Automatic Melting Point Determination of Fats

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ABSTRACT

The Mettler FP3 automatic dropping point apparatus was used for the determination of melting points of a variety of edible fat products. The instrument was particularly suitable for this purpose because of the availability of different heating rates. Advantages were the fully automatic heating, the automatic and objective endpoint determination, the application for melted as well as solidified samples (shortening, margarine, butter), and good reproducibility of results. A standard laboratory method for melted fat samples has been suggested.

INTRODUCTION

The determination of the melting point of edible fat samples is a routine procedure in oil laboratories. Since natural fats do not have a true "melting point" but a "melting range," melting points are dependent on the method used for their determination. Examples are the Wiley melting point, (AOCS Official Method Cc2-38) and the capillary tube melting point (AOCS Official Method Cc1-25) (1). These methods are widely used in the North American edible oil industry. The Ubbelohde dropping point (Deutsche Gesellschaft fuer Fettwissenschaft [DGF] Einheitsmethode C-IV 3b) (2), is more popular in Europe. The different methods give results not directly related to each other, and even small changes in the established procedures can produce large variations in the results. Often the endpoint determinations depend upon a subjective interpretation. The reproducibility of test results between different laboratories is sometimes poor. Examples are the ranges given for the various official methods or reported in the literature: AOCS Wiley mp, 1.0 C; AOCS capillary tube mp, 0.5 C; and DGF dropping point (dp), 4.0 C. Mehlenbacher (3), standard deviation of Wiley mp tests: 0.59; standard deviation of capillary mp tests: 0.92. AOCS Smalley edible fat series (check samples) (4).

Harangozo (5) has described the Mettler FP3 unit and its use with lubricating grease, wax, cosmetic products and edible fats. With a heating rate of 1 C/min and 3-5 determinations per sample, the dropping point results of six fat samples showed standard deviations of 0.1-0.5. Rotger (6) also published test results with the FP3. He had found a reproducibility of better than 0.5 C.

The aim of the present work was to investigate more fully the usefulness of the FP3 apparatus for the edible oil industry (7). Especially the melted fat samples from the manufacturing process of an oil refinery require an easily applicable, rapid melting point method. The automatic temperature regulation and the objective endpoint determination made this instrument very attractive.

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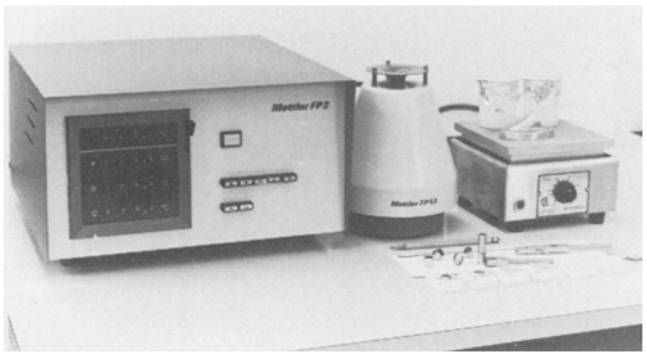

FIG. 1. Mettler FP3 dropping point unit.

METHODS AND MATERIALS

The Mettler automatic dropping point instrument consists of an electronic control unit (FP3) and the furnace (FP31 or FP53). The units, their working principle and technical data have been described by Harangozo (5) and by the Mettler Instrumente AG in the Instruction Manual (8).

The control unit regulates the automatic and linear temperature increase in the furnace, records the endpoint, and also makes the preselection of several heating rates possible (0.2, 1, 2, 3 and 10 C/min). The furnace holds the sample cartridge with the small sample cup. Temperatures are measured with a built-in platinum resistance thermometer. Below the sample a light beam is directed horizontally against a photocell, and the first drop falling from the sample cup interrupts this beam and stops the test. This temperature is recorded automatically as the dropping point. The metal sample cups have been designed according to American Society for Testing and Materials (ASTM) Method D566-64 (9), and have a bottom opening with a diameter of 2.8 mm. Harangozo (5) reported identical test results with sample cups with 2.8 mm (ASTM) or 3 mm openings (DGF).

The sample preparation depends on the nature of the material. Solidified fat samples can be filled into the cups with a spatula, or the cups can be placed on a smooth surface and filled with liquid fat. Completely filled sample cups are used in the DGF Ubbelohde method (2), whereas a conical section of the test material is removed in the ASTM method (9).

