Critical Aspects of Slip Melting Point Measurements

Ringkasan

Aspek penting mengenai ukuran paras titik lebur minyak seperti masa/waktu dan suhu, cara-cara pewajaan, cara menyediakan sampel, ukuran tinggi lemak di dalam salur rerambut dan saiz salur rerambut dibincangkan secara terperinci.

Ketetapan cara di laporkan dan juga cadangan-cadangan yang dibuat untuk membaiki keputusan percubaan telah diberikan.

Introduction

The melting point is usually defined as the point at which a material changes from the solid to liquid state. Oils and fats, unlike pure compounds do not show sharp melting points. Being a complex mixtures of triglycerides, they go through an extended softening period before gradually changing to a completely liquid oil upon heating. The process of melting is further complicated by the fact that fat crystals can exist in several polymorphic forms which may be governed by time temperature pretreatments. The melting point of a fat can therefore be defined only if rigid and specific conditions of fat pretreatment in the test method are strictly adhered to.

It is the objective of this paper to present the differences which may arise in slip melting point measurements using the open capillary tube method and also to suggest some specific recommendations for further standardisation between laboratories in order to obtain reproducible values.

Review of Slip Melting Point Methods

Table 1 shows some basic differences between methods with regard to size of capillary tube, and tempering procedure. Internal diameter of capillary tubes ranges from 0.8 — 1.1 mm for the Indian standards to 1.1 — 1.3 mm for British standards. *Table 2* shows the slip point of palm oil and other products using different methods. It is obvious that results vary with the methods and that these variations depend on the type and nature of the sample. With palm oil and palm olein, large variations exist between methods. The Cocks and Van Rede method results in higher values for palm oil, while the British Standard method 2 appears to give lower values.

With palm oleins, problems occasionally exist with the Cocks and Van Rede and the Indian Standard methods, as the shorter time of tempering does not allow for complete solidification and formation of stable crystals; hence lower values are obtained.

It is imperative therefore that for comparisons and especially in commercial transactions, a mutually agreed method should be used.

Factors Affecting Slip Melting Point

Height of the Fat Column. (Reference method AOCS Cc3-25).

While a 10 mm fat column is suggested in the AOCS method, it is not always possible to be able to retain this height in the capillary tube. Hence we have tried out a range of

Table 1. Basic Differences Between Slip Point Methods

Method	Internal Diameter of Capilary Tubes	Tempering Procedure	
		Initial Treatment	Further Treatment
Cocks and Van Rede	0.9 — 1.1 mm	Chill against ice till solid	Hold at –10°C for 5 minutes.
AOCS Cc3-25	1 mm	Chill against ice till solid	Hold at 4–10°C for 16 hours.
BS 1.3 Method 1	1.1 — 1.3 mm	Cool to 15°C	Hold at 15–17°C for 16 hours.
BS 1.3 Method 2	1.1 — 1.3 mm	Cool with stirring till a paste is formed. Fill capillary tube with paste.	Hold at 15–19°C for at least 24 hours.
Indian Standard (IS 9.1)	0.8 — 1.1 mm	Chill against ice till solid	Hold at 4–10°C for 1 hour.

Table 2. Slip Point of Different Fats Using Various Methods

Sample / Method	Palm Oil				Palm Olein		Palm Stearin		Hydrogenated Palm Oil		
	1	2	3	4	1	2	1	2	1	2	3
Cocks and Van Rede	40.4	39.0	41.7	36.1	20.7	10.5	50.9	50.4	40.9	40.8	43.4
AOCS Cc3–25	36.2	35.2	37.5	35.3	21.8	19.9	51.4	50.7	41.5	40.9	43.9
BS 1.3 Method 1	36.5	35.9	38.0	34.3	—	—	51.2	49.3	40.1	40.3	43.0
BS 1.3 Method 2	34.5	33.0	35.6	33.9	—	—	50.9	49.4	40.6	40.7	43.9
IS 9.1	36.4	35.8	38.0	34.8	20.4	10.0	51.1	51.0	40.9	41.0	43.6

heights varying from 7mm to 12mm *(Table 3)*. It appears that a longer column of fat in the capillary tubing may result in slightly higher slip point values.

Effect of Different Sizes of Capillary Tubing

Table 4 shows results obtained from two sizes of capillary tubing, differing widely in internal diameter and wall thickness. No significant effect was obtained.

Tempering Time

The slip melting point obtained under different tempering times of 1 to 20 hours were compared in *Table 5*. Except for palm olein, the difference in slip point for the other samples tempered for 1, 8 or 16 hours were not significant. For palm olein, longer tempering times generally lead to higher slip points.

Tempering Temperature

Samples tempered at various temperatures ranging from –10°C to 15°C were found to result in large variations in slip melting point. This is shown in *Figure 1*.

