Melting-Point Determination of Fat Products[1]

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ABSTRACT

A variety of methods exist for the determination of the melting point (mp) of fats. These include the Wiley mp (AOCS Method Cc 2-38), open capillary slip point, softening point and Mettler dropping point. The conditions under which the tests are performed influence the values obtained. Several of these methods were compared using a variety of fats, including margarine and soft margarine oils, lard, butter and hydrogenated Canola oils. The Mettler dropping-point values were found to coincide with the extrapolated solid fat curves obtained using wide-line NMR for all fats except butterfat. The reproducibilities of the Mettler dropping point and softening point were excellent; that of the slip point was poor.

INTRODUCTION

Although it is customary to speak of melting points of fats, they really have no melting point in the proper sense of the word. Pure substances have a sharp melting point, i.e., the temperature of transition of the solid to the liquid state. Fats are invariably mixtures of mixed triglycerides and each individual triglyceride has its own melting point. The fat, therefore, has a melting range. What we understand by melting point of a fat is really the end of the melting range. Melting points of fats can be determined in a variety of different ways and the results are not necessarily the same, nor have different methods the same degree of reliability. Some methods require elaborate and expensive equipment, others can be done with relatively simple tools.

In the AOCS Official and Tentative Methods, mention is made of melting-point determination by the capillary tube method (Cc 1-25), the Wiley method (Cc 2-38), the softening point (Cc 3-25) and the slipping point (Cc 4-25). The Official Methods of Analysis of the AOAC list the Wiley method and the capillary tube method. Several other methods have been described in the literature and it is of some interest to bring the information on these procedures together.

The reproducibility of test results between different laboratories or even when done by the same analyst is sometimes poor. Mertens and deMan (1) quoted ranges given for official methods. AOCS Wiley mp 1.0 C; AOCS capillary tube mp 0.5 C; and results for check samples Wiley mp 0.59 C and capillary tube mp 0.92 C.

Description of Methods

Some of the simpler melting-point methods include the capillary tube methods. There are two versions of this test.

Closed capillary tube method. This procedure is similar to the one commonly used for crystalline organic compounds. It is not widely used for fats.

Open capillary tube method. In this procedure, the fat is solidified in an open capillary tube and the tube heated in a water bath. When the temperature is high enough, the fat rises in the tube. This test is described as softening point by the AOCS (Method Cc 3-25). It is known as the slip point in Great Britain and rise melting point in Germany.

Slipping point. In this method (AOCS Cc 4-25), the sample is contained in a brass ring and heated in a water bath until the fat is forced out of the ring. The method is used for finished products such as margarine. It should not be confused with the previously mentioned slip point.

Wiley melting point. In this method (AOCS Cc 2-38), a disc of chilled fat is heated in a bath of alcohol and water. The Wiley melting point is the temperature at which the disc assumes a spherical shape.

Ubbelohde melting point. This method has been used in several European countries. The fat is contained in a small glass cup with a restricted opening in the bottom. The cup is heated in a water bath. The temperature at which the fat starts to protrude from the opening is called flow point. When the first drop falls from the opening, the temperature is indicated as dropping point (2).

Mettler dropping point. This is an automated version of the Ubbelohde dropping-point method. The sample cup is placed in an automatically heated furnace and the falling of the first drop of fat is sensed photometrically and indicated on a digital display (3).

Photoelectric method. The fat is contained in a capillary tube and placed in a light beam of a photoelectric instrument. The temperature is raised and when the fat melts the transmittance of the sample increases, indicating the melting point (3).

Conductivity method. A fat sample is solidified in an open capillary tube containing a fine electrode. Another electrode is placed in the heating bath. The solidified fat prevents passage of current. As soon as the fat melts, it flows away and current can pass, indicating the melting temperature (4).

Softening point. In this method, the fat is solidified in a small test tube and a steel ball bearing placed on top of the fat. The tube is heated in a water bath. The temperature at which the ball has fallen through half the height of the fat column is taken as the softening point (5).