The present work has been done with an electronic control unit FP2 (which was available and is identical to the control unit FP3), and a furnace FP53. Metal cups and cup holders were provided with the instrument. The sample holder has a handle for easy positioning of the cups in the furance; the lower part is the collecting sleeve for the melted sample.

In order to work easily with melted fat samples, small rectangular pieces of styrofoam were cut (35 x 30 mm, 10 mm thick), and a 12 mm diameter hole, equivalent to the outside diameter of the metal cups, was drilled into each one. Aluminum foil squares, 35 x 35 mm, were placed on top of the small plastic trays and pressed into the holes with empty sample cups. A firm support for the cup was thus obtained, along with a foil lining which sealed the

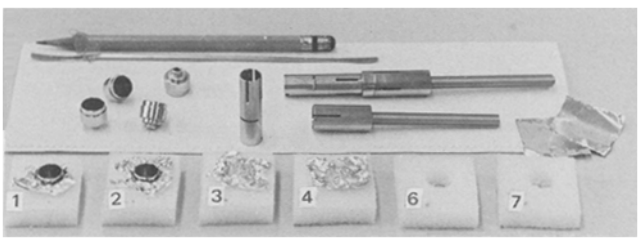

FIG. 2. Accessories for the FP 3 dropping point unit: sample cups, cup holders (cartridge), plastic foam trays, aluminum squares.

TABLE I

Dropping Points (°C) of Seven Fat Samples at Different Heating Rates[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
1 C/min							
Mean dp	44.35	41.68	44.92	41.10	37.05	32.58	32.73
Range	0.3	0.2	0.2	0.2	0.3	0.5	0.3
Standard deviation	0.12	0.08	0.08	0.11	0.14	0.18	0.12
2 C/min							
Mean dp	44.87	42.20	45.37	41.68	37.62	33.98	33.50
Range	0.3	0.4	0.4	0.1	0.5	0.5	0.2
Standard deviation	0.10	0.19	0.16	0.04	0.22	0.19	0.06
10 C/min							
Mean dp	48.07	46.48	48.27	46.22	41.08	38.45	37.17
Range	0.8	1.0	1.0	0.8	0.7	1.1	0.9
Standard deviation	0.34	0.33	0.38	0.34	0.33	0.37	0.31
Wiley mp	44.3	42.1	44.5	41.1	37.6	35.6	33.2
Beginning of programing	30	30	30	30	25	20	20

[a]Six determinations per test.

[b]dp = Dropping point. Range = difference between highest and lowest test result.

bottom opening of the sample cup. Aside from simplifying numbering and handling of the metal cups, the foam trays serve another important function: once the fat has been solidified and is ready for the test, the hand of the analyst never needs to touch the sample cup, thereby avoiding premature and uncontrollable heating.

A temperature-controlled hotplate with a surface thermometer was used for uniform melting of the fat samples; freezing was done in a refrigerator freezing cabinet at -10 C. All cups were filled completely with the fat sample. The instrument is presented in Figure 1, and details of the accessories (cups, cup holders, plastic trays and foil squares) are shown in Figure 2.

Test methods used are described below.

Liquid Fat Samples, Standard Procedure

(a) After filtering of the oil, a 30 ml sample in a 100 ml beaker (or a similar small amount in a relatively large beaker to make dropwise filling of the sample cups possible) was heated to 85 C on the hotplate. (b) Two sample cups in the plastic trays were prechilled in the freezer cabinet at -10 C for 15 min. (c) Both cups were filled at the same time. (d) The cups were transferred directly from the freezer cabinet into the FP53 furnace, the first sample after 30 min. The second sample was tested as soon as possible after the first one, when the furnace had again reached the starting temperature. Total freezing time of this sample depended on the programing rate and was 45 ± 5 min. (e) Prior to the sample transfer, the furnace had been adjusted to the starting temperature, which was 10-15 C below the dropping point: tests started at 20 C for dropping points from 30-35 C; tests started at 25 C for dropping points from 35-40 C; tests started at 30 C for dropping points above 40 C. Most melting point methods specify a starting temperature of at least 8-10 C below the endpoint. (f) The heating rates were 1, 2 and 10 C/min. (g) The average of two determinations was taken as the dropping point. (h) All fat samples were taken from the

TABLE II

Dropping Points (°C) of Different Fat Samples[a]