Table 3. Effect of Different Levels of Fat Column in Capillary Tubes on Melting Point °C

Sample	7 mm	10 mm	12 mm	Difference Between 7 mm + 12 mm
Palm Oil	33.9	35.1	35.6	1.7
	35.2	36.3	36.9	1.7
Palm Olein	20.6	20.3	20.9	0.3
	20.2	20.8	20.7	0.5
Palm Stearin	39.9	40.5	40.8	0.9

Table 4. Effect of Different Tube Diameter and Thickness on Slip Point

Sample	Size of Capillary Tubes		Difference
	Internal diameter 1.1 — 1.2 mm; wall thickness 0.20 ± 0.02 mm	Internal diameter 2 mm; wall thickness approx. 0.4 mm	
Palm Oil	37.5	37.3	+0.2
	36.4	36.2	+0.2
Palm Olein	22.0	22.3	—0.3
	21.3	21.3	0
Palm Stearin	51.5	52.3	+0.2
	51.9	52.2	—0.3
Hydrogenated	41.5	41.4	+0.1
Palm Oil	40.9	40.6	+0.3
	43.9	44.1	—0.2

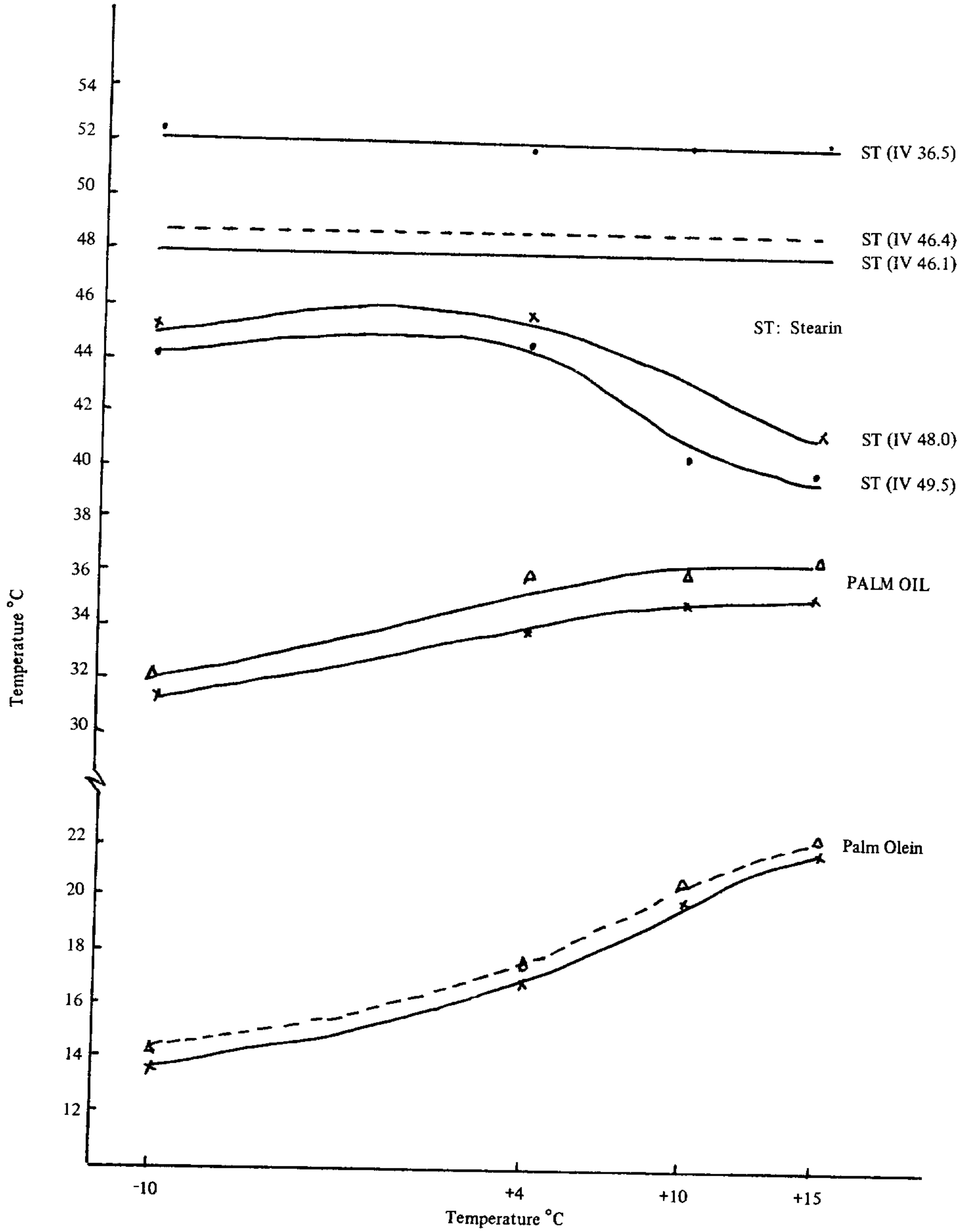

Fig. 1. Effect of Tempering Temperature on Slip Point.

Table 5. Effect of Time of Tempering

Time (hrs)	Palm Oil		Palm Olein			Palm Stearin
1	38.2	35.8	18.4	19.0	16.6	53.1
6	38.2	35.9	20.9	21.3	19.8	52.9
16	37.8	35.5	20.4	21.4	19.5	52.7
18	37.8	35.5	20.3	21.4	20.3	52.8
20	37.5	35.5	20.5	21.1	18.5	52.7

Palm oil and palm olein show lower slip point values at low temperature of tempering such as –10°C, and 4°C.

The Differential Scanning Calorimetry (DSC) thermograms of the samples tempered under different temperatures are shown in *Figures 2 — 6*. The melting thermograms for palm oil and olein *(Figures 2 and 3)* show that samples kept at –10°C and 4°C were in the least stable form, absorbing the least amount of heat during melting, hence low slip point values. Samples kept at 10°C were more stable.

