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Dilatometric Measurements

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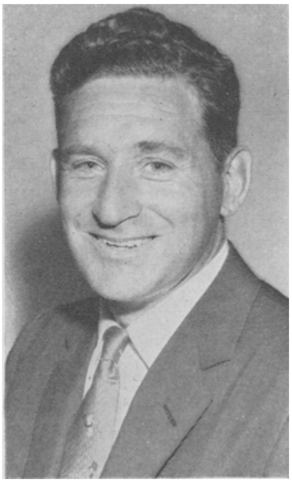
Dilatometry is essentially a measurement of changes in specific volume. It is useful in the field of fats and oils to detect or analyze phase transformations because fats expand when they melt and generally contract when they undergo polymorphic change to a more stable form.



W. Q. Braun

Dilatometric measurements have great value in the margarine and shortening industries because they characterize fats over a wide temperature range. Plastic fats are mixtures of liquid oil and small crystals of solid fat, and their consistency is largely dependent upon their solid fat content. It is, of course, advantageous to know if a fat will produce a product with desirable consistency characteristics before the product is plasticized. Since dilatometry provides a fairly simple means of estimating solid fat contents at various temperatures. it is useful both for consistency control and for formulation work.

According to Andersen (1), dilatometry has been used as an analytical method in some margarine establishments since the early 1920's. The first publication on this subject appears to have been by Norman in 1931 (2). Hofgaard published dilatometric data on a large number of fats in 1938 and also pointed out the relationship between dilatometric curves and solid fat content (3). Since his work was published in Danish, it was not widely read in this country at that time.

Interest in dilatometric measurements in this country before 1940 is indicated by a number of publications (4, 5). However the first extensive studies which appeared in the literature were by Bailey and co-workers in a series of articles beginning in 1944 (6, 7, 8).

When the specific volume of a fat is plotted against temperature over a wide temperature range, one obtains an irregular curve similar to the one in Figure 1. There is a linear volume-temperature relationship only at temperatures below $T_{.S.}$, where the fat is completely solidified and above $T_{.L.}$, where the fat is completely liquefied. When extending the solid and liquid fat expansion lines to T.$_{M.}$, it becomes apparent that fat expands when it melts.

If the melting dilations and the coefficients of expansion of all triglycerides were the same, the fraction ab/bc would represent the solid fat content. The melting dilations of different triglycerides vary greatly however, as can be seen from the figures reported by Craig (9) in Table 1. The fraction ab/bc in Figure 1 therefore is only a rough approximation. Any attempt to determine the actual solid fat content of a natural fat from dilatometric measurements would become extremely complex and would require previous knowledge of the amounts of the individual components and their properties. An excellent discussion of the problems involved, even with simple mixtures of triglycerides, has been published by Lutton (10).

TABLE I

Melting Dilations of Single Triglycerides

Triglyceride	Melting Dilation
	ml./gm.
Triolein	0.0665
Stearodiolein	0.0905
Oleodistearin	0.0925
Oleodipalmitin	0.0965
Palmitodistearin	0.1406
Stearodipalmitin	0.1460
Tristearin	0.1516
Tripalmitin	0.1621

Even though the results are not absolute, they do have a great deal of comparative value. Bailey (11) has proposed a simplified calculation of solid fat content. In commercial plastic fats one usually is interested only in the relative solid fat contents at temperatures above 10°C. The average melting dilation of fats over the range 10 to 50°C. is approximately 0.1 milliliter per gram. Each .001 milliliter per gram melting dilation then corresponds to 1% solids. The melting dilation is the total fat dilation minus the dilation due to the thermal expansion of the liquid fat. This method of calculating solid fat contents is now commonly used, but the results are generally referred to as solid fat indices instead of percentages of solid fat. Some laboratories report their results only as melting dilations. While this is technically more correct, the term "solid fat index" is probably more graphic for many of the people that are concerned in the production of fat products.

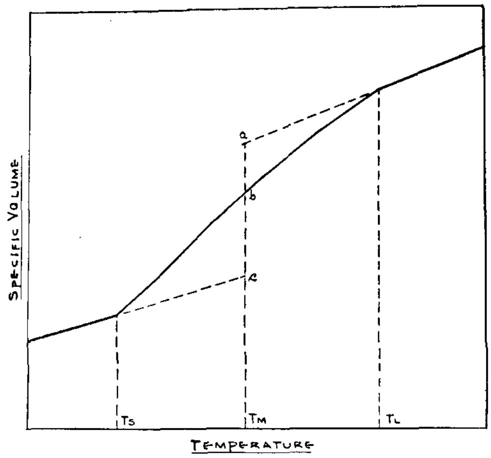


FIG. 1. Schematic drawing of dilatometric curve showing method used for estimating solid fat content.

