Dilatometric Investigations of Fats
I. Apparatus and Techniques for Fat Dilatometry[1]

A. E. BAILEY and E. A. KRAEMER
Southern Regional Research Laboratory,[2] New Orleans, Louisiana

IT is somewhat surprising that dilatometry has not been more extensively employed in phase investigations of fats. The dilatometric method, which combines simplicity with a high degree of accuracy, was used with notable success by McBain and Field (7) in 1933 as well as by a number of subsequent workers (11, 12, 13) for detecting phase transformations in soaps.

Publications on fat dilatometry are few, and for the most part, superficial. The utility of dilatometry in the examination of fats was pointed out in a general way by Normann (8). Van Roon (10), Jensen (6), and Reinders, Doppler, and Oberg (9) recorded the dilatometric behaviour of cocoa butter. Coffey and Spannuth (2) reported the examination of a number of samples of shortening. The application of dilatometry to the evaluation of hydrogenated fats was discussed by Hügel (5). The only dilatometric investigations which have been carried out on a comprehensive scale, and with a full appreciation of both the practical and theoretical significance of the results, are those of Hofgaard (4). However, Hofgaard's monograph, published in Denmark, has not been widely distributed, and is generally unavailable in this country.

In the course of recent work carried out in this Laboratory, dilatometry has been employed, alone and in conjunction with calorimetric methods, for investigating phase changes in fats and oils over the partial or complete melting range of these materials. The apparatus and techniques used in this work merit some discussion, for while dilatometry is simple in principle, useful and reliable results can be obtained only by using a well designed apparatus and observing a number of precautions—some of which are by no means obvious.

Volume Changes Associated with Phase Transformations in Fats

Fats have a considerably higher density in the solid than in the liquid form, hence the dilation accompanying transformations from solid to liquid is considerable. Preliminary data obtained in this Laboratory (Figure 1) indicate that in the case of a completely saturated fat, such as tristearin, this dilation amounts to approximately 11 percent on the basis of the volume of the solid phase. At present, comparable data are not available on glycerides containing unsaturated acids.

Published information on the volume changes accompanying polymorphic transformations of fats is very meagre. However, according to Ferguson and Lutton (3), simple triglycerides, as exemplified by tristearin, become progressively more dense as they are converted from less stable or lower-melting to more stable or higher-melting crystal forms. According to work quoted by these authors, tristearin contracts 2.3 percent in changing from the gamma to the alpha form, and 0.8 percent in changing from the alpha to the beta form.

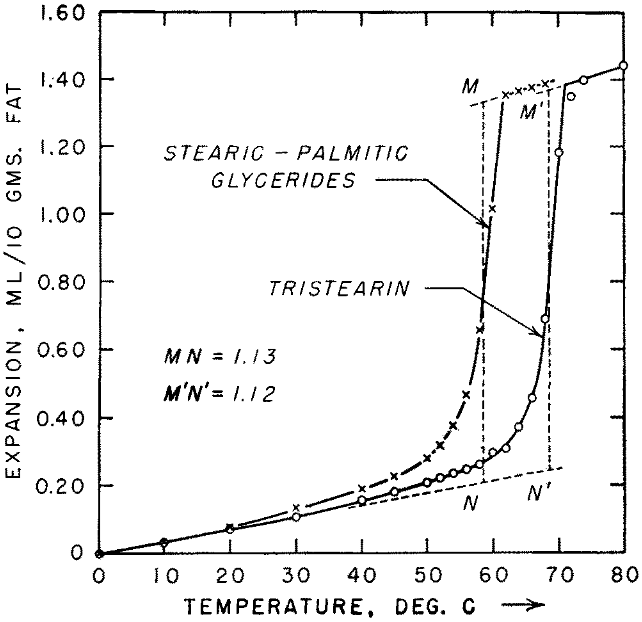

FIG. 1. Dilatometric curves, tristearin and glycerides from co-esterification of equal molar proportions of stearic and palmitic acids.

