Standard Test Method for Determining Flammability Characteristics of Plastics and Other Solid Materials Using Microscale Combustion Calorimetry[1]

This standard is issued under the fixed designation D7309; 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, which is similar to thermal analysis techniques, establishes a procedure for determining flammability characteristics of combustible materials such as plastics.

1.2 The test is conducted in a laboratory environment using controlled heating of milligram specimens and complete thermal oxidation of the specimen gases.

1.3 Specimens of known mass are thermally decomposed in an oxygen-free (anaerobic) or oxidizing (aerobic) environment at a constant heating rate between 0.2 and 2 K/s.

1.4 The heat released by the specimen is determined from the mass of oxygen consumed to completely oxidize (combust) the specimen gases.

1.5 The rate of heat released by combustion of the specimen gases produced during controlled thermal or thermoxidative decomposition of the specimen is computed from the rate of oxygen consumption.

1.6 The specimen temperatures over which combustion heat is released are measured.

1.7 The mass of specimen remaining after the test is measured and used to compute the residual mass fraction.

1.8 The specimen shall be a material or composite material in any form (fiber, film, powder, pellet, droplet). This test method has been developed to facilitate material development and research.

1.9 *This standard is used to measure and describe the response of materials, products, or assemblies to heat and flame under controlled conditions, but does not by itself incorporate all factors required for fire hazard or fire risk assessment of the materials, products, or assemblies under actual fire conditions.*

1.10 *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.*

NOTE 1—There is no known ISO equivalent to this test method.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics

D5865 Test Method for Gross Calorific Value of Coal and Coke

E176 Terminology of Fire Standards

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

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

E1591 Guide for Obtaining Data for Fire Growth Models

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms relating to plastics, refer to Terminology D883.

3.1.2 For definitions of terms relating to fire, refer to Terminology E176.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *combustion residue, n*—the non-volatile chemical species remaining after controlled thermal oxidative decomposition of a specimen.

3.2.2 *combustion temperature, n*—the specimen temperature at which the specific combustion rate is a maximum during controlled thermal oxidative decomposition.

3.2.3 *controlled heating, n*—a controlled temperature program used to effect thermal decomposition or oxidative thermal

---

[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.30 on Thermal Properties.

Current edition approved Nov. 1, 2013. Published November 2013. Originally approved in 2007. Last previous edition approved in 2011 as D7309 – 11. DOI: 10.1520/D7309-13.

[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.

decomposition in which the temperature of the specimen is uniform throughout and increases with time at a constant rate.

3.2.4 *controlled thermal (or thermal oxidative) decomposition, n*—thermal (oxidative) decomposition under controlled heating.

3.2.5 *heat release capacity, n*—the maximum specific heat release rate during a controlled thermal decomposition divided by the heating rate in the test.

3.2.6 *heating rate, n*—the constant rate of temperature rise of the specimen during the controlled temperature program.

3.2.7 *heat release temperature, n*—the specimen temperature at which the specific heat release rate is a maximum during controlled thermal decomposition.

3.2.8 *maximum specific combustion rate, n*—the maximum value of the specific combustion rate recorded during the test.

3.2.9 *maximum specific heat release rate, n*—the maximum value of the specific heat release rate recorded during the test.

3.2.10 *net calorific value, n*—the net heat of complete combustion of the specimen measured during controlled thermal oxidative decomposition per unit initial specimen mass.

3.2.11 *oxidative thermal decomposition, n*—a process of extensive chemical species change caused by heat and oxygen (thermal oxidation, oxidative pyrolysis).

3.2.12 *pyrolysis residue, n*—the fraction of the initial specimen mass remaining after controlled anaerobic thermal decomposition.

3.2.13 *specific combustion rate, n*—the rate at which combustion heat is released per unit initial mass of specimen during controlled thermal oxidative decomposition.

3.2.14 *specific heat of combustion of specimen gases, n*—net calorific value of gases.

3.2.15 *specific heat release rate, n*—the rate at which combustion heat is released per unit initial mass of specimen during controlled thermal decomposition.

3.2.16 *specific heat release, n*—the net heat of complete combustion of the volatiles liberated during controlled thermal decomposition per unit initial specimen mass.

3.2.17 *specimen gases, n*—the volatile chemical species liberated during controlled thermal (oxidative) decomposition of a specimen.

3.3 *Symbols:*

β = heating rate, K/s
E = 13.1 kJ/g-O_2 is the average heat released by complete combustion of organic compounds per unit mass of oxygen consumed
F = volumetric flow rate of the combustion stream at ambient temperature and pressure measured at the terminal flow meter, cm^3/s
h_c = specific heat release of sample, J/g
h_c^o = net calorific value of sample, J/g
$h_{c,gas}$ = specific heat of combustion of specimen gases, J/g
η_c = heat release capacity, J/g-K
m_o = initial specimen mass, g
m_c = residual specimen mass after oxidative pyrolysis, g
m_p = residual specimen mass after the anaerobic pyrolysis, g
$\Delta[O_2]$ = the change in the concentration (volume fraction) of O_2 in the gas stream due to combustion measured at the oxygen sensor at time t, cm^3/cm^3
$Q(t)$ = specific heat release rate at time t, W/g
Q_{max} = maximum specific heat release rate, W/g
$Q_{max}{}^o$ = maximum specific combustion rate, W/g
ρ = density of oxygen at ambient conditions, g/cm^3
t = time synchronized to temperature, x - τ, s
T_{max} = heat release temperature, K
$T_{max}{}^o$ = combustion temperature, K
τ = transit time of the gas stream between the specimen location and the oxygen analyzer, s
x = time at which the oxygen analyzer signal is recorded, s
Y_c = combustion residue, g/g
Y_p = pyrolysis residue, g/g

4. Summary of Test Method

4.1 This test method provides two procedures for determining flammability characteristics of materials in a laboratory test using controlled heating (controlled temperature programming) and oxygen consumption calorimetry. This test measures flammability characteristics using a controlled temperature program to force the release of specimen gases, thermal oxidation of the specimen gases (and optionally the specimen residue) in excess oxygen, and measurement of the oxygen consumed to calculate the amount, rate, and temperature of heat released by combustion of a solid specimen during controlled heating.

