



Standard Test Method for Determination of Purity by Differential Scanning Calorimetry¹

This standard is issued under the fixed designation E 928; 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 (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of purity by use of differential scanning calorimetry and the evaluation of the results using the van't Hoff equation.

1.2 This test method is generally 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 Computer- or electronic-based instruments, techniques, or data treatments equivalent to this test method may also be used. Users of this test method are expressly advised that all such instruments or techniques may not be equivalent. It is the responsibility of the user of this test method to determine the necessary equivalency prior to use.

1.5 The values stated in SI units are to be regarded as the 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:

E 473 Terminology for Thermal Analysis²

E 793 Test Method for Enthalpies of Fusion and Crystallization by Differential Scanning Calorimetry²

E 967 Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers²

E 968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters²

3. Terminology

3.1 *Definitions*—The definitions relating to thermal analysis appearing in Terminology E 473 shall be considered applicable to this test method.

¹ This test method is under the jurisdiction of ASTM Committee E-37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Test Methods and Recommended Practices.

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² *Annual Book of ASTM Standards*, Vol 14.02.

4. Summary of Test Method

4.1 This test method consists of melting the test specimen that is subjected to a temperature-controlled program while recording the heat flow (power) into the specimen as a function of time. The resulting endotherm area is often measured to yield the enthalpy of fusion. 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). Each fractional area is assigned a temperature. A plot of the reciprocal fractional areas and their corresponding temperatures is then produced. The resulting plot is seldom a straight line. To linearize the plot, an incremental amount is added to the enthalpy of fusion and the fractional areas recalculated and plotted. The purity level is then calculated from the slope of this straight line.

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 (power) into the specimen as a function of time or 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 mol percent); enthalpy of fusion (expressed as joules per mol); 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 (x) 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 must display 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.

6.3 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.

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

6.5 Sublimation 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/furnace temperature to ± 0.1 K; a differential sensor to detect a difference (temperature or heat flow) between the specimen and reference equivalent to $10 \mu\text{W}$; and a means of sustaining a test chamber environment of N_2 at a purge rate of 15 to 25 ± 1 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 $\pm 1\%$ K/min.

7.1.1.3 *Recording Device*, either digital or analog, to record the display of the DSC curve with a y -sensitivity of 0.1 mW/cm and an x -sensitivity of 2 min/cm.

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 $\pm 1\%$ precision.

7.3 *Balance*, 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 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 Accurate calibration of the absolute temperature or enthalpy of fusion is not necessary to determine the mol percent purity. However, if the accurate melting temperature or enthalpy of fusion of the pure compound is desired, calibrate the instrument in accordance with Practice E 967 and E 968. Perform calibrations at the heating rate used for the purity determination (see 11.7) and in the temperature range of the melting temperature of the pure material.

9.2 When metals are used with aluminum specimen holders, it is best to use a fresh sample each time as alloying of the metallic standard with aluminum may result on reheating.

10. Procedure

10.1 **Caution**—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 holder.

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 1—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 25 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 to equilibrate.

10.8 Select a heating rate within the range from 0.3 to 0.7 K/min.

10.9 Scan the specimen from the temperature selected in 10.7 to completion of the melt process. If data are recorded on a strip chart recorder, a chart speed of at least 1 cm/min is necessary. If automatic data acquisition is used, a minimum of 200 data points should be taken in the melt region.

10.10 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

11.1 All calculations shall use all available decimal places before rounding the final result.

11.2 Measure the total area under the fusion curve ($ABCA$) as shown in Fig. 1.

11.3 Divide the area by drawing at least ten perpendicular lines from the baseline to the fusion curve as illustrated by the typical line (DE) in Fig. 1.