Stearins behaved in a different manner depending on the nature of their composition. Hard stearins were very much unaffected by the different procedures of tempering. The DSC thermograms *(Figure 4)* show that the melting point is essentially determined by the hard fraction which is indicated by the major peak. This fraction crystallises in the same form under all the different tempering temperatures, hence very little variation in slip point exists. In fact, in a collaborative test conducted by PORIM, the results from various laboratories were most consistent for hard stearins.

Soft stearins fall into two groups depending on its iodine value and triglyceride composition. It has been found that some soft stearins of iodine value 46 shows higher slip point values at –10°C and 4°C of tempering and lower slip point values at 10°C and 15°C of tempering. A 5°C difference in the slip point exists between these two groups of temperature. However this behaviour is not always true and there are other soft stearins of similar iodine value which are not affected very much by different tempering temperatures. Examples of these behaviours are shown in the DSC thermograms *(Figures 5 and 6)*. The triglyceride composition of these stearins are shown in *Table 6*. It is observed that the slip point of soft stearin with a high C48 triglyceride are unaffected by the tempering procedures while stearins with lower C48 triglycerides are more susceptible to changes. The extra C48 triglyceride present appears to help in stabilisation of the crystal form during tempering.

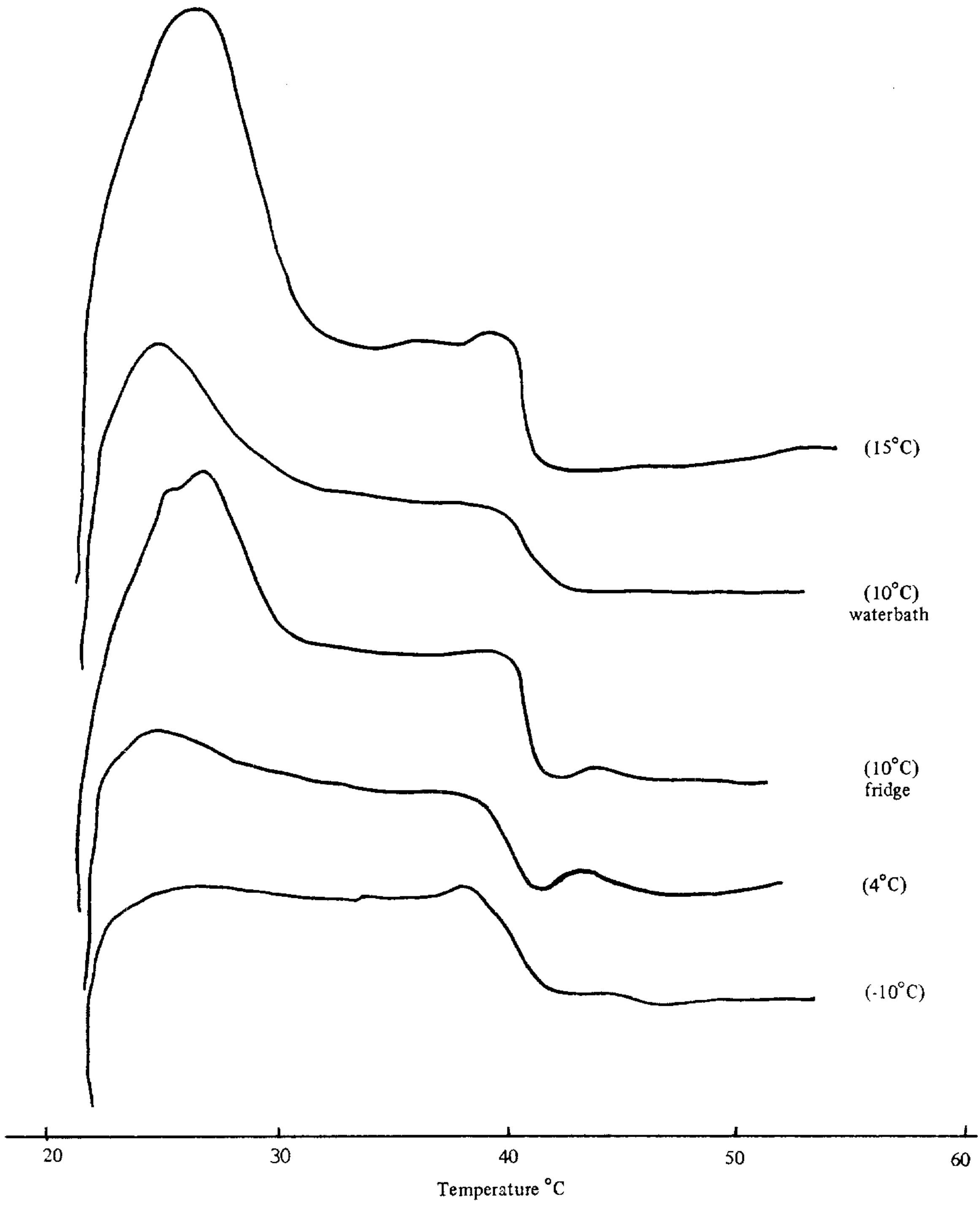

Fig. 2. DSC Melting Thermograms Sample — Palm Oil.