FAT DILATOMETERS MAY vary considerably in size and construction (see Figure 2). Basically those used for general analytical work consist of a bulb which is attached to a calibrated capillary tube. The fat in the bulb is confined by a liquid, such as water or mercury, and as the fat expands, the confining liquid is displaced into the capillary bulb. The bulb size is usually approximately 5 or 10 ml., but larger ones are also used.

Dilatometers similar to A in Figure 2 are used quite extensively for routine work. A definite amount of deaerated colored water solution is first pipetted into the dilatometer. The dilatometer is then weighed, filled with liquid fat which is free of dissolved gases, sealed, and reweighed. Since the temperatures of interest in margarine and shortening control are above 0°C., water is a satisfactory confining fluid. One dilatometer of this type that is quite widely used has a bulb of approximately 10-ml. capacity and a 1.400-ml. capillary scale graduated in .005-ml. marks. Two ml. of a 1% dichromatic solution are used as the confining fluid.

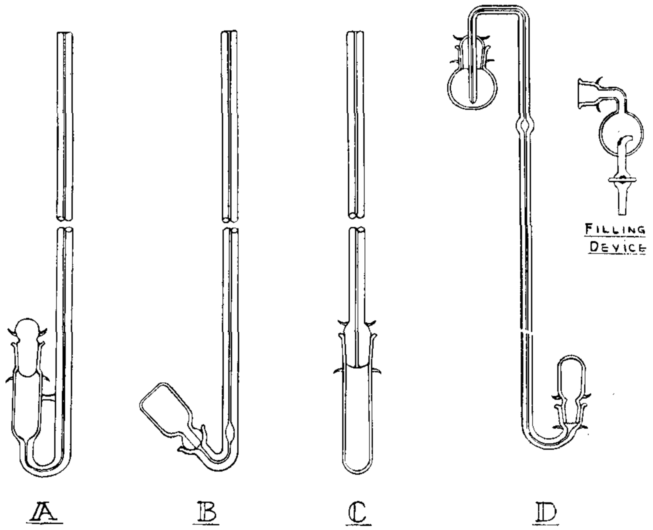


FIG. 2. Diagramatic drawings of some of the types of dilatometers used for dilatometric measurements.

Type B in Figure 2 uses mercury as a confining liquid and therefore can also be used for low temperature work. In this instrument (12) the bulb and capillary are joined by a ground glas joint, and different-sized bulbs can be used when this is advantageous.

Type C uses an 80% alcohol solution as confining fluid. The bulbs have equal volumes to the 0 mark of the capillary when the capillary is inserted. A definite volume of fat at 60°C. is pipetted into the bulb and layered with the alcohol solution. The capillary is then inserted to bring the alcohol to a definite height in the capillary. Since the amount of alcohol and fat in each dilatometer is very nearly the same, comparative differences in dilation can be read directly without correcting for sample weight and expansion of the confining fluid. A disadvantage of this method is that the alcohol solution has some solvent effect, especially on fats with high monoglyceride or free fatty acid contents.

Type D measures fat expansion by the weight of the mercury which has been displaced. This type of instrument is capable of determining very small volume changes (6, 9), such as those occurring during polymorphic changes, but is cumbersome for general analytical use.

In order to obtain good dilatometric results it is essential that the oil and confining fluid be free of dissolved or occluded gases. The melted oil can be degassed with a good mechanical vacuum pump. When water is used as confining fluid, it can also be degassed quickly by vigorous boiling under reduced pressure. The dilatometer should be sealed as quickly as possible after degassing. It is especially important that the dilatometer be sealed before any of the fat has solidified because solidification of the fat seems to occlude quite a bit of air. For routine analytical work it is usually unnecesary to make any corrections other than those for the thermal expansion of the confining fluid when Pyrex dilatometers are used. For very precise measurements, corrections should be made for stem immergence and glass expansion. Some data on expansion of Pyrex glass have been published by Buffington and Latimer (13). The water baths that are used should be capable of maintaining a temperature constant to a plus or minus .05°C. Mercury thermoregulators with relay are generally used to control temperatures. A refrigerating coil in the bath is also needed for low temperatures.

