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Standard Test Method for Purity by Differential Scanning Calorimetry¹

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1. Scope

1.1 This test method describes the determination of purity of materials greater than 98.5 mole percent purity using differential scanning calorimetry and the van't Hoff equation.

1.2 This test method is applicable to thermally stable compounds with well-defined melting temperatures.

1.3 Determination of purity by this test method is only applicable when the impurity dissolves in the melt and is insoluble in the crystal.

1.4 There is no ISO method equivalent to this test method.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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*:²

E473 Terminology Relating to Thermal Analysis and Rheology

E793 Test Method for Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry

E794 Test Method for Melting And Crystallization Temperatures By Thermal Analysis

E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers

E968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters

¹ This test method is under the jurisdiction of ASTM Committee E37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Calorimetry and Mass Loss.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

E1970 Practice for Statistical Treatment of Thermoanalytical Data

3. Terminology

3.1 *Definitions*—The definitions relating to thermal analysis appearing in Terminology E473 shall be considered applicable to this test method.

4. Summary of Test Method

4.1 This test method is based upon the van't Hoff equation:³

$$T_s = T_o - (RT_o^2 \chi) / (HF) \quad (1)$$

where:

T_s = specimen temperature, K

T_o = melting temperature of 100 % pure material, K

R = gas constant (= 8.314 J mol⁻¹ K⁻¹),

χ = mole fraction of impurity,

H = heat of fusion, J mol⁻¹, and

F = fraction melted.

4.2 This test method consists of melting the test specimen that is subjected to a temperature-controlled program while recording the heat flow into the specimen as a function of temperature. The resulting melting endotherm area is measured to yield the enthalpy of fusion, H . The melting endotherm area is then partitioned into a series of fractional areas (about ten, comprising the first 10 to 50 % of the total area). The fractional area, divided by the total area, yields the fraction melted, F . Each fractional area is assigned a temperature, T_s .

4.3 Eq 1 has the form of $Y = mX + b$ where $Y = T_s$, $X = 1/F$, $m = -(RT_o^2 \chi) / H$, and $b = T_o$. A plot of Y versus X should produce a straight line with slope m and intercept b .

4.4 In practice, however, the resultant plot of T_s versus $1/F$ is seldom a straight line. To linearize the plot, an incremental amount of area is added to the total area and to each fractional area to produce a revised value for F . The process of incremental addition of area is continued until a straight line is obtained.

$$F = (A_{part} + c) / (A_{total} + c) \quad (2)$$

³ Brennan, W. P., DiVito, M. P., Fynas, R. L., Gray, A. P., "An Overview of the Calorimetric Purity Measurement", in *Purity Determinations by Thermal Methods*, R. L. Blaine and C. K. Schoff (Eds.), Special Technical Publication 838, American Society for Testing and Materials, West Conshohocken, PA, 1984, pp. 5–15.

where:

A_{part} = area of fraction melted, mJ

A_{total} = total area, mJ and

c = incremental area, mJ.

NOTE 1—The best fit straight line may be determined by the least squares method. See Practice E1970.)

4.5 The values of mole fraction impurity χ and melting temperature of the 100 % pure material T_o are determined from the slope m and intercept b of the resultant straight line. This is Method A.

4.6 An alternative form of the van't Hoff equation is given by:⁴

$$A_{part} = -c + [T_o c - R T_o^2 \chi m / M] / T_s + T_o A_{part} / T_s \quad (3)$$

where:

m = mass of the sample, mg, and

M = molecular weight, g mol⁻¹.

4.7 Eq 3 has the form of $Y = \alpha W + \beta X + \gamma Z$ where $Y = A_{part}$, $\alpha = -c$, $W = 1$, $\beta = [T_o c - R T_o^2 \chi m / M]$, $X = 1 / T_s$, $\gamma = T_o$, and $Z = A_{part} / T_s$. Eq 3 may be evaluated by multiple linear regression and χ and T_o determined from the resultant values of α , β and γ . This is Method B.

5. Significance and Use

5.1 The melting temperature range of a compound broadens as the impurity level rises. This phenomenon is described approximately by the van't Hoff equation for melting point depressions. Measuring and recording the instantaneous heat flow into the specimen as a function of temperature during such a melting process is a practical way for the generation of data suitable for analysis by the van't Hoff equation.