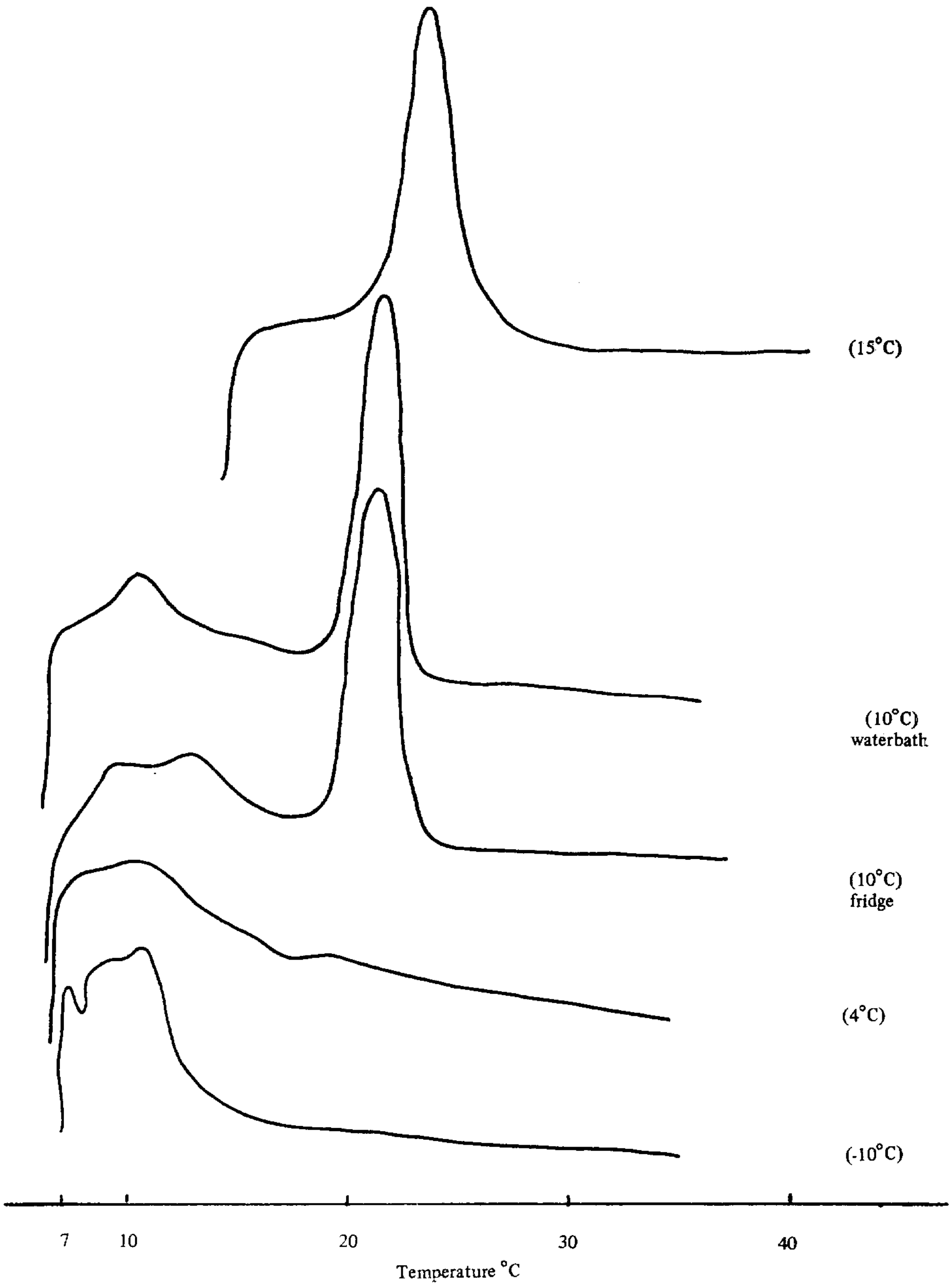

Fig. 3. DSC Melting Thermograms Sample — Olein.

