



# Standard Test Method for Measurement of Transition Temperatures of Petroleum Waxes by Differential Scanning Calorimetry (DSC)<sup>1</sup>

This standard is issued under the fixed designation D 4419; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method measures the transition temperatures of petroleum waxes, including microcrystalline waxes, by differential scanning calorimetry (DSC). These transitions may occur as a solid-solid transition or as a solid-liquid transition.

1.2 The normal operating temperature range extends from 15°C to 150°C (Note 1).

1.3 The values stated in SI units are to be regarded as the standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 87 Test Method for Melting Point of Petroleum Wax (Cooling Curve)<sup>2</sup>

D 1160 Test Method for Distillation of Petroleum Products at Reduced Pressures<sup>2</sup>

D 3418 Test Method for Transition Temperatures of Polymers by Differential Scanning Calorimetry<sup>3</sup>

E 472 Practice for Reporting Thermoanalytical Data<sup>4</sup>

E 473 Terminology Relating to Thermal Analysis<sup>4</sup>

E 474 Test Method for Evaluation of Temperature Scale for Differential Thermal Analysis<sup>5</sup>

## 3. Terminology

### 3.1 Definitions of Terms Specific to This Standard:

3.1.1 *Differential Scanning Calorimetry (DSC)*—A technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature, while the substance and a reference material are subjected

to a controlled temperature program. The record is the DSC curve. Two modes, power-compensation DSC and heat-flux DSC, can be distinguished depending on the method of measurement used. For additional background information refer to Practice E 472, Terminology E 473, and Test Method E 474.

## 4. Summary of Test Method

4.1 Separate samples of petroleum wax and a reference material or blank (empty sample container) are heated at a controlled rate in an inert atmosphere. A sensor continuously monitors the difference in heat flow to the two samples. The DSC curve is a record of this difference versus temperature. A transition in the wax involves the absorption of energy relative to the reference, resulting in an endothermic peak in the DSC curve. While the transition occurs over the temperature range spanned by the base of the peak, the temperature associated with the peak apex is designated the nominal transition temperature (Note 1).

NOTE 1—Test Method D 87 also monitors energy transfer between wax and a standard environment. The highest temperature DSC transition may differ from the melting point because the two methods approach the solid/liquid phase transition from different directions.

## 5. Significance and Use

5.1 DSC is a convenient and rapid method for determining the temperature limits within which a wax undergoes during transitions. The highest temperature transition is a solid-liquid transition associated with complete melting; it can guide the choice of wax storage and application temperatures. The solid-solid temperature transition is related to the properties of the solid, that is, hardness and blocking temperature.

NOTE 2—For a relatively narrow cut petroleum wax, the lowest transition will be a solid-solid transition. A narrow cut wax is one obtained by deoiling a single petroleum distillate with a maximum range of 120°F between its 5 % and 95 % vol in accordance with Test Method D 1160 boiling points (converted to 760 torr). The DSC method cannot differentiate between solid-liquid and solid-solid transitions. Such information must be predetermined by other techniques. In the case of blends, the lower temperature transition may be envelopes of both solid-liquid and solid-solid transitions.

5.2 Since petroleum wax is a mixture of hydrocarbons with different molecular weights, its transitions occur over a temperature range. This range is one factor that influences the

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 08.02.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 14.02.

<sup>5</sup> Discontinued; see 1985 *Annual Book of ASTM Standards*, Vol 14.02.

width, expressed in °C, of the DSC peaks. The highest temperature transition is a first-order transition. If, for a series of waxes, there is supporting evidence that the highest temperature transition of each wax is the major first-order transition, its relative width should correlate with the relative width of the wax's molecular weight distribution.

## 6. Interferences

6.1 The test specimen must be homogeneous and representative. The small sample size (10 mg) makes these requirements particularly important.

6.2 Intimate thermal contact, sample-to-pan and pan-to-sensor, is essential to obtain accurate and reproducible results.

6.3 The heating rate must be the specified  $10 \pm 1^\circ\text{C}/\text{min}$ . Faster or slower rates will produce a different transition temperature and transition peak width.