General Procedure in Conducting Dilatometric Tests

IN carrying out the dilatometric examination of a fat, the liquid sample is first cooled until it is wholly or partially in the solid form. Its temperature is then increased stepwise, in small increments, and its volume is measured at each step, until the sample is completely melted. The expansion of the sample, in terms of the original volume, is plotted against temperature. The resulting curve represents the phase changes occurring over the melting range, in terms of the dilations or contractions associated with these changes. The dilation of the sample due to simple thermal expansion of the liquid and solid phases is, of course, superimposed upon the volume changes due to phase transformations.

In order that the results may be reproducible and significant, the sample must be held at each temperature for a sufficient time to allow substantial equilibrium to be established between the solid and liquid phases.

The Apparatus

Two different forms of dilatometer have been used with good results; the construction of these is shown in Figures 2 and 3. Type A (Figure 2) is of the

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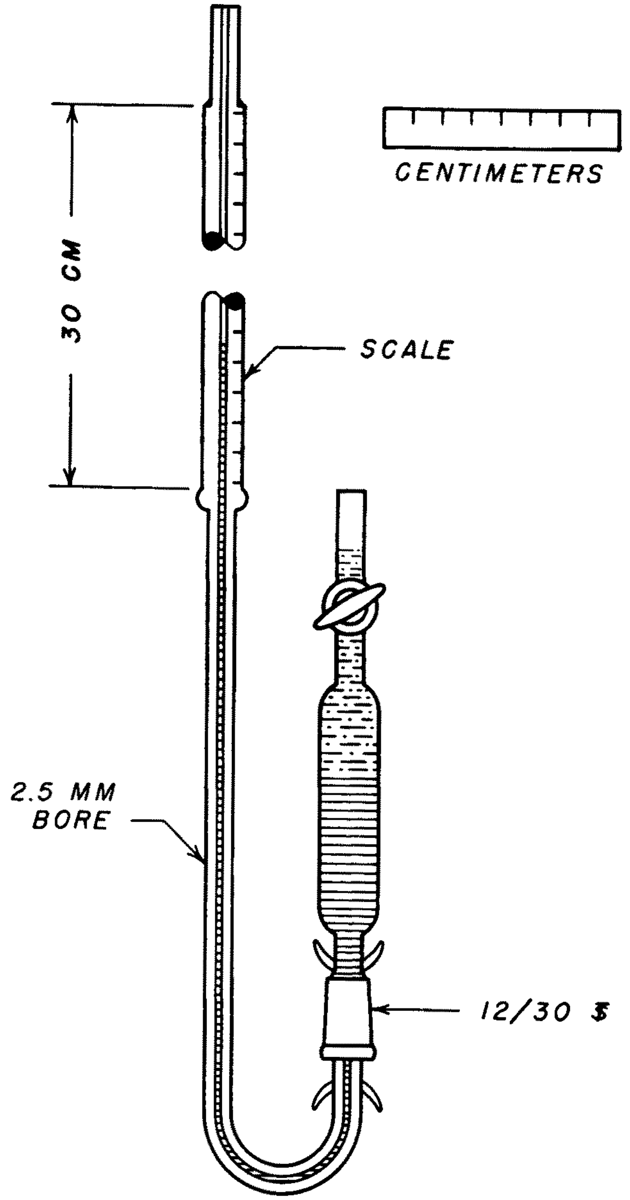

FIG. 2. Dilatometer, Type A or volumetric type.

usual volumetric variety, not essentially different from that first described by Normann. Its novel features consist in the introduction of a ground-glass joint between the bulb and the side arm, to facilitate filling and cleaning, and the provision of a scale of new design. The scale is made from a section of a 50-ml. burette, and is attached permanently to the side arm. The capillary must of course be calibrated. In this dilatometer water is usually employed as the confining liquid, although mercury may also be used. It is chiefly useful for the examination of fats of relatively low melting point, in cases where extreme accuracy in the measurements is not required.