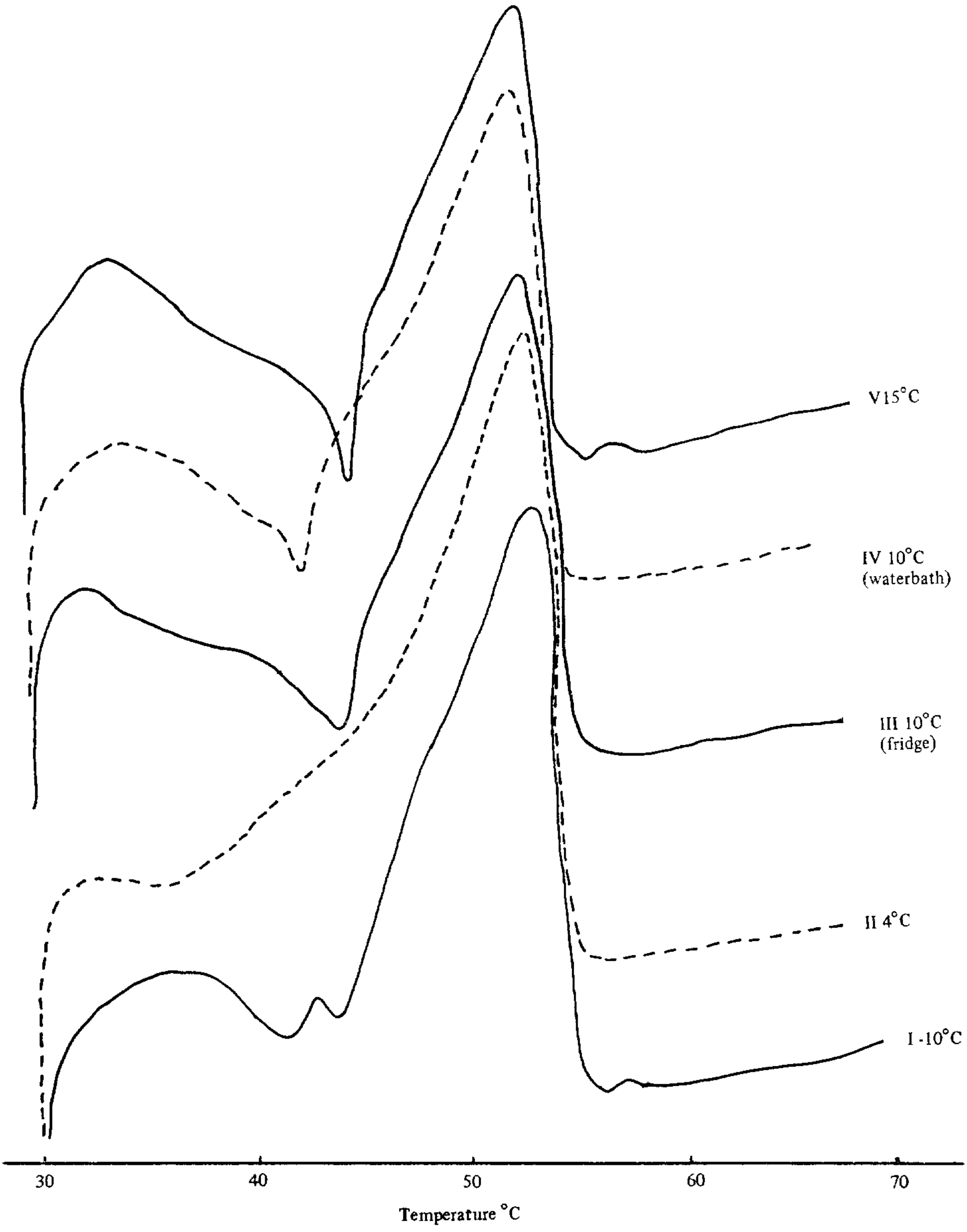

Fig. 4. DSC Melting Thermograms Sample — Hard Stearin.