	Freezing time, hr									
	Without tempering				With tempering					
Fat[b]	0.5	1	2	16	0.5	1	2	16	Beginning of programing	Mean of all ranges
67-1 (Animal)										
Mean dp	45.10	45.10	44.87	44.30	45.20	44.87	44.37	44.0	30	0.18
Range	0.2	0.2	0.1	0.2	0	0.2	0.3	0.2		
Standard deviation	0.10	0.10	0.06	0.08	0	0.12	0.15	0.08		
69-2 (Vegetable)										
Mean dp	37.83	37.70	37.60	37.23				37.33	20	0.24
Range	0.1	0.2	0.6	0.2				0.1		
Standard deviation	0.06	0.10	0.35	0.12				0.06		
68-2 (Lauric fat)										
Mean dp	33.97	34.37	33.93	33.85				33.83	20	0.48
Range	0.5	0.7	0.4	0.4				0.4		
Standard deviation	0.25	0.35	0.23	0.19				0.17		
69-4 (Vegetable)										
Mean dp	33.43	33.53	33.40	33.13				33.47	20	0.30
Range	0.5	0.3	0.2	0.2				0.3		
Standard deviation	0.29	0.15	0.10	0.12				0.15		
68-1 (Animal)										0.16
67-3 (Vegetable)										0.28
68-3 (Vegetable)										0.28

[a]Heating rate 2C/min, with and without tempering. Three to four determinations per test.

[b]dp = Dropping point. Range = difference between highest and lowest test result.

TABLE III

Dropping Points (°C) of Three Shortenings at Different Heating Rates[a]

Programing[b]	Shortening sample					
	1. Blended		2. All vegetable		3. Hydro coconut	
	Original	Melted	Original	Melted	Original	Melted
1 C/min						
Mean dp	45.77	45.50	45.73	45.23	38.87	37.92
Range	0.3	0.4	0.6	0.2	0.6	0.4
Standard deviation	0.12	0.14	0.22	0.10	0.23	0.15
2 C/min						
Mean dp	46.50	46.43	46.42	46.03	39.72	38.85
Range	0.2	0.3	0.6	0.1	1.1	0.3
Standard deviation	0.06	0.10	0.22	0.05	0.42	0.11
10 C/min						
Mean dp	50.40	50.17	49.85	49.87	43.92	44.47
Range	0.6	0.3	0.6	0.5	1.2	0.8
Standard deviation	0.21	0.12	0.24	0.26	0.48	0.28
Mean difference between original and melted	0.19		0.30		0.79	
Wiley mp	---	45.0	---	44.6	---	40.6
Beginning of programing	30	30	30	30	25	25

[a]Six determinations per test.

[b]dp = Dropping point. Range = difference between highest and lowest test result.

AOCS Smalley edible fat series, and the average Wiley melting points are reported for comparison.

Liquid Fat Samples, Preliminary Tests

The temperatures listed previously were used. (a) Tempering for 15 or 30 min at 26 C or 20 C prior to the determination has been investigated. (b) Different freezing times for the fat sample cups were used (0.5, 1, 2 and 16 hr). (c) The heating rate in all cases was 2 C/min.

Solidified Fat Samples

Solidified fat samples, commercial shortenings, margarine and butter samples were tested as received, or after melting, phase separation, and filtering of the oil. The melted oil samples were tested according to the procedure listed above. All solidified samples were filled into the sample cups with a spatula at a temperature equal to or lower than the lowest test temperature (usually at room temperature). (a) In preliminary tests, six solidified fat samples were tested at a heating rate of 1 C/min; starting temperature 20 C, three to four determinations per sample. (b) Three shortening samples were tested at heating rates of 1, 2 and 10 C/min. Each individual test condition was repeated six times on at least two different days. (c) Tests with four randomly selected butter and margarine samples were all started at 25 C, and a programing rate of 2 C/min was used exclusively. Each test was repeated eight times on two different days.

RESULTS AND DISCUSSION

Liquid Fat Samples, Standard Procedure

Seven AOCS fat samples were tested at different heating rates. The samples and test results are listed in Table I.

All results obtained with heating rates of 1 and 2 C/min showed good reproducibility. Poorest results were obtained with lauric acid fat 68-2. The greatest variations in absolute values and in the test precision were caused by the rapid heating rate of 10 C/min. This rate is intended only for a rough estimation of the dropping point. The mean ranges of all tests show the improved precision at decreasing heating rates; with heating rates of 1, 2 and 10 C/min the mean ranges were 0.29, 0.34 and 0.90 C, respectively.