In filling this dilatometer, complete displacement of air is effected by permitting the confining fluid to enter through the side arm and force a small portion of the sample out through the stopcock. The weight of the fat actually retained in this bulb is determined at the conclusion of the experiment by washing out the interior of the bulb through the ground glass joint, weighing the bulb plus fat retained in the outlet tube and stopcock bore, and subtracting the weight of this fat from the weight of the original sample. The weight of the confining fluid must also be determined, so that the total observed expansion can be properly distributed between sample and confining fluid.

Dilatometer B (Figure 3) is of the gravimetric type, and may be considered a modification of the instrument described by Burlew (1). In this dilatometer mercury is used as the confining liquid; the mercury thread in the capillary side arm communicates with a reservoir of mercury in the small flask, *F*. Volume changes in the fat cause mercury to be expelled into the reservoir or withdrawn therefrom. Readings are made by detaching and weighing the flask and its contents. In the event of an air bubble forming in the capillary as a result of the flask being detached for weighing, it may be eliminated by raising the dilatometer from the bath a sufficient distance to expose the expansion bulb, *E*, and gently warming the latter.

After the sample is placed in the bulb, the side arm is sealed on by fusion. The filling device illustrated in Figure 3 is provided for filling the dilatometer with mercury. The dilatometer containing the sample is connected to the filling device by means of the ground joint provided for the purpose, and the sample is melted and degassed under vacuum. The assembly of dilatometer and filling device is then tilted, to bring the mercury in the latter over the tip of the capillary, and the stopcock is turned to shut off the vacuum and admit air which forces mercury into the dilatometer. Manipulation of the assembly is simplified if the fat is chilled until pasty before the mercury is admitted to the system. A high vacuum should be employed, to completely eliminate air bubbles in the bulb.

Before the reservoir flask is attached, lubricant should be removed from the male joint on the end of the capillary, to insure constant weight of the flask and to permit the joint to pass sufficient air to avoid building up pressure in the flask as the mercury expands.

This latter type of dilatometer is recommended for all precise work, and particularly for use with highly saturated fats, which must be carried to relatively high temperatures, and which are inclined to undergo very slow polymorphic transformations. Since the instrument is sealed to form one solid, all-glass apparatus the possibility of leakage is eliminated. Ordinarily mercury can be weighed with greater accuracy than its volume can be measured; hence smaller volume changes can be detected with this dilatometer than with those of the usual type. The use of mercury as the confining fluid eliminates slight inaccuracies due to the appreciable solubility of water in fats.

Method of Calculating Volume Changes in the Fat

In calculating the volume changes in the fat, allowance must be made for the thermal expansion of the confining liquid, and where extreme accuracy is desired, of the dilatometer bulb. It is to be particularly emphasized that the results should be expressed in terms of the actual expansion or contraction of the fat, and not simply as dilatometer readings, as has been done by most previous workers. If water is used as the confining fluid in the dilatometer, a plot of dilatometer readings against temperature will bear little resemblance to the true dilatometric curve of fat, owing to the uneven thermal expansion of water over different temperature ranges.

Solidification of the Sample

The procedure adopted for solidifying the sample must depend upon the phase transformations which are to be investigated. If the test is to reveal any possible polymorphic transformation, the sample should be chilled as rapidly as possible, by plunging the dilatometer bulb containing the molten sample into ice water or other cold liquid. If only the most stable solid phase is desired in the fat, the sample must be cooled slowly, or first solidified rapidly, then tempered for a time—usually 24 to 72 hours—at a temperature approaching its melting point, and then chilled to a low temperature corresponding to the beginning of the test. A great many fats show no evidence of the formation of unstable crystal forms even when chilled rapidly; hence the manner in which they are solidified is unimportant.