Materials. Margarines, lard and butter were obtained from local supermarkets. The hydrogenated Canola oils were made from refined and bleached Canola oil by hydrogenation in a Parr laboratory hydrogenator.

Discussion of Methods

Since melting points of fats are not precise physical constants, the values obtained with various methods depend to a certain extent on the pretreatment of the sample as well as on the rate of heating during measurement. For this reason, melting-point measurements are carefully standardized. Because new methods have become available recently, it is of interest to compare the results of such methods with those obtained with the standardized tests.

Soltoft (6) investigated the effect of temperature treatment on the melting point (open capillary tube) of fats. He found that when the cooling period at 0 C increased, the melting point first decreased, then went through a minimum and, as the cooling further increased, the melting

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point increased again. He attributed this phenomenon to the fact that fat crystallization requires a certain time to go to completion and also to the fact that fat may initially crystallize in unstable polymorphic modifications. He followed the melting behavior of fats with a microdilatometer and found that easily reproducible melting points were obtained when the fats were stabilized by a tempering treatment.

A method which has not received much attention but which may be useful is the softening-point method. This method is easy to perform and requires only inexpensive equipment. First described by Barnicoat (5), the method involves putting 1 mL of fat in a small test tube. The fat is solidified and an 1/8-inch ball bearing is placed on top of the fat. The softening point is the temperature at which the ball has fallen half-way through the fat. The tubes were originally held in the bath by weighting with mercury or lead shot. However, the tubes can be easily clamped so that weighting is not necessary. The original method as described by Barnicoat (5) involved chilling the melted sample in ice water for 30 min and keeping in a refrigerator overnight. The tube was then kept in a 20C water bath for 30 min and the temperature raised at a rate of 0.5C/min. Subsequently, the ice-water chilling was eliminated and the time in the 20C bath reduced to 15 min. Dolby (7) investigated these changes and found that the ice-water cooling resulted in a highly significant difference in dropping point. He demonstrated that the ice-water cooled samples changed much less in dropping point during 8-day storage than did the air-cooled ones. Black (8) suggested the elimination of overnight storage in a refrigerator to shorten the time required for the test. The shortened version of the dropping-point test is a useful addition to the melting-point methods available.

Automated methods for melting-point measurement appeared in the literature in the late sixties. Keim (3) described a photoelectric method using a fat sample contained in a glass capillary which was closed at one end. The equipment used was a Mettler FP-1 unit. Chabanne (4) described a conductivity method in which the sample covered a microelectrode inside a capillary tube. As soon as the fat melted, the electrode was uncovered and current passed through the electrode. A method based on automation of the Ubbelohde dropping point was first described by Harangozo (2). This procedure uses the Mettler FP-3 unit and has subsequently been widely studied and accepted. Bürki and Flückiger (9) used this method for butter and found a standard deviation of 0.1C. Mertens and deMan (1) used the Mettler dropping-point method for a variety of fat products. The advantages of this instrument include the automatic endpoint detection, availability of different heating rates from 0.2 to 10C/min, and good precision. The manufacturer claims a precision of ± 0.3C at heating rates from 1-3C/min, and this was confirmed by the results of Mertens and deMan (1). It is also possible to use the method for finished products such as margarine and shortening since it is easy to fill the sample cups with the aid of a spatula. In this study, the fat samples contained in the sample cups were solidified in the freezer for 1 hr at -10C and a heating rate of 2C/min was used. The effect of tempering the samples was investigated. Tempering mainly affected the animal fat samples. Short time tempering at 20C had almost no effect on the dropping point. Lauric acid containing fats had a lower precision than the other fats. In general, the Mettler dropping points corresponded well with the Wiley melting points.

Timms (10) used the Mettler dropping-point method for milkfat, fractionated milkfat and butter. Heating rate was found to be the most important factor affecting the dropping point. A method involving overnight chilling of the sample and heating at 1C/min gave results equal to those of the Barnicoat softening point. A rapid method was suggested which included chilling for 15 min and heating at 2C/min. The results with the latter method were 1.3C higher than with the former.

