Fat Melting Point Determinations: a Review[1]

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ABSTRACT

The many melting point methods can be grouped in different ways: (a) Some methods determine the point of complete melting of all crystalline material; others use a point farther removed from there and are more correctly called softening, slipping or dropping points. (b) Some are only being used for melted fat samples, others for finished products, or both. (c) Some depend on the subjective interpretation of the endpoint by the operator; others use objective indications. (d) Some depend upon manual controls; others employ a certain degree of automation. Especially in this last group, modern instrumentation has shown the way for possible improvements. The use of automatic temperature control, linear heating rates and objective endpoint determinations, as shown in some of the examples given, is an encouraging sign. These methods promise a noticeable improvement in the precision of melting point tests.

DISCUSSION

General

The melting point is usually defined as the point at which a material changes from the solid to the liquid state. Smith (1) states: "The melting point is the temperature at which a solid assumes the liquid condition," and Brunner (2) says: "The melting point is represented by the temperature at which previously solidified fat transforms completely into the liquid state."

Many methods have been devised to determine accurately this point or a point close to it, sometimes by direct observation, sometimes by an indirect and objective process. For an edible fat product this melting point in its relation to the body temperature can give some indication of the "mouth feel," of gumminess, workability and general behavior at elevated room temperatures. It is no wonder, then, that melting point determinations have for a long time belonged to the group of the most frequently and routinely performed analytical tests in industrial oil laboratories. They are useful to identify unknown samples, to duplicate approved standards and to control production, especially in the critical area of finished product formulation.

The most important consideration at this moment is the well known fact that natural fats do not have a true melting point. Only pure compounds have sharp melting points, whereas natural fats, being complex mixtures of many glycerides, upon heating go through a more or less extended softening period, only gradually changing to a completely liquid oil. This melting procedure is further complicated by the other well known fact that fat crystals can exist in several polymorphic modifications, depending not only on the specific triglycerides involved, but also on the temperature-time pretreatment of the sample. These different crystal forms are often sufficiently stable to exhibit distinctive melting points (Swern [3]). Therefore, instead of a melting point, it is more correct to speak of a melting range or melting interval. If the expression "melting point" is to be used, one point within the melting range has to be selected arbitrarily and defined—together with the corresponding method—as the melting point. Only if rigid and specific conditions of fat pretreatment and of the test itself are being used, is it possible to define such a point.

Advantages of most melting point methods are their relative simplicity and their reasonably low requirements for instrumentation, time, and amount of sample.

The dependence of the melting point on the sample pretreatment and on the method used must be listed as a main disadvantage of all determinations. Many different methods are being used in different laboratories or countries. These define endpoints not necessarily identical with the definition of complete melting given above; they often measure different properties, and usually give results not directly related to each other (Hannewijk et al. [4], Bailey [5], and Niiya et al. [6]). Changes in the methods can lead to variations in the results, and manually controlled tests have a built-in tendency towards slightly changing heat transfer conditions. Often the endpoint determination