At the present time there is no standard method for making dilatometric measurements. The method used to chill and condition the fat in the dilatometer has a great bearing upon the results which are obtained. Since most laboratories use the results empirically for control and formulation work, this does not make too much difference provided that they use a standard procedure. Results from different laboratories are not always comparable however, because of this.

SINCE IT WOULD BE desirable to have a uniform method, a subcommittee of the Fat Analysis Committee of the American Oil Chemists' Society is now studying dilatometric methods. It seems that most laboratories are now using one or the other of the following two methods of conditioning the fat, or slight modifications thereof.

Method A

1. The filled dilatometer containing completely melted fat is placed in a 0°C. bath and chilled for 90 min.
2. The dilatometer is then transferred to a constant temperature bath set at the lowest desired temperature. When the reading is constant, it is recorded.
3. The dilatometer is then placed in a bath at the next highest desired temperature and kept there until a constant reading is obtained. This is continued through the whole desired temperature range, including a reading at a temperature at which the fat is completely melted.

Method B

1. The dilatometer containing melted fat is placed in an 0°C. bath and chilled for 15 min. It is then transferred to a 26.7°C. (80°F.) bath for 30 min. After this it is again chilled for 15 min. at 0°C.
2. The dilatometer is transferred to a bath at the lowest desired temperature, and readings are taken at various temperatures as in method A1.

Most fats give constant readings in 30 to 45 min. Some fats however slowly change in volume over fairly long periods of time. Because of this some laboratories record their readings at a specified time such as 30 or 45 min.

Corrections are then made for the expansion of the confining liquid and for the liquid expansion of the melted oil. For fats consisting largely of C_{16} and C_{18} acids, the thermal expansion of the completely melted oil is approximately .00083 ml. per gram per degree C. This can be taken as a standard liquid slope. However better checks are usually obtained when an experimentally obtained thermal expansion is used. Very slight occlusion of air or not quite thorough degassing will cause differences in the thermal expansion.

Where T_M is a temperature at which the fat is completely melted, the solid index at any temperature T will be:

$$\left[\left(\frac{\text{Total fat dilation between } T_M \text{ and } T}{\text{sample weight}}\right) - \left(\begin{matrix}\text{Thermal expan-}\\ \text{sion per gram}\\ \text{per deg.}^\circ\text{C.}\end{matrix}\right)\left(T_M - T\right)\right] \times 100$$

The total fat dilation is the total expansion minus the expansion due to the confining liquid.

Results on the same fat at four different temperatures by methods A and B are shown in Table 2. Although either method can be used for comparative purposes, it is obvious from these results that the method of conditioning the fat has great effect on dilatometric results. Proponents of method B point out that chilling followed by tempering more nearly represents the condition of a commercially plasticized fat than does method A.

TABLE II
Effect of 80°F. Tempering on Dilatometric Results

Temp.	Solid Index	
	Non-tempered	Tempered
10°C.	33.1	28.2
21.1°C.	18.8	14.6
26.7°C.	10.6	10.1
33.3° C.	3.7	3.6

A probable explanation for the differences in the results of the two methods is that some of the lower melting glycerides go into solid solution with higher melting glycerides when the liquid fat is rapidly chilled. Upon tempering, the more unsaturated glycerides go out of solid solution while the higher melting ones remain solid. Upon chilling, the lower melting glycerides do not have the opportunity of going back into solid solution.

A difficulty encountered when working with a fat of very high solid fat content or when working at very low temperatures is the formation of vacuoles. These are caused when the fat solidifies very rapidly at the interface between the confining fluid and the fat. This acts as a dam and prevents the confining fluid from being drawn into the bulb as the fat shrinks. Instead the fat shrinks away from the dilatometer bulb, forming vacuoles. Normally, vacuoles are not formed with oils of margarine or shortening consistencies at 0°C., but they are a problem at this temperature with certain coating fats. Some people try to eliminate this by alternately chilling and partially melting the fat. This is not always successful, and it can also cause variation in the conditioning of individual samples. A novel way of overcoming vacuole formation has been described by Lutton (10), in which the chilled fat in the dilatometer bulb is placed in a pressure bomb and the block is broken by applying high pressure. Another method which has been described in an effort to get away from vacuole formation has been by making small individual pellets which are placed in the dilatometer bulb (8, 9).

It has been mentioned previously that dilatometric measurements are used quite extensively to predict product consistency. However comparisons are valid only when similar fats are plasticized under nearly identical conditions. Crystal size has a bearing on consistency, and this varies not only with plasticization conditions but also with the characteristics of the fat. For example, lard and soybean oil which have been hydrogenated to equal solid indices at 70°F. and plasticized under identical conditions will not necessarily have the same consistency at 70°F. Molecular rearrangement of certain fats also affects their crystallization habits.