Comparison of Some Methods

A comparison of some of the simple methods was made with the Mettler dropping-point method. It was previously shown that the Mettler procedure gives results closely corresponding to the Wiley melting points. The following methods were used:

Mettler dropping point. The procedure of Mertens and deMan (1) was used. Samples were chilled in the freezer at -10C for one hour. Heating rate was 2C/min.

Falling ball. This is the softening-point method of Barnicoat (5). This method is commonly described as softening point but to avoid confusion with the AOCS softening-point method, the term falling ball is used. Samples were chilled in ice water for ½ hr, tempered at 20C for 20 min and the heating rate used was 2C/min.

Slip point. This is the open capillary melting point described by Cocks and van Rede (11).

Softening point. The open capillary melting point AOCS Cc 3-25.

These four methods were used in triplicate on a total of 15 samples of margarine fat, lard, butter and hydrogenated Canola oil. The means and ranges are listed in Table I. The overall mean of the ranges of the Mettler dropping point and the falling ball method were almost identical. The overall mean of the ranges of the slip point and softening point were much higher. The slip point overall mean was lower than the softening point overall mean.

The reproducibility of these methods was further checked by performing 10 replicate tests on each of four different fats. Results are presented in Table II. Dropping point and falling ball methods had better reproducibility than slip point and softening point. The standard deviation for butterfat in the dropping point and falling ball methods was higher than for other fats. A similar observation was made by Mertens and deMan (1) for lauric acid fats.

There was a close correlation between Mettler dropping point and falling ball softening point as indicated in Figure 1. The relationship is expressed as $Y = .9895X + .2126$, and the correlation coefficient was $r = .9948$.

When a fat reaches the melting point, virtually all of the solid should be melted. The 15 fats mentioned above were analyzed for solid fat content by wide-line NMR. Results are presented in Figures 2 and 3. The last point on the NMR solid fat line was connected with the Mettler dropping-point value on the abscissa. In all cases but one, the lines were virtually straight extensions of the solid fat lines. The only exception was butterfat. In this case, the Mettler dropping-point value was at a temperature where about 2.5% solid fat was present.

Melting points can also be derived from DSC curves. The 15 fats were analyzed with a series 99 DuPont system and the inflection points of the melting curve and the solid line taken as the melting point. Sample size was 10-20 mg and the heating rate was 5C/min. All samples were run in duplicate. The DSC melting points were generally considerably higher than the Mettler dropping points (Table III). The mean for all samples was 2.4C higher than the mean of the Mettler dropping points.

TABLE I

Mean and Range of 3 Replicates of 4 Melting-Point Methods using 15 Fat Products

Sample	Mettler dp		Falling ball		Slip point		Softening point	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Blue Bonnet stick	35.0	0.2	34.9	0.2	33.3	0.5	34.4	0.3
Parkay stick	34.5	0.2	35.0	0.1	32.4	0.8	33.8	0.5
Imperial stick	34.7	0.1	34.4	0.3	32.7	1.5	33.6	1.4
A & P stick	34.2	0.3	33.7	0.2	33.5	1.0	32.8	1.0
Fleischmann's corn	32.7	0.1	32.6	0.2	30.6	1.2	32.4	0.4
Fleischmann's sunflower	35.7	0.1	36.0	0.3	35.1	1.0	34.6	0.6
Imperial soft	33.5	0.3	33.0	0.4	32.2	1.6	34.5	0.3
Blue Bonnet soft	32.2	0	31.7	0.2	31.5	0.5	31.6	0.8
Parkay soft	28.6	0.2	28.4	0.2	27.4	0.3	27.5	0.7
Lard	40.0	0.2	39.7	0.1	37.2	2.6	40.5	0.3
Becel	29.0	0.1	28.5	0.2	28.5	0.5	27.0	1.0
Butter	32.7	0.2	33.7	0.2	30.1	1.2	29.9	0.4
Canola IV 66	44.7	0.2	44.2	0.1	41.3	0.3	43.0	0.5
Canola IV 70	41.9	0.2	41.6	0.1	38.2	0.1	39.3	2.7
Canola IV 80	33.5	0.1	33.2	0.3	30.4	1.0	28.9	0.3
Overall mean	34.86	0.17	34.70	0.20	32.96	0.94	33.59	0.73