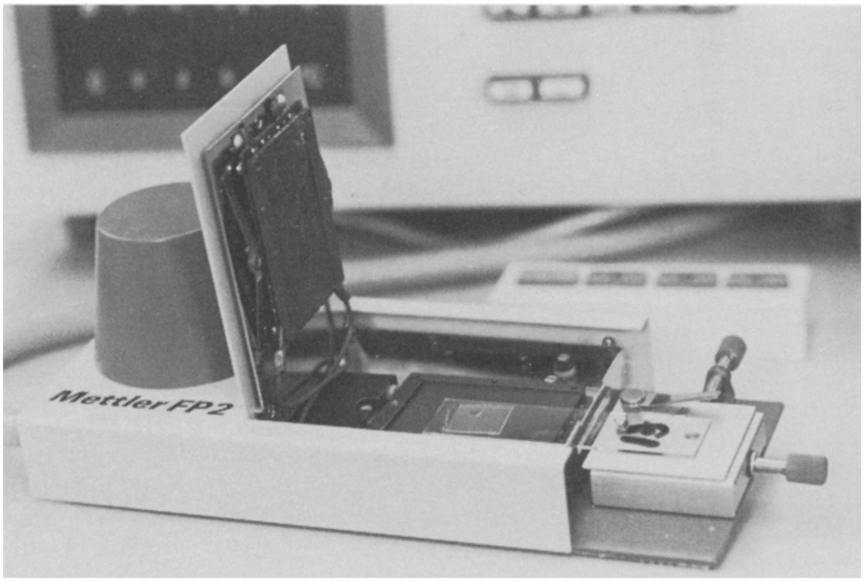

FIG. 1. Mettler FP2 hot stage.

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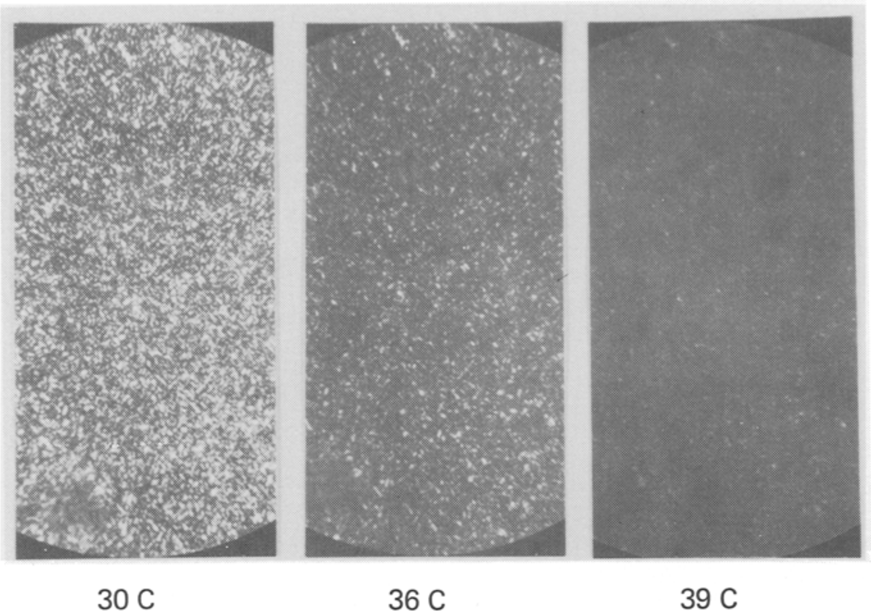

FIG. 2. Photomicrographs of a fat sample at 30, 36 and 39 C. Magnification 300x.

requires a subjective interpretation, a wide open area for differences of opinion and errors. All these difficulties must have been the reasons that led Hannewijk et al. (4) to summarize that: "it is impossible to draft a uniform standard method applicable to all fats. Any method, therefore, is bound to be a compromise. The results obtained have only comparative value, and the reproducibility is reasonable only when the method is accurately standardized."

Several melting point methods have been standardized by the AOCS (7), the British Standards Institution (8), the Deutsche Gesellschaft für Fettwissenschaft (DGF) (9), and similar societies in many countries. In spite of this standardization, the precision of melting point tests is not very satisfactory, and the desirability of improvements can easily be seen from some results taken from the literature: (a) The AOCS melting point methods (7) list reproducibilities as being in the range of 0.5-1.0 C. (b) The DGF dropping point method (Einheitsmethode C-IV 3b) (9) lists a reproducibility of 4.0 C. (c) Smalley edible fat series (check samples) (10). The melting point results (Wiley melting point, AOCS Official Method Cc2-38, and capillary tube melting poing, AOCS Official Method Ccl-25) (7) from 1968 and 1969 are shown in Table I. With the participation of 30-42 laboratories the mean range (difference between lowest and highest test result) was 2.6 C for the Wiley melting point and 4.4 C for the capillary tube melting point. The lauric acid oil sample no. 68-2 showed especially poor results. (d) Seher (11) listed results from an international test with the open capillary tube melting point (15 laboratories), in which the ranges were 3.2 C for tallow, 7.0 C for lard and 8.6 C for a lard-tallow blend. Results like these are indeed discouraging.