5.2 The results obtained include: sample purity (expressed as mole percent); enthalpy of fusion (expressed as joules per mole); and the melting temperature (expressed in Kelvin) of the pure form of the major component.

5.3 Generally, the repeatability of this test method decreases as the purity level decreases. This test method is ordinarily considered unreliable when the purity level of the major component of the mixture is less than 98.5 mol % or when the incremental enthalpy correction (c) exceeds 20 % of the original detected enthalpy of fusion.

5.4 This test method is used for quality control, specification acceptance, and research.

6. Interferences

6.1 This test method is nonspecific. Many impurities may cause the melting temperature broadening. Thus, it is not useful in identifying the nature of the impurity or impurities but only the total mol percent of impurity present.

6.2 The van't Hoff theory assumes the following:

6.2.1 The impurities dissolve in the melt of the major constituent forming a solution approximately described by ideal solution theory;

6.2.2 The solubility of the impurity in the solid of the major constituent is negligible; and

6.2.3 The major constituent displays a single well-defined melting endotherm in the temperature range of interest. Microscopic investigations of the melt and the solid may help to establish whether or not solid or liquid solutions have been formed.

6.2.4 The solute and solvent are close in molecular size.

6.3 In some cases the sample may react with air during the temperature cycle, causing an incorrect transition to be measured. Where it has been shown that this effect is present, provision shall be made for sealing the specimen and running the test under an inert gas blanket. Since some materials degrade near the melting region, carefully distinguish between degradation and transition. See Appendix X1.

6.4 Since milligram quantities of sample are used, ensure that samples are homogeneous and representative.

6.5 Sublimation or decomposition will lead to a different heat consumption and, perhaps, a change in composition of the specimen. The specimen holder should be examined after the measurement for crystals not part of the resolidified melt.

7. Apparatus

7.1 The essential equipment required to provide the minimum instrument capability for this test method includes:

7.1.1 *Differential Scanning Calorimeter (DSC)*, consisting of:

7.1.1.1 *DSC Test Chamber*, composed of a furnace(s) to provide uniform controlled heating of a specimen and reference to a constant temperature or at a constant rate within the applicable temperature range of this test method; a temperature sensor to provide an indication of the specimen temperature to ± 0.1 K; a differential sensor to detect a heat flow difference between the specimen and reference equivalent to 10 μ W; and a means of sustaining a test chamber environment of N₂ at a purge rate of 15 to 50 \pm 5 mL/min.

7.1.1.2 *Temperature Controller*, capable of executing a specific temperature program by operating the furnace(s) between selected temperature limits at a rate of temperature change of 0.3 to 0.7 K/min constant to ± 0.01 K/min.

7.1.1.3 *Data Collection Device*, to provide a means of acquiring, storing, and displaying measured or calculated signals, or both. The minimum output signals required for DSC are heat flow, temperature, and time.

7.1.2 *Containers*, that are inert to the specimen, and that are of suitable structural shape and integrity for use in the DSC test chamber, made of materials of high thermal conductivity, such as aluminum.

7.2 *Planimeter*, computer- or electronic-based data treatment or other instrumentation to determine area to within ± 1 % precision.

7.3 *Balance*, with a capacity of at least 100 mg capable of weighing to an accuracy of 0.01 mg.

8. Sampling

8.1 The test sample (liquid or solid) should be mixed prior to sampling and sampled by removing portions from various

⁴ Widman, G., Scherrer, O., "A New Program for DSC Purity Analysis", *Journal of Thermal Analysis*, 371987, pp. 1957–1964.

parts of the container. Combine the portions and mix well to provide a representative sample for the purity determinations. Only 1 to 3 mg is required for each analysis.

8.2 Avoid any physical or mechanical treatment of the material that will cause chemical changes. For example, grinding the sample for size reduction often introduces such changes as a result of heat generated by friction.

9. Calibration

9.1 Perform any calibrations procedures called for by the instrument manufacturer as described in the operations manual.

9.2 Calibrate the apparatus temperature signal at the heating rate to be used in this test method (see 10.8) using Test Method E967. High purity (>99.99 %) indium metal is a convenient material to use for this purpose.