Dilatometric measurement takes too long a time actually to control the individual hydrogenation batches. Most operators depend upon the refractive index reading and some type of congeal or setting point. The dilatometric method however shows up differences in selectivity of hardening much better than these faster analytical methods and is therefore of great value in blending two or more batches of hardened fat to a desired consistency. Dilatometric results on a particular product may also point out slight changes which should be made in subsequent converter batches to obtain the desired degree of hydrogenation. Figure 3 shows the dilatometric curves of two soybean oils hardened to approximately the same iodine number. This happens to be a fairly exaggerated case, and congeal points and Wiley melting points together with the iodine numbers or refractive indices show up differences in selectivity here. Figure 4 however gives the dilatometric curves of two samples of soybean oil in which the differences in melting points, congeal points, and refractive indices expressed as butyro numbers are within experimental error. There is a considerable difference in dilatometric curves and also in penetrometer readings of the plasticized product at 70°F. Figure 5 shows the effect of rearrangement on lard. Again the differences in the dilatometric curves are much greater than one might expect from the differences between melting points and congeal points.

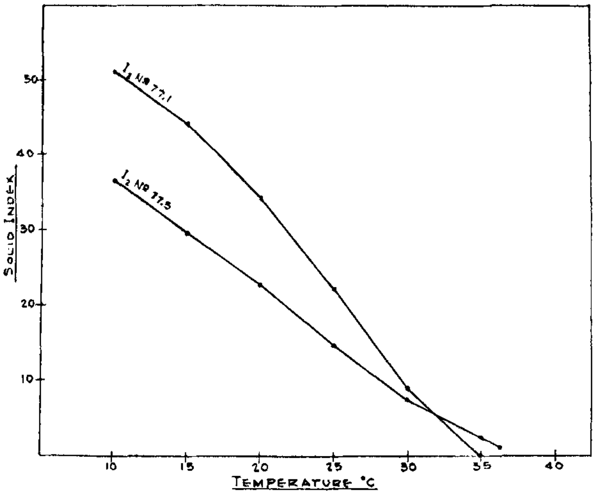


FIG. 3. Effect of differences in hydrogenation selectivity on dilatometric results of soybean oil samples hardened to equal iodine values.

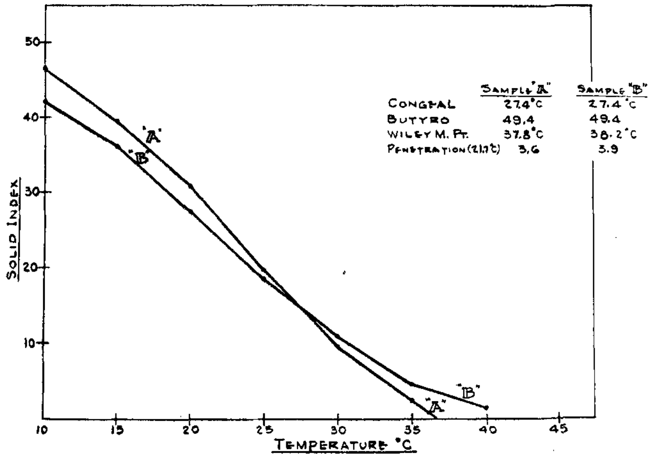


FIG. 4. Dilatometric results on two hydrogenated samples of soybean oil in which differences in melting point, congeal point, and refractive index are within experimental error.

DILATOMETRIC RESULTS CAN BE used empirically to to predict the temperature range over which shortenings will incorporate air properly into a cake batter. In other words, certain oil formulations will have minimum and maximum solid fat indices for optimum performance. Similarly these results may be used to predict storage temperatures above which a shortening's ability to incorporate air will be irreversibly harmed.