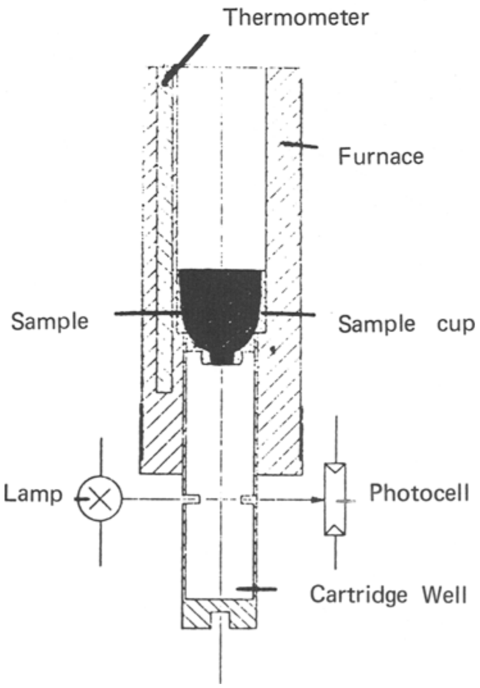

FIG. 3. Mettler FP3 dropping point instrument furnace, schematic (Harangozo [17]).

Different Melting Point Methods

A detailed description of the many melting point methods would be beyond the scope of this paper, but the principles employed or suggested will be discussed briefly.

A) *Observation under the microscope*: Microscopy offers itself as a melting point method, because under polarized light the fat crystals appear brightly on the dark background of liquid oil and the melting of an individual crystal can be observed. This possibility was listed by Bailey (5) and Hoerr (12). Practical applications were, however, limited because of the difficulties with available hot stages, because other, simpler melting point methods were available and because the melting of a particular crystal group is not necessarily closely related to the physical properties of a fat. This fact was already expressed by Bailey (5). The development of the Mettler hot stage FP2 with automatic and linear temperature control has opened new possibilities and has led us to conduct some feasibility studies. The results have been published elsewhere (13). Figure 1 shows the FP2 hot stage, which was used with a polarizing microscope at 375x magnification. The fat samples on microscope slides were frozen (15 min at -10 C), tempered (5 min at 25 C) and observed at different heating rates; the melting of the last crystals was taken as the micro melting point.

Some results obtained are listed in Table II. The ranges of these determinations look reasonable, but all tests were done by one operator and should therefore be compared cautiously with the Wiley melting point results from a check series. A main disadvantage of the micro melting

TABLE I

Melting Point Ranges (0 C) of Check Samples from 1968-69 Smalley Edible Fat Series (10)

Fat sample	Capillary tube melting point			Wiley melting point		
	Range[a]	SD[b]	No. of labs.	Range[a]	SD[b]	No. of labs.
68–1	2.4	0.54	42	1.8	0.43	38
68–2	14.9	3.33	41	4.3	0.96	40
68–3	2.6	0.54	39	1.9	0.45	38
68–4	3.2	0.97	32	2.5	0.61	31
69–1	2.3	0.54	33	2.0	0.44	32
69–2	4.4	0.91	34	3.7	0.90	30
69–3	3.4	0.89	40	2.6	0.61	37
69–4	2.0	0.51	33	1.8	0.45	35

[a] Range = difference between highest and lowest test result.

[b] SD = standard deviation.

point method was the subjective interpretation of observations and a noticeable influence of light conditions. In addition, the observations became more and more difficult during the gradual melting of the crystalline phase. At the endpoint, when a sharp contrast would be most desirable, this contrast had largely disappeared. Figure 2 illustrates this point. The results obtained in these tests were not good enough to recommend the micro melting point as a practical method for commercial fats.

