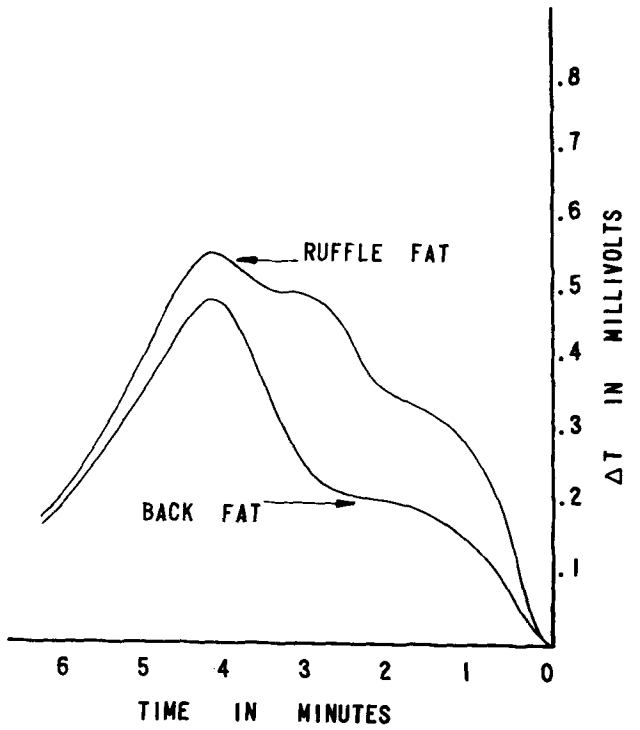

FIG. 5. Differential cooling curves of pig ruffle fat and back fat.

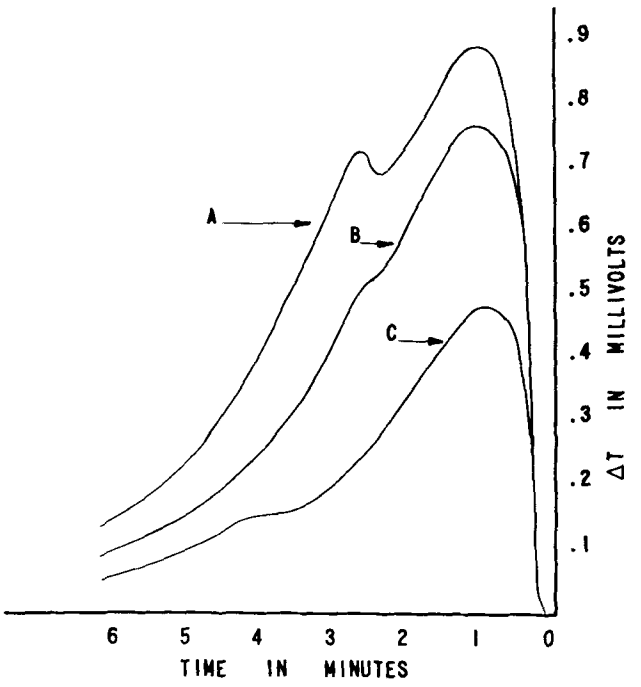

FIG. 7. Differential cooling curves of monoglyceride preparations from different fats.
Curve A, hydrogenated cottonseed oil
Curve B, hydrogenated peanut oil
Curve C, corn oil

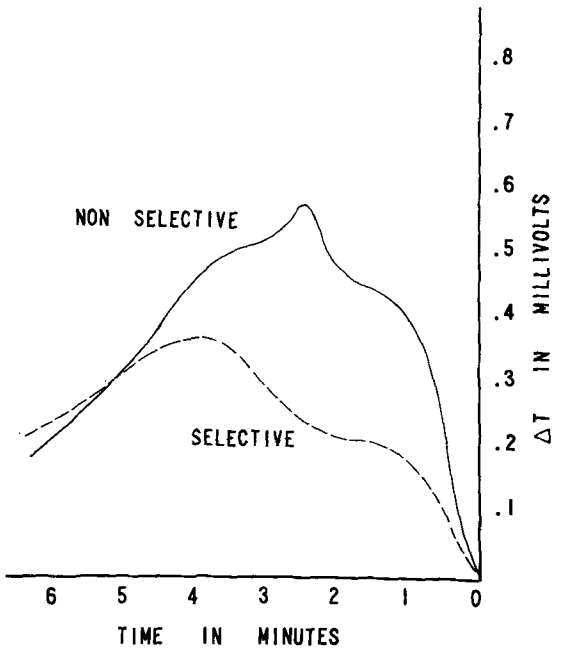

FIG. 6. Differential cooling curves of cottonseed oil, hydrogenated to the same refractive index, selectivity and nonselectively.

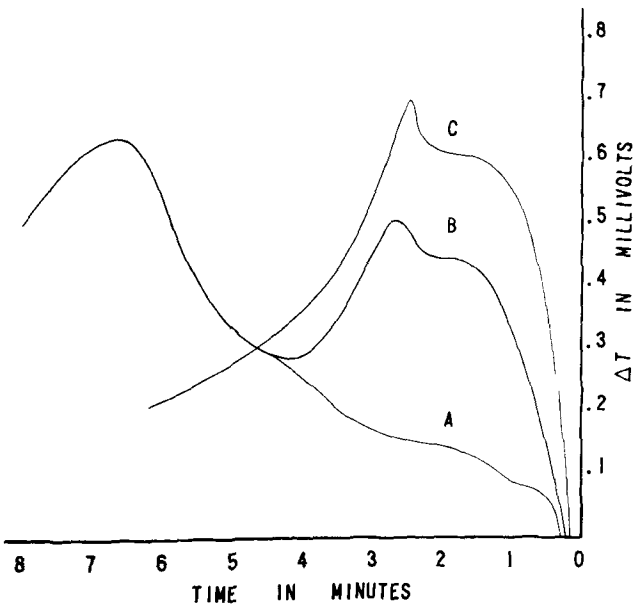

FIG. 8. Differential cooling curves.
A. Coconut oil.
B. 50% coconut oil, 50% tallow
C. 65% lard, 35% tallow

the blend with a minimum of interference between the curves (Figure 8). A blend of 65% lard and 35% tallow, on the other hand, produces a curve which is characteristic of the tallow, the minor component (Figure 8). Here the typical S_2U peak of lard has been obliterated, and other means of detection of the lard component would have to be relied upon for identification of the fat.

REFERENCES

1. Quimby, O.T., Wille, R.L., and Lutton, E.S., J. Am. Oil Chemists' Soc., *30*, 186 (1953).
2. Luddy, F.E., Morris, S.G., Magidman, P., and Riemenschneider, R.W., J. Am. Oil Chemists' Soc., *32*, 522, (1955).
3. Haighton, A.J., and Hannewijk, J., J. Am. Oil Chemists' Soc., *35*, 344 (1958).
4. Lavery, H., J. Am. Oil Chemists' Soc., *35*, 418 (1958).
5. Hannewijk, J., and Haighton, H.J., J. Am. Oil Chemists' Soc., *35*, 457 (1958).
6. Wiedermann, L.H., Weiss, T.J., Jacobson, G.A., and Mattil, K.F., J. Am. Oil Chemists' Soc., in press.
7. Weiss, T.J., Jacobson. G.A., and Wiedermann, L.H., J. Am. Oil Chemists' Soc., in press.
8. Riemenschneider, R.W., Luddy, F.E., Swain, M.L., and Ault, W.C., Oil and Soap, *23*, 276 (1946).

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