Increased programing rates resulted in higher dropping points. This was to be expected, since the difference between true sample temperature and instrument signal increases with a more rapid heating.

The relatively slow heating rate of 1 C/min was investigated because it is specified in the DGF (2) and ASTM (9) methods. When compared to 2 C/min programing, precision of the results was not greatly improved. A heating rate of 2 C/min is therefore suggested as a standard laboratory method, as outlined under Methods and Materials. It is interesting to note that the dropping points (1 and 2 C/min heating rates) were often close to the Wiley melting points.

The results with temperature programing of 1 and 2 C/min were satisfactory. If similar results could be obtained with different FP3 units in other laboratories, the method would represent an improvement in the precision of results over the most popular melting point methods now in use.

Liquid Fat Samples, Preliminary Tests

This series included the same seven oil samples listed in Table I; all were tested with a 2 C/min heating rate. As an example the results of dropping point determinations of animal fat 67-1 and of three fat samples with a Wiley melting point below 40 C (AOCS samples 69-2, 68-2, 69-4) are shown in Table II. Tempered sample 67-1 was held for 15 min at 26 C, the other tempered samples for 30 min at 20 C. For the work with samples 69-2, 68-2 and 69-4, the FP3 unit was transferred to a temperature-controlled room at 16 C. Reproducibility was good in all cases, and tempering had only a minimal effect on reproducibility. Some oils seemed to be more suited for the dropping point method than others. The lauric acid oil sample (68-2) gave the largest variations.

With the exception of fat 68-2, the mean ranges never exceeded 0.3 C. Longer freezing times resulted in slightly lower dropping points, but these changes were small at freezing times of 0.5-2 hr, when no tempering was used. Tempering mainly affected the animal fat samples. The effect of short time tempering at 20 C was almost negligible. To achieve the best uniformity at short freezing times, the tempering step was omitted in the standard procedure.

The dropping points were generally close to the Wiley melting point, which is an advantage for practical applications. All dropping points of lauric acid fats were lower than the Wiley melting points.

The influence of sample size in the cup on the dropping

TABLE IV

Dropping Points (°C) of Two Butter and Two Margarine Samples and Their Oil Phases[a]

Sample[b]	Finished product	Oil sample	Wiley mp	Difference in dp, product-oil
Butter no. 1				
Mean dp	34.96	34.65	35.2	0.31
Range	0.2	0.5	---	
Standard deviation	0.07	0.15	---	
Butter no. 2				
Mean dp	34.81	34.69	34.3	0.12
Range	0.2	0.2	---	
Standard deviation	0.06	0.06	---	
Margarine no. 3				
Mean dp	37.03	35.88	35.6	1.15
Range	0.3	0.4	---	
Standard deviation	0.10	0.15	---	
Margarine no. 4				
Mean dp	35.86	35.28	35.0	0.58
Range	0.2	0.5	---	
Standard deviation	0.07	0.21	---	

[a]Heating rate 2 C/min; starting temperature 25 C; eight determinations per test.
[b]dp = Dropping point. Range = difference between highest and lowest test result.

point was investigated with two oils (samples 68-3 and 67-1). Sample size fluctuations (from two-thirds to fully filled cups) influenced dropping point results only slightly. The results differed by not more than 0.3 C. The amount of sample per full cup, filled at 85 C, was 0.55-0.56 g.

Solidified Fat Samples

a) The dropping points of six solidified fat samples gave ranges varying from 0.2-0.8 C.

b) Three commercial shortenings were tested at different heating rates, both as finished products (as received), and after melting. These were: shortening no. 1, and animal and vegetable blend; no. 2, a vegetable formula; no. 3, hydrogenated coconut oil. The suggested standard procedure (Methods and Materials) was used for the melted samples. Results are listed in Table III.

When the sample cups are filled with a spatula, the breakdown of the structure will probably contribute to fluctuations of the results. Shortenings 1 and 2 were smooth and plastic at 25 C and could easily be filled into the cups. Shortening 3 was firm below 20 C. Sample cups were filled at 20 C for the test with 2 and 10 C/min heating rates, and at 25 C for the tests at 1 C/min; the shortening was much less brittle at the higher temperature.

The precision of the method was good, but poorer at 10 C/min heating than at the slower rates. The 1 C/min heating rate was not better than the 2 C/min rate, as is indicated by the mean ranges of all tests which were 0.42, 0.43 and 0.67 C at 1, 2 and 10 C/min, respectively.