## 7. Apparatus

7.1 *Differential Scanning Calorimeter*, operating in either power compensation or heat flux mode, capable of heating at  $10 \pm 1^\circ\text{C}/\text{min}$  from  $15^\circ\text{C}$  to  $150^\circ\text{C}$ . Controlled cooling capability is preferred but not essential. The calorimeter must be able to record automatically the differential signal (WE or WT) versus temperature with a temperature repeatability of  $\pm 0.5^\circ\text{C}$ . If the differential record is versus time, the calorimeter must have the capability to make a simultaneous record of temperature versus time.

7.2 *Sample Pans*, of aluminum or other metal of high thermal conductivity, excluding copper and its alloys.

7.3 *Reference Material*—Glass beads, alumina powder, silicon carbide, or any material known to be unaffected by repeated heating and cooling and free from interfering transitions. The specific heat capacity of the reference should be as close as possible to that of the test material.

7.4 *Recorder*, capable of recording heat flow versus temperature.

## 8. Reagent

8.1 *Nitrogen*, or other dry inert gas supply for flushing the sample compartment.

## 9. Calibration

9.1 Using the instrument manufacturer's recommended procedure, calibrate the instrument's temperature scale over the temperature range of interest with appropriate standards. These include, but are not limited to:

Standard 99 % Purity Min.	Melting Point	
	°C	K
Phenoxybenzene (2) <sup>6</sup>	26.9	300.0
<i>p</i> -Nitrotoluene (3)	51.5	324.8
Naphthalene (4)	80.3	353.6
Benzoic Acid <sup>A</sup>	122.4	395.7
Adipic Acid (5)	153.0	426.3
Indium Metal (2)	156.6	429.9

<sup>A</sup>See Test Method D 3418. 99.98 % purity available from U.S. Bureau of Standards as SRM 350.

<sup>6</sup> The boldface numbers in parentheses refer to the list of references at the end of this test method.

9.2 The specimen weight and test procedure should be those specified in Section 10, except that the precycle (11.3) is omitted.

## 10. Specimen Preparation

10.1 To ensure homogeneity, completely melt the entire sample by heating it to  $10^\circ\text{C}$  above the temperature at which the wax is completely molten. Using a clean eyedropper, transfer a few drops to the surface of a clean sheet of aluminum foil to form a thin wax film. Separate the wax from the foil, and break it into pieces.

## 11. Procedure

11.1 Weigh  $10 \pm 1$  mg of the wax pieces into a sample pan, and insert the pan in the calorimeter sample compartment.

NOTE 3—Intimate thermal contact, sample-to-pan and pan-to-sensor, is essential. Ensure that pan bottoms are flat and also that sensor surfaces where pans rest are clean. If the equipment is available, it is advantageous to ensure maximum sample-to-pan thermal contact by crimping a metal cover against the pan with the sample sandwiched in between. A thermal precycle (see section 10.3) improves pan contact and establishes the same thermal history for every sample.

11.2 Flush the sample compartment of the test cell with inert gas throughout the test; a flow of 10 to 50 mL/min is typical.

11.3 Perform a thermal precycle (Note 3). Heat the test cell at  $10 \pm 1^\circ\text{C}/\text{min}$  to  $20 \pm 5^\circ\text{C}$  beyond the end of melting, beyond the return to the base line (Note 4 and Note 5). Then cool the test cell to  $15 \pm 5^\circ\text{C}$  at  $10 \pm 1^\circ\text{C}/\text{min}$ . Hold the test cell at  $15^\circ\text{C}$  for 30 s.

NOTE 4—During the precycle heating scan, note the height of the first thermo transition peak, and adjust instrument sensitivity so it is 50 to 95 % of full scale.

NOTE 5—The exposure of the sample to high temperatures should be minimized to prevent decomposition. Hold the maximum temperature only for the time required to prepare for cooling.

11.4 Perform and record the thermal scan of record. Heat the test cell at  $10 \pm 1^\circ\text{C}/\text{min}$  to  $20 \pm 5^\circ\text{C}$  beyond the end of melting (Note 6). Record the DSC curve using a heating rate of  $10 \pm 1^\circ\text{C}/\text{min}$  from  $15^\circ\text{C}$  to  $20 \pm 5^\circ\text{C}$  beyond the end of melting.

NOTE 6—A cooling (solidification) scan is also possible, but the transition peak apex will be several degrees celsius lower than that obtained using a heating scan.