B) *Capillary tube melting point*: A very accurate but slow method with a closed capillary tube was described by Francis and Collins (14). The final heating rate of 0.1 C/4 min eliminates this as a routine laboratory method. The AOCS Official Method Ccl-25 (7) specifies 1 mm diameter glass tubes, which are partly filled with liquid fat, fuse sealed, refrigerated and then heated in a water bath at a rate of 0.5 C/min. The temperature at which the sample becomes completely clear is taken as the endpoint. Bailey (5) was of the opinion that the results were not related closely enough to the consistency of the fat at ordinary temperatures, but it can probably be stated that all melting point methods are poor indicators of fat consistency at room temperatures. The subjective interpretation of the "completely clear" endpoint by the analyst is one obvious disadvantage.

Open capillary tube melting point methods avoid this disadvantage by using the physical movement of the fat column under a standardized hydrostatic pressure as the endpoint indicator. This objective determination is a definite advantage. The method is also known as the slip point or softening point (AOCS Official Method Cc3-25) (7). It can be used for melted fat samples as well as for solidified finished products, and in the latter case differences in the slip point are sometimes used as indicators for "melt in mouth" differences.

Recently there have been welcome attempts to improve several melting point methods with more uniform conditions and better endpoint determinations, usually obtainable by some automation. Such an improvement of the open capillary tube method has been suggested by Chabanne (15).

The AOCS slipping point (AOCS Official Method Cc4-25) (7) is based on the same principle as the open capillary tube melting point. Metal cylinders with a diameter of 10 mm are filled with the sample and then heated at 0.5 C/min while immersed. The temperature at which the fat sample rises from the metal ring is taken as the slipping point. This method is useful for finished products and the endpoint is determined objectively, but the samples lack uniform pretreatment so that the results are influenced by the prior history of the product.

C) *Wiley melting point*: This test (AOCS Official Method Cc2-38) (7) is probably the most popular melting point method in North America. A solidified fat disc is heated slowly in a tube filled with deaerated water and alcohol, and the temperature at which the disc becomes completely spherical is defined as the Wiley melting point. The final heating rate is specified as 0.2 C/min. Smith (1) called it the most widely used method, and very useful and reliable. He stated that the results of one analyst should check within ±0.2 C. The subjective interpretation of the endpoint is again a major disadvantage and can lead, together with slight changes in the temperature treatment of the samples (freezing, heating rate), to such variations as were listed earlier (see Table I).

D) *Dropping point*: This method is based on an

TABLE II

Micro Melting Points (0 C) of Four Fat Samples at Different Heating Rates after Tempering at 25 C for 5 min[a]

Programing[b]	Fat sample			
	67–1	68–1	67–3	68–3
	Animal	Animal	Vegetable	Vegetable
1 C/min				
Mean mmp	44.3	44.9	41.7	40.5
Range	1.2	1.0	0.9	0.6
SD	0.32	0.30	0.27	0.24
2 C/min				
Mean mmp	44.4	44.9	41.0	40.3
Range	0.6	0.3	1.1	0.8
SD	0.12	0.10	0.36	0.24

[a] Nine determinations per test.

[b] mmp = Micro melting point; range = difference between highest and lowest test result; SD = standard deviation.

TABLE III

Dropping Points (0 C) of Seven Fat Samples, at Heating Rate of 2 C/min without Prior Tempering, vs. Wiley Melting Points[a]

	Fat sample						
	67–1	67–3	68–1	68–3	69–2	68–2	69–4
Programing[b]	Animal	Vegetable	Animal	Vegetable	Vegetable	Lauric fat	Vegetable
Mean dp	44.9	42.2	45.4	41.7	37.6	34.0	33.5
Range	0.3	0.4	0.4	0.1	0.5	0.5	0.2
SD	0.10	0.19	0.16	0.04	0.22	0.19	0.06
Wiley mp							
Mean	44.3	42.1	44.5	41.1	37.6	35.4	33.2
Range	4.2	4.3	1.8	1.9	3.7	4.3	1.8
SD	0.72	0.75	0.43	0.45	0.90	0.96	0.45

[a] Six determinations per test.