The dropping points, as expected, increased with increased rate of heating. The precision was better for melted and resolidified samples than for the original shortenings. This might be partly due to the nonuniform working with the spatula during the filling of the sample cups. The mean range of melted samples was 0.37 C and of the finished shortenings, 0.64 C.

Different results were obtained for the same fat material when it was analyzed as a finished product or after remelting. The results after remelting were usually slightly lower. These differences changed from one shortening to another, as can be seen in Table III.

If a certain shortening, manufactured under specific standard conditions, shows a typical and reproducible difference between the dropping point of the melted fat and the solidified, finished product, such a method might be useful for production control. Factors which might influence this difference could be "run-off" conditions (chilling rates), air content of a product, tempering conditions, tempering times, etc.

c) The dropping point test results of two butter and two margarine samples, and the oil phases separated from these are listed in Table IV.

As in the case of shortenings, the dropping point method could be used for butter and margarine, both for the ingredient oil phase and for the finished product. The precision of results was good for all tests. The dropping points of the finished products were higher than those of the ingredient oils. These differences were smaller for the butter than for the margarine samples, as can be seen from Table IV.

Knowledge of these differences might be useful for evaluation of a variety of factors, such as water phase distribution, chilling rates, working during manufacturing, recrystallization during handling and storing, etc. More work will be required to determine whether these differences are consistent and typical for certain oils, manufacturing procedures, or tempering conditions. These differences may also indicate organoleptic preferences of products (mouth feel).

General Comments

Some disadvantages of the Mettler FP3 dropping point unit should be mentioned. Only one sample can be analyzed at one time. The connection of two furnace units to the same electronic control unit for duplicate determinations would be an advantage. Handling and cleaning of the relatively small cups and cartridge parts could cause difficulties, and the lower cartridge section (the well for the liquid drops) should be larger to reduce the frequency of cleaning. Since the furnace is air-cooled, the surrounding air temperature limits the starting temperature of the test. With the present trend towards softer fats, starting temperatures of 15-20 C are often needed. This requires a cold room or cabinet for the furnace.

The main advantages of the instrument are the availability of different heating rates, the fully automatic control of heating rates, and the automatic endpoint determination. This eliminates subjective interpretation. The precision of the results at heating rates of 1-2 C/min was good in all cases, even though some fats were less suited for this test than others (example lauric acid fat).

A standard procedure has been suggested for melted fat samples as an automatic, objective and precise melting

point method. The method is rapid and practical for quality control work.

The manufacturer (8) claimed a precision of ± 0.3 C at heating rates from 1-3 C/min. The results reported in this work confirm this. The ranges were below 0.7 C, with a mean of all tests (at 1 and 2 C/min heating) of about 0.3 C.

The ability to test finished products (shortenings, butter, margarine) as well as their ingredient oils opens possibilities for the study of manufacturing processes, handling, storing, etc. The advantages far outweigh the disadvantages and make the FP3 instrument a very useful tool for the determination of the melting point of fats.

ACKNOWLEDGMENT

This work was done during a Post Industrial Experience Research Fellowship awarded by the National Research Council of Canada to W.G. Mertens.

REFERENCES

1. "Official and Tentative Methods of the American Oil Chemists' Society," Vol. I, Third edition, AOCS, Champaign, Ill., 1964, Method Cc2-38 and Cc1-25.
2. "Deutsche Einheitsmethoden zur Untersuchung von Fetten, Fettprodukten and verwandten Stoffen," Deutsche Gesellschaft fuer Fettwissenschaft, 1961, DGF Einheitsmethode C-IV 3b.
3. Mehlenbacher, V.C., "The Analysis of Fats and Oils," The Garrard Press, Champaign, Ill. 1960.
4. "Smalley Edible Fat Series," AOCS, Champaign, Ill., Results published yearly and distributed to participating laboratories.
5. Harangozo, D., Fette, Seifen, Anstrichm. 71:826 (1969).
6. Rotger, K., Ibid. 70:857 (1968).
7. Mertens, W.G., "An Investigation of Several Methods for the Study of Fat Crystallization," M. Sc. thesis, University of Guelph, Guelph, Ontario, 1971.
8. "Mettler Instrumente AG," Greifensee-Zurich, Switzerland, Instructions Mettler FP3 and FP31.
9. "ASTM Standards," Part 17, American Society for Testing and Materials, 1968, Method D566-64.

[Received December 13, 1971]