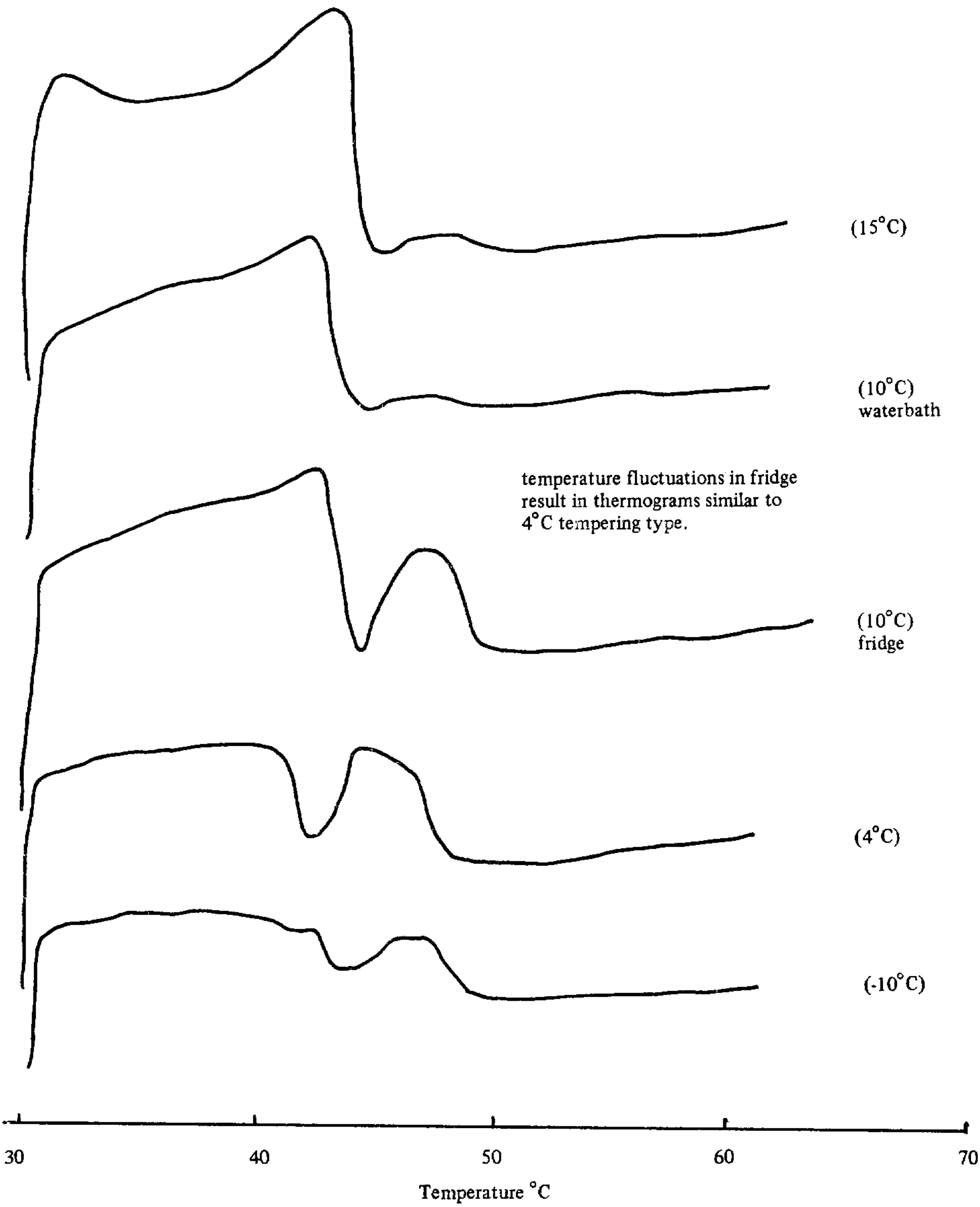

Fig. 5. DSC Melting Thermograms Sample — Soft Stearin A.

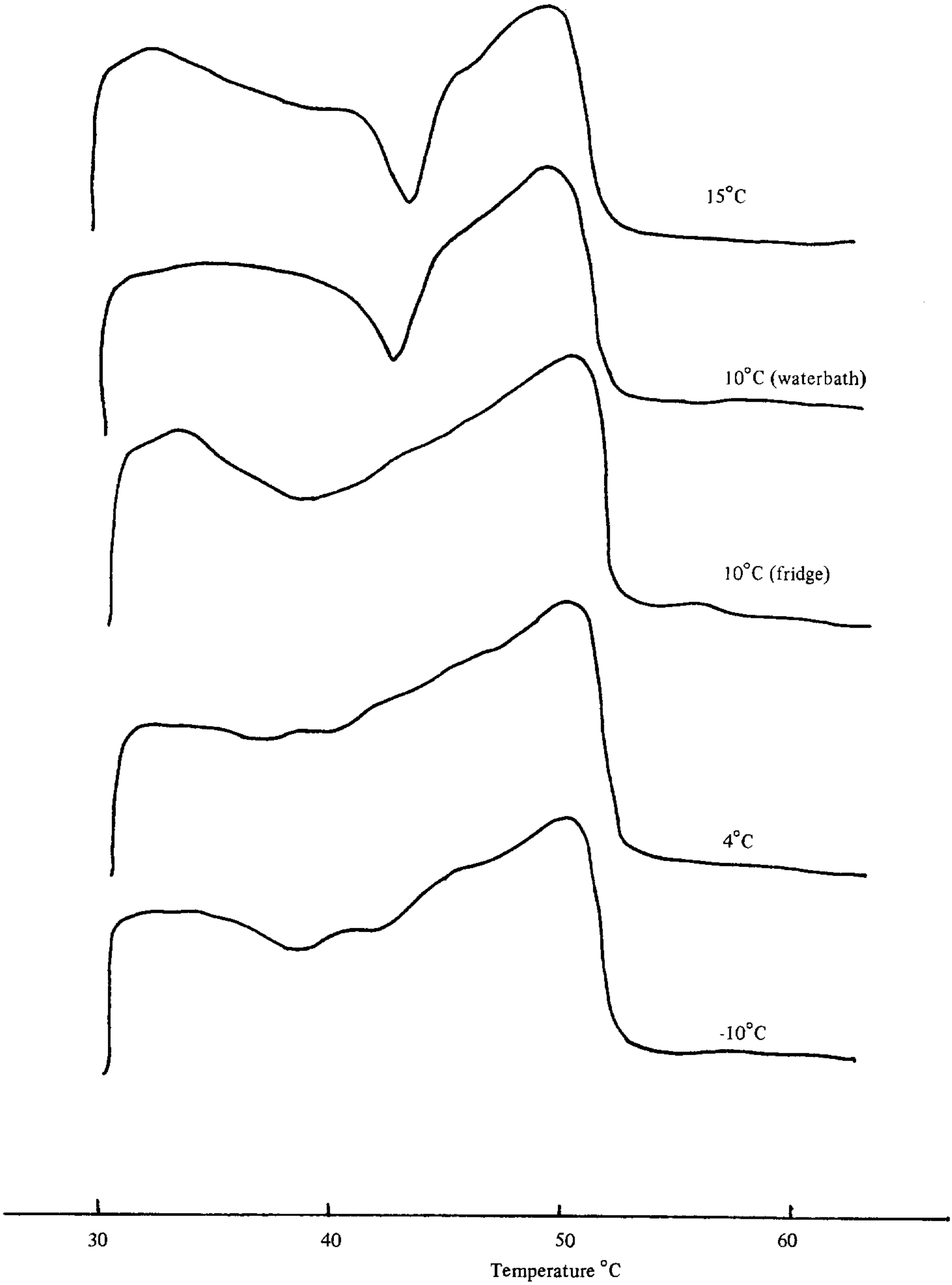

Fig. 6. DSC Melting Thermograms Sample — Soft Stearin (81 CS).