TABLE II

Reproducibility of Different Melting-Point Methods using 4 Different Fat Products (10 Replicates)

Method		Parkay soft margarine	Parkay stick margarine	Lard	Butterfat
Dropping point	Mean	28.67	34.53	40.11	32.76
	Range	0.4	0.4	0.4	0.8
	SD	0.125	0.125	0.102	0.276
Falling ball	Mean	29.70	35.44	40.32	34.01
	Range	1.0	0.6	1.0	1.7
	SD	0.093	0.184	0.093	0.263
Slip point	Mean	27.05	33.80	39.19	31.78
	Range	2.3	1.7	3.9	0.8
	SD	0.712	0.665	1.174	.308
Softening point	Mean	31.36	34.28	40.51	30.28
	Range	5.3	1.5	0.8	2.2
	SD	1.908	.442	.300	.600

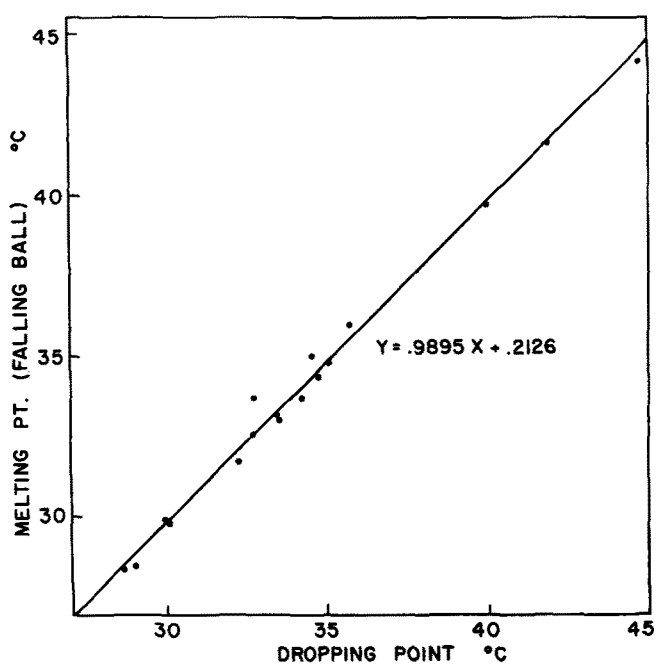

FIG. 1. Correlation between Mettler dropping point and falling ball softening point.

TABLE III

Comparison of DSC Melting Points and Mettler Dropping Points

Sample	DSC mp (C)	Mettler dropping point (C)	Difference
Blue Bonnet stick	35.5	35.0	+ 0.5
Parkay stick	36.5	34.5	+ 2.0
Imperial stick	37.5	34.7	+ 2.8
A & P stick	37.0	34.2	+ 2.8
Fleischmann's corn	38.5	32.7	+ 5.7
Fleischmann's sunflower	36.5	35.7	+ 0.8
Imperial soft	38.0	33.5	+ 4.5
Blue Bonnet soft	35.0	32.2	+ 2.8
Parkay soft	32.0	28.6	+ 3.4
Lard	43.5	40.0	+ 3.5
Becel	31.0	29.0	+ 2.0
Butter	33.0	32.7	+ 0.3
Canola IV 66	44.5	44.7	- 0.2
Canola IV 70	42.5	41.9	+ 0.6
Canola IV 80	38.5	33.5	+ 5.0
		Mean	+ 2.4