Dilatometric results can also be used to predict appearance deterioration which will result from widely fluctuating storage temperatures. Figure 6 shows the results of storage tests of various shortenings conducted at temperatures ranging from 70 to 95°F. After the storage period the samples were again brought back to 70°F. The shortenings were then given an appearance score by a panel, using a 1 to 10

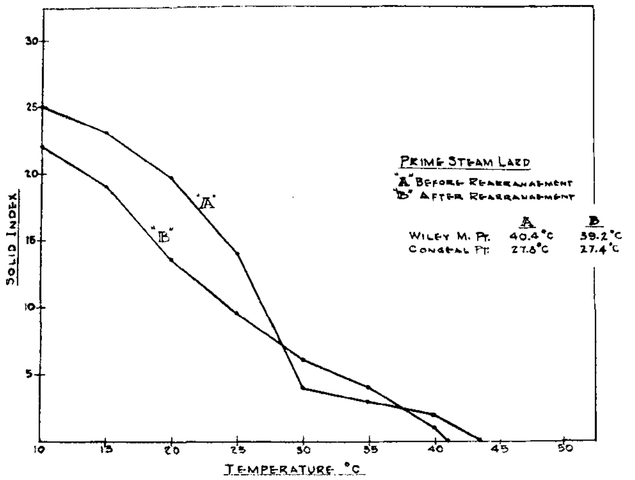


FIG. 5. Effect of molecular rearrangement on the dilatometric curves of lard.

score in which 1 designates excellent appearance and 10 designates a very poor appearance. Differences between the scores of the 70°F. storage samples and the scores of the samples stored at higher temperatures denote appearance deterioration. It will be noted that there is a good correlation between visual scores of appearance deterioration and the amount of solid fat which had melted during storage and then recrystallized when brought back to 70°F.

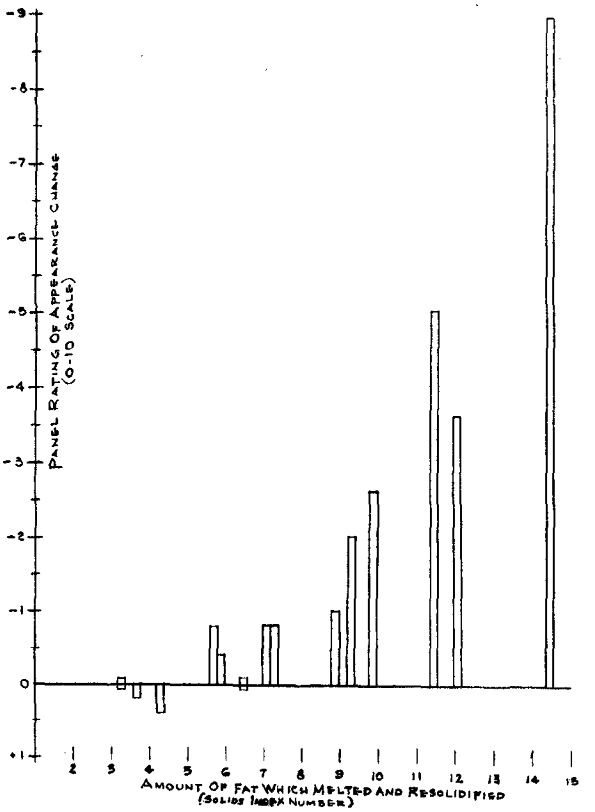


FIG. 6. Relationship between appearance deterioration of shortening during storage and the amount of fat which melted and resolidified because of temperature variations.

Dilatometers can also be used to compare rates of crystallization. Some fats which have similar dilatometric curves may have a greatly different rate of solidification at some temperatures. Figure 7 shows solidification rates of two fats, one of which has a solid fat index of 56% and the other one 53% at 39°F. The oils were originally at 125°F. in the dilatometer and then immersed in a 39°F. bath. The results are plotted in terms of completeness of solidification rather than actual solid fat indices.

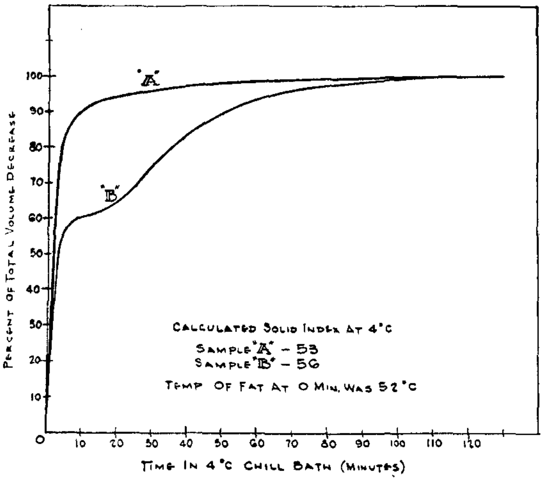


FIG. 7. Differences in the rate of crystallization of two fats as measured by decrease in volume.

The above examples are just a few to indicate that after sufficient dilatometric data have been obtained by a laboratory, dilatometry can be of considerable research value in addition to its general use as a control instrument.

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