[b] dp = Dropping point; range = difference between highest and lowest test result; SD = standard deviation. Wiley melting point from Smalley edible fat series (10).

instrument designed by Ubbelohde and is standardized in Germany (DGF Einheitsmethode C-IV 3b) (9) and England (British Standard 894) (8). A small cup with a round bottom opening is filled with the sample, attached to a thermometer and heated under controlled conditions until the first drop falls from it; this is the dropping point. The objective endpoint determination is a great advantage, but the method is slightly cumbersome and is used mainly for solidified fat samples. The reproducibilities listed by the DGF Einheitsmethode (9) or the similar American Society for Testing and Materials (ASTM) method D566-64 (16) for lubricating grease are not good enough for good quality control.

The Mettler FP3 dropping point instrument has made automatic determinations possible. Different heating rates are available, heating is linear and automatic, and the endpoint is determined automatically. The furnace of the instrument is shown schematically in Figure 3 (Harangozo [17]).

Testwork with the Mettler FP3 has been published earlier this year (18). From this work, Table III is shown as an example of the results obtained with different fat samples. The most interesting findings were that this method determines endpoints automatically, without subjective interpretation and with good precision. The mean range of all tests at 1 and 2 C/min heating rates was ca. 0.3 C. A similar precision of results has been reported by Harangozo (17) and Seher (11), and the different Mettler instruments have also been discussed recently by Kunzmann (19). A further advantage was that the method could be applied both to melted fat samples (solidified in the cups) and finished products like shortening, margarine or butter. This makes it possible to analyze an ingredient fat as well as the product made from it with the same method and opens possibilities to study the influence of manufacturing conditions.

The combination of many desirable features in the FP3 instrument outweighs certain disadvantages, e.g., that only one sample can be analyzed at a time and that without a refrigerated cabinet the air-cooled furnace is limited at the low temperature end by the surrounding room temperature.

E) *Other melting point methods*: Dilatometry can be used to determine melting points, as was already pointed out by Bailey (5). He called it a very precise and "virtually the only strictly accurate method available for commercial fats," since at each determination point the sample reaches full liquid-solid equilibrium. Subjective interpretations are eliminated. Several points have to be determined close to the melting point to see the change from the melting curve to the straight-line thermal expansion curve, and the whole method is time consuming.

In a similar way, other methods which can be used for the determination of the solid-liquid ratio of fats offer themselves as melting point methods. Examples are differential scanning calorimetry (DSC) or differential thermal analysis (DTA).

A photoelectric determination of the melting point, in which the increasing transparency of a fat sample during melting is measured and registered automatically, is the principle of the Mettler FP1 instrument, which has been described by Keim (20). Since the gradual melting of a fat sample is reflected in a similarly gradual change in light transmittance, it is not easy to obtain a sharp "break" in the resultant curve at complete melting, except for fats or fat fractions with a very narrow melting range.

An interesting instrument, the Fus-O-Mat by Heraeus, has been used by Seher (11) to determine melting and solidification temperatures. One of the shortcomings of almost all melting point methods—the indirect measurement of the fat sample temperature in the surrounding medium (oven, water bath, etc.)—has been overcome by placing a temperature probe directly inside the sample. The sample tube is heated automatically, and crystal changes are reflected in changes in the sample temperature. Seher (11) reported the useful application of this instrument to the study of polymorphic changes and melting points, and obtained good precision of results.

Softening points can be determined for resolidified fat samples as well as for finished products. The principle is to place a standardized small metal sphere on the sample surface and to determine the temperature at which the product can no longer support the sphere. Several such methods might still be in use, but they more often give an indication of a certain degree of softness than a melting point.

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