Procedure in Making the Measurements

Measurements made at intervals of about 2°C. will generally define the dilatometric curve of a plastic fat satisfactorily. In the examination of highly saturated fats, or other fats with a short melting range, it may be desirable to make readings at temperature intervals of 1°, or even less.

It is difficult to specify hard-and-fast rules concerning the highly important factor of the time interval over which the sample should be maintained at each temperature. However, the behavior of the sample immediately after the temperature of the bath is increased will usually provide a clue as to the proper procedure. In the case of fats which do not exhibit polymorphism, and which have a relatively long plastic range, equilibrium will be established practically by the time the entire sample has come to the temperature of the bath. With the dilatometers described here, this will require about 20 to 30 minutes. Fats of this type exhibit a regular cycle of volume changes with each increment of temperature, and any irregularities introduced by the appearance of polymorphic transformations are quite easily recognized.

Highly saturated fats containing only stable crystal forms behave similarly to plastic fats, except that in the range near the melting point an appreciable time is required for the absorption of sufficient heat to correspond to the latent heat of the melting glycerides, and therefore equilibrium is attained more slowly.

Polymorphic transformations are manifested by a contraction following the original dilation due to thermal expansion and the melting of glycerides. Such transformations are usually in evidence within 20 to 30 minutes after the temperature is raised, but they invariably require hours for completion. In the case of polymorphous materials, the most satisfactory practice is to take readings at intervals of 8 to 24 hours until the readings become constant.

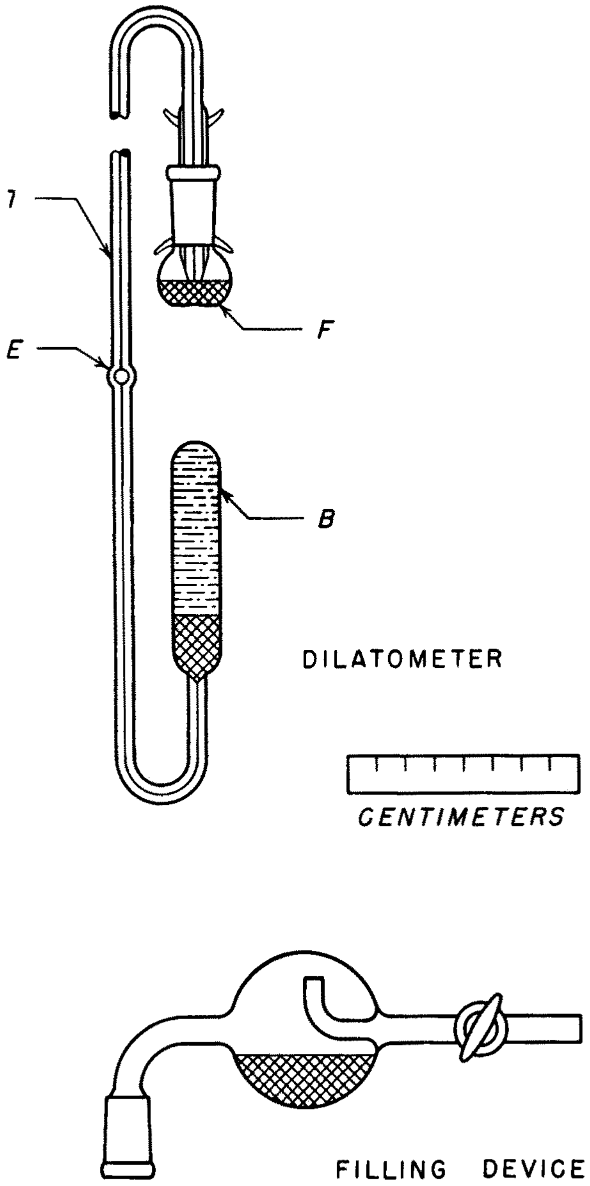

FIG. 3. Dilatometer and filling device, Type B or gravimetric type.

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