Table 6. Triglyceride Composition of Soft Palm Stearins
(a) Slip Point Sensitive to Tempering

Triglyceride Carbon Number	Stearins IV 48–49			Stearins IV 46–47		
	63CS	143CS	65CS	A*	127CS	128CS
C46	0.8	0.8	1.6	1.1	1.0	1.1
C48	**12.8**	**8.2**	**12.2**	**10.8**	**9.9**	**12.4**
C50	42.2	48.9	43.4	43.0	49.8	48.0
C52	36.0	35.7	35.5	36.6	33.9	33.2
C54	8.2	6.3	7.2	8.5	5.4	5.2
Slip Point After Tempering						
at 4°C	45.1	44.2	46.0	45.5	44.6	45.8
10°C	41.8	40.0	42.4	40.4	39.7	43.7

(b) Slip Point Not Sensitive to Tempering

Triglyceride Carbon Number	Stearins IV 46–47		
	125CS	98CS	81CS*
C46	1.2	1.5	1.3
C48	**14.0**	**16.2**	**19.4**
C50	47.5	45.4	41.8
C52	32.3	30.0	30.9
C54	5.0	6.9	6.6
Slip Point After Tempering			
at 4°C	46.1	48.0	48.2
10°C	46.1	48.1	49.6

Note * DSC Melting Thermograms shown in Figures 5 and 6.

It is obvious therefore that the temperature of tempering plays an important role in slip point measurements depending on the nature of the oil. It also appears that tempering between 10° and 15°C is more suited for palm oil and its fractions than at other temperatures. To be more specific, one should temper at a fixed temperature of 10° ± 1°C in order to reduce variations in results.

Modes of Tempering

Differences in sample preparation and tempering may give rise to inconsistency in results between laboratories. This is implicitly shown in an experiment conducted between laboratories A and B. The results are summarised in *Table 7*. Methods 1 and 2 are different ways of sample preparation. Method 1 involves capillary tubes being filled, held against ice and left in ambient conditions before being transferred to the refrigerator for tempering.

In method 2, the capillary tubes after being filled and held against ice are inserted into narrow test tubes held in a beaker of water which has been pre-equilibrated to the refrigerator temperature (10°C). The beaker with the test tubes is then transferred to the refrigerator for tempering. In addition the test tubes containing filled capillary tubings were also kept in a water bath at 10°C (method 2a). Method 1 is laboratory B's normal procedure for preparation of the samples and is more subjected to temperature variations under ambient conditions during transfer of the tubings. These two procedures resulted in differences of 4–5°C in the slip point values. Method 1 appears to result in higher values.

The difference observed between 1 and 2 can be explained by the DSC melting thermogram *(Figure 7)*. The samples prepared under method 1 shows a higher melting point fraction (peak A) hence higher slip point values were obtained.

Precision and Reproducibility Between Laboratories

The precision of slip point measurements within the laboratory was measured at 10°C using a refrigerator and a thermostated waterbath *(Table 8)*. The precision of the method is much better for palm oil fractions, than for palm oil itself as noted from the standard deviations. Moreover better precision could be obtained using the waterbath as a tempering medium. This may be explained by the possible fluctuation in temperature that may occur in a refrigerator.

The results of two ring tests of slip melting point carried out on palm oil products are summarised in *Table 9*. In the first ring test, 41 laboratories reported. In the second test 13 laboratories took part, all using a thermostated bath set at 10°C for tempering. *Table 7* records the expected agreement between two single determinations within and between laboratories calculated according to AOCS MI — 59.

For the first ring test, the results of all laboratories (tempering from −10° to 10°C range) are compared with those tempering at 4 — 10°C range. A significant improvement in the expected agreement is obtained. A further improvement resulted in the second ring test where a thermostat bath was used.