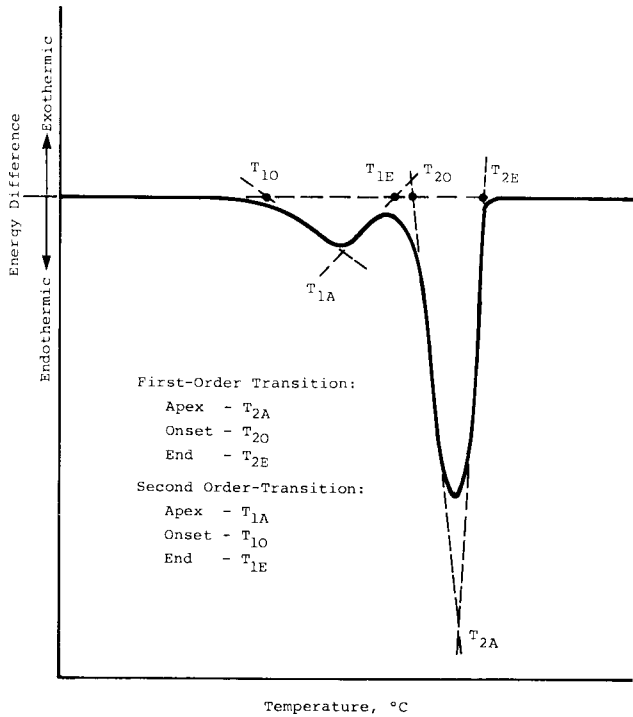
## 12. Calculation

12.1 Several transitions may be present. Number them consecutively in order of appearance. Draw tangents to each transition peak (see Fig. 1). The transition peak apex ( $T_A$ ) is located by the intersection of the tangents to the peak slopes (Note 7 and Note 8).

NOTE 7—The extrapolated onset ( $T_O$ ) and end ( $T_E$ ) temperatures are located by the intersection of the peak tangents with the base line (see Fig. 1). The difference between the onset and end temperatures of each transition peak is a measure of peak width.

NOTE 8—Some microcrystalline waxes may exhibit shoulders on the transition peaks. If this occurs, exclude the shoulder in drawing in the extrapolated onset ( $T_O$ ) and end ( $T_E$ ) temperatures.

12.2 Read the temperature associated with each transition peak apex from the curve, and apply any correction indicated



<sup>A</sup> Sample determined to have solid-liquid and solid-solid transitions by another technique.

**FIG. 1 Schematic of Petroleum Wax<sup>A</sup> DSC Curve (Heating Cycle)**

by the temperature-scale calibration.

**13. Report**

13.1 Report the corrected apex and end temperatures for each of the transition peaks to the nearest 0.5°C in order of occurrence. First thermal transition apex ( $T_{1A}$ ), first thermal transition end temperature ( $T_{1E}$ ), second thermal transition apex temperature ( $T_{2A}$ ), and second thermal transition end temperature ( $T_{2E}$ ), transition temperature of petroleum waxes by DSC.

**14. Precision and Bias**

14.1 *Precision*—The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

14.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

	°C	°F
Solid-Liquid Transition Temperatures		
Apex, $T_{2A}$	0.8	(1.4)
End, $T_{2E}$	1.0	(1.8)
Solid-Solid Transition Temperatures		
Apex, $T_{1A}$	1.2	(2.2)
End, $T_{1E}$	1.4	(2.5)

14.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

	°C	°F
Solid-Liquid Transition Temperatures		
Apex, $T_{2A}$	3.5	(6.3)
End, $T_{2E}$	6.1	(11.0)
Solid-Solid Transition Temperatures		
Apex, $T_{1A}$	2.3	(4.1)
End, $T_{1E}$	11.2	(20.2)

NOTE 9—DSC will not differentiate between solid-liquid and solid-solid transitions; other techniques must be used for example, melting point in accordance with Test Method D 87.

14.1.3 The first thermal transition temperature precision data are based on duplication determinations on five different petroleum waxes in an interlaboratory study among six laboratories. The second thermal transition temperature precision data are based on duplicate determinations on two different petroleum waxes in an interlaboratory study among six laboratories.

14.2 *Bias*—The procedure in this test method has no bias because the value of transition temperatures can be defined only in terms of a test method.

**15. Keywords**

15.1 differential scanning calorimetry; petroleum wax; thermal properties; transition temperature

**REFERENCES**

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