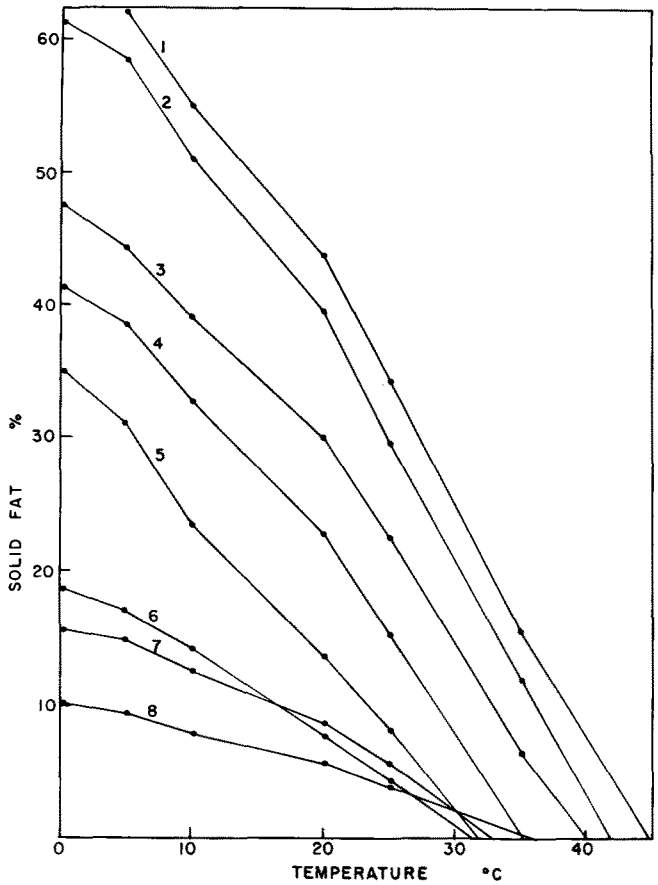

FIG. 2. Solid fat curves for different fat products. The highest temperature of the solid fat curves has been connected with the corresponding Mettler dropping point on the temperature axis. (1) hydrogenated Canola oil IV-66, (2) hydrogenated Canola oil IV-70, (3) lard, (4) Blue Bonnet stick, (5) hydrogenated Canola oil IV-80, (6) Blue Bonnet soft, (7) Fleischmann's corn, (8) Fleischmann's sunflower.

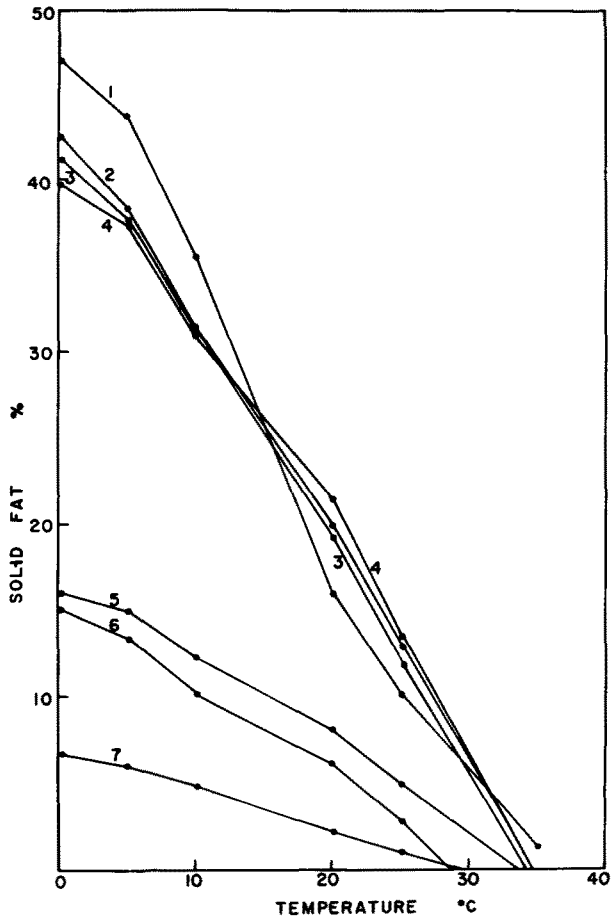

FIG. 3. Solid fat curves for different fat products. The highest temperature of the solid fat curves has been connected with the corresponding Mettler dropping point on the temperature axis except for curve 1. (1) butter, (2) Imperial stick, (3) A & P stick, (4) Parkay stick, (5) Imperial soft, (6) Parkay soft, (7) Becel.

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