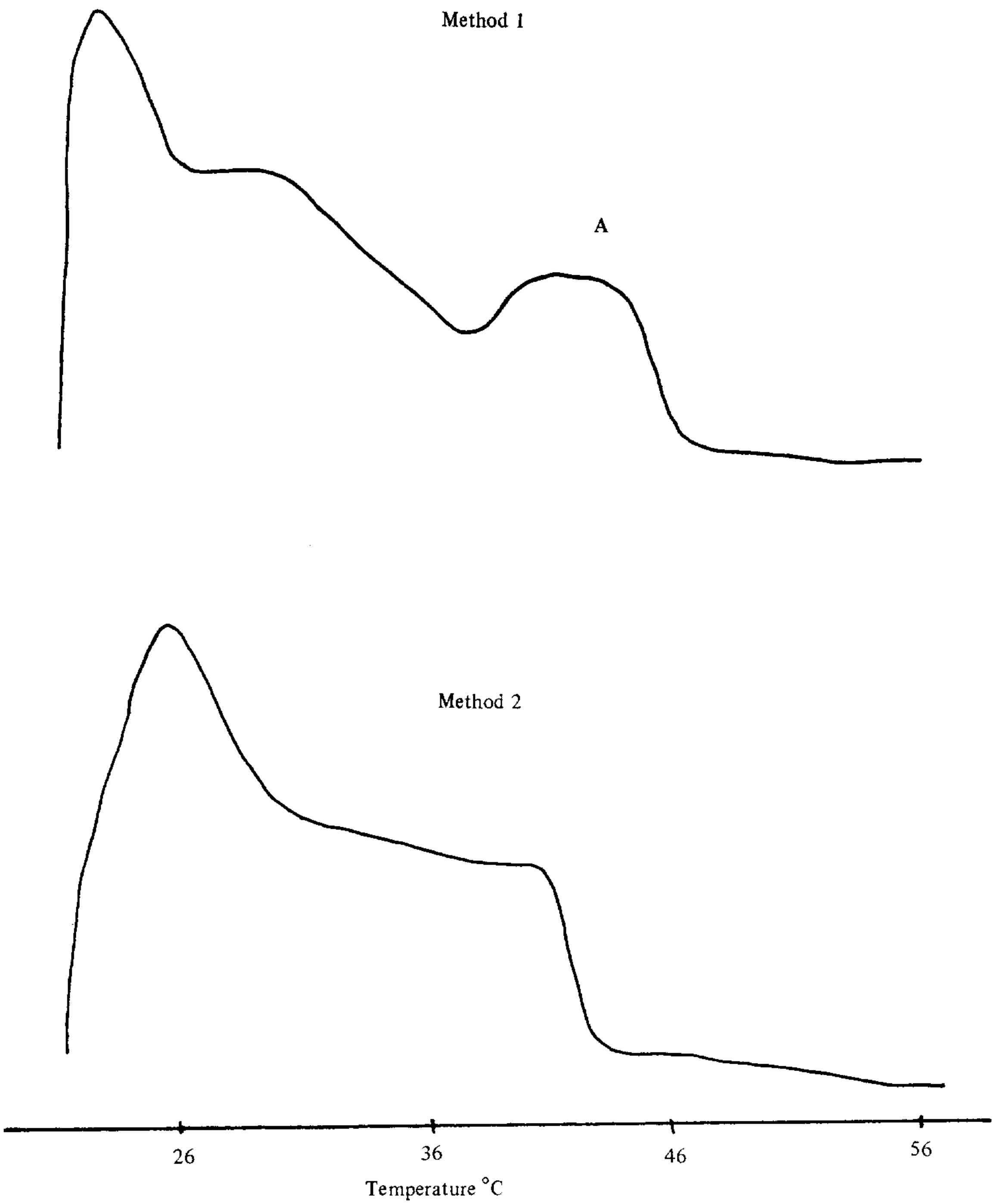

Fig. 7. DSC Melting Thermograms of Method 1 and 2 Procedures of Tempering.

Table 7. Effect of Different Modes of Sample Preparation

Sample Crude Palm Oil	Slip Melting Point (AOCS Cc 3 – 25)				
	Method 2 Temper at 10°C in fridge		Method 2a Temper at 10°C (waterbath)		Method 1
	Lab A	Lab B	Lab A	Lab B	Lab B
P.O. (1)	36.5	37.3	37.0	37.3	40.4
P.O. (2)	36.2	36.8	36.8	37.0	39.6
P.O. (3)	36.0	36.5	36.1	36.5	40.1
P.O. (4)	35.8	36.4	36.1	36.3	39.9
P.O. (5)	35.8	36.3	35.9	36.2	36.3

Table 8. Precision of Slip Point of Palm Oil and Its Fractions

a) Tempering at 10°C in a refrigerator

b) Tempering at 10° C in a thermostated waterbath.

	Palm Oil		Palm Stearin		Palm Olein	
	(a)	(b)	(a)	(b)	(a)	(b)
Mean	37.5	37.2	52.3	52.9	20.4	20.9
Standard Deviation	0.27	0.18	0.19	0.09	0.14	0.08
Coefficient or Variation	0.72	0.47	0.36	0.18	0.68	0.37

Table 9. Reproducibility of Slip Melting Point

	Expected Agreement of Single Determinations (0)	
	Within Laboratory	Between Laboratories
PALM OIL		
1st test 41 results (1)	1.8	6.4
1st test 35 results (2)	0.8	3.9
2nd test (3)	0.8	2.4
PALM OLEIN		
1st test 41 results (1)	0.6	5.9
1st test 35 results (2)	0.6	6.1
2nd test (3)	0.5	1.9
PALM STEARIN		
1st test 41 results (1)	1.3	1.9
1st test 35 results (2)	0.8	2.6
2nd test (3)	0.5	1.6

(0) Calculated according to AOCS M1-59

(1) First collaborative test (Tempering at -10°C to 10°C)

(2) Eliminating those laboratories using -10°C for tempering

(3) Second collaborative test (Tempering at 10°)

Standardisation of the Method

Since procedures for sample preparation and tempering are not specified in detail in the AOCS method it is expected that different laboratories would adopt their own interpretations of sample preparations and tempering using available facilities in the laboratories. It is shown that these differences do give rise to variations in results. In order to further improve on the reproducibility between laboratories we feel that it is necessary to standardise and specify the method of sample preparation and tempering for the test method. The following recommendations are proposed as additional precautions to be adopted for the AOCS method.

(i) Samples must be filtered and free from moisture. Samples are to be shaken thoroughly and left in the oven for 10 minutes till free from air bubble before preparation.

(ii) In order to minimise effects due to changes in temperatures, the capillary tubes should be filled with the sample up to 10 mm in length, and held against ice.

(iii) The capillary tubes should then be placed in a test tube (8 mm i.d., 1 mm thickness) held in a beaker of water which has been pre-equilibrated in the refrigerator to the tempering temperature. The samples should be tempered for 16 hours preferably in a thermostated water-bath or incubator held at 10°C. A refrigerator set for 10°C may be used if neither of the above is available. The opening and closing of the refrigerator door in this case should be minimised. A close check of the temperature should be maintained as the temperature of the refrigerator may be more subjected to fluctuations.

Article Credit: W. L. Siew, Augustine S. H. Ong, Flingoh C. H. Oh and K. G. Berger.