9.3 Calibrate the apparatus heat flow signal at the heating rate to be used in this test method (see 10.8) using Practice E968. High purity (>99.99 %) indium metal is a convenient material to use for this purpose.

9.4 Determine the leading edge slope (S) in mW/K from the heat flow calibration curve obtained in 9.3. See Fig. 1.

NOTE 2—The value of S is negative.

10. Procedure

10.1 **Warning**—Toxic and corrosive effluents may be released upon heating the material. It is the responsibility of the user of the standard to take appropriate safety measures.

10.2 Wash the empty specimen container in an appropriate solvent, such as hexane, then heat to 700 K for 1 min.

10.3 Cool the specimen container and store in a desiccator until ready for use.

10.4 Weigh 1 to 3 mg of the sample to an accuracy of 0.01 mg in a pre-cleaned specimen container.

10.5 Under ambient conditions, hermetically seal the specimen container so there will be no mass loss during the scan. Minimize the free space between the specimen and the lid to avoid sublimation onto the lid.

NOTE 3—If oxidation is suspected, hermetically seal in an inert atmosphere.

10.6 Purge the cell with dry nitrogen at a flow rate of 15 to 50 mL/min throughout the experiment.

10.7 Place the encapsulated specimen in the specimen container and heat rapidly up to 25 K below the melting temperature. Allow the instrument temperature to stabilize.

10.8 Heat the specimen from the temperature selected in 10.7 to completion of the melt at the rate of 0.3 to 0.7 K min⁻¹. A minimum of 200 data points should be taken in the melt region.

10.9 Reweigh the specimen after completion of scan, examine contents (see 6.5) and discard. Do not accept data if mass loss exceeds 1 %.

11. Calculation – Method A

NOTE 4—All calculations shall use all available decimal places before rounding the final result.

11.1 Construct a linear baseline under the melting endotherm by connecting a straight line between the baseline before and after the transitions shown in Fig. 2.

11.2 Integrate as a function of time the total area under the fusion curve ($ABCA$) as shown in Fig. 2. Report this value as $ABCA$ in mJ.

11.3 Partition the total area by drawing at least ten perpendicular lines from the baseline to the fusion curve as illustrated

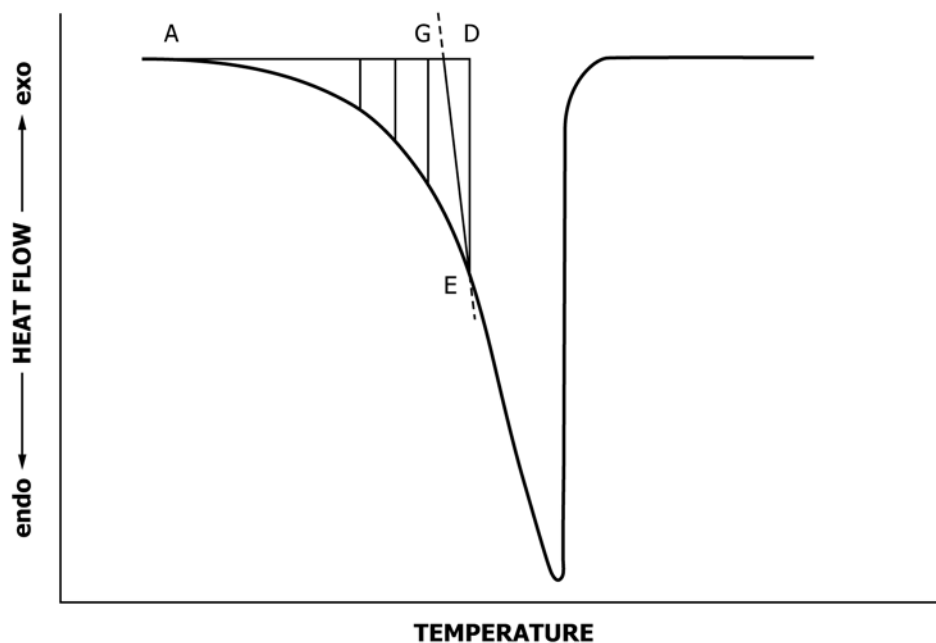


FIG. 1 Fusion Curve for Method B