4.2 *Controlled Thermal Decomposition, Method A*—In this procedure the specimen is subjected to controlled heating in an oxygen-free/anaerobic environment, that is, controlled thermal decomposition. The gases released by the specimen during controlled thermal decomposition are swept from the specimen chamber by a non-oxidizing/inert purge gas (typically nitrogen), subsequently mixed with excess oxygen, and completely oxidized in a high temperature combustion furnace. The volumetric flow rate and volumetric oxygen concentration of the gas stream exiting the combustion furnace are continuously measured during the test to calculate the rate of heat release by means of oxygen consumption. In Method A the heat of combustion of the volatile component of the specimen (specimen gases) is measured but not the heat of combustion of any solid residue. Table X1.1 of Appendix X1 shows data for η_c, h_c, Y_p, and T_{max} for 14 different commercial plastics tested in triplicate (n = 3).

4.3 *Controlled Thermal Oxidative Decomposition, Method B*—In this procedure the specimen is subjected to controlled heating in an oxidizing/aerobic environment, that is, controlled thermal oxidative decomposition. The specimen gases evolved during the controlled heating program are swept from the specimen chamber by the oxidizing purge gas (for example, dry air) and mixed with additional oxygen, if necessary, prior to entering a high temperature combustion furnace where the gases are completely oxidized. The volumetric flow rate and volumetric oxygen concentration of the gas stream exiting the combustion furnace are continuously measured during the test to calculate the specific combustion rate by means of oxygen consumption. In Method B the net calorific value of the specimen gases and solid residue are measured during the test.

5. Significance and Use

5.1 This laboratory test method measures thermal combustion properties of materials (**1-5**).[3]

5.2 The test uses controlled thermal decomposition of specimens and thermal oxidation of the specimen gases as they are released from the specimen to simulate the condensed and gas phase processes of flaming combustion, respectively, in a small-scale laboratory test (**1-7**).

5.3 The thermal combustion properties measured in the test are related to flammability characteristics of the material (**4-7**).

5.4 The amount of heat released in flaming combustion per unit mass of material is the fire load and the potential fire load (complete combustion) is estimated in Method A as h_c.

5.5 The net calorific value of the material (see Test Method D5865) is determined directly using Method B as h_c^o without the need to know the atomic composition of the specimen to correct for the latent heat of evaporation of the water produced by combustion, or to perform titrations to correct for the heat of solution of acid gases. See Table X1.2 for comparison of Microscale Combustion Calorimetry (MCC) data with Test Method D5865.

5.6 The heat release temperature T_{max} of Method A approximates the surface temperature at piloted ignition in accordance with Ref. (**5-7**) for purposes of fire modeling (See Guide E1591).

5.7 The heat release capacity η_c (J/g-K) is a flammability parameter measured in Method A that is unique to this test method.

6. Limitations

6.1 The heat release capacity (η_c) is independent of the form, mass, and heating rate of the specimen as long as the specimen temperature is uniform at all times during the test (**1-5**).

6.2 Test results obtained from small (milligram) samples by this method do not include physical behavior such as melting, dripping, swelling, shrinking, delamination, and char/barrier formation that can influence the results of large (decagram/kilogram) samples in flame and fire tests.

6.3 Test results obtained from small (milligram) samples by this method do not include extrinsic factors such as thickness, sample orientation, external heat flux, ignition source, boundary conditions, and ventilation rate that influence the results of large (decagram/kilogram) samples in flame and fire tests.

6.4 The specific combustion rate and combustion temperature of Method B are not generally reproducible because sample geometry can affect the rate of surface oxidation and gas phase ignition can occur in the sample chamber at appropriate fuel/oxygen ratios. Reproducibility of Q_{max}^o and T_{max}^o are improved by using low oxygen concentration in the purge gas, small samples, and low heating rates in this test.

7. Apparatus

7.1 The equipment used in this test method shall be capable of displaying changes in combustion heat release rate as a function of specimen temperature during controlled heating and shall have the capability of subjecting the specimen to different atmospheres of oxygen concentration at ambient pressure.

7.2 Commercial thermogravimetric analyzers, pyrolysis probes, and electrically-heated ceramic tubes in thermal contact with a combustor, or attached gas analyzers, or both, have been found suitable. Detailed apparatus design criteria are given in Annex A1.

NOTE 2—In typical materials tests a material is exposed to a particular set of test conditions and the material's response to those particular test conditions is measured and reported as the test result. In these tests changing the test conditions has an effect on the result of the test. In this test, the heat release capacity (η_c) is independent of the test parameters as it is a material property and not a response of a material to a particular set of conditions. Thus, changing the test condition (within certain constraints) will have no effect on the test result. As such, the apparatus required to perform this test shall operate to provide test parameters that remain within certain constraints for each section of the device, for example, specimen chamber, mixing section, combustor. The diameter, length and shape of each section will have no effect on the test result provided the section meets the performance given in Annex A1.

7.3 Figure 1 illustrates the basic components of an apparatus, (**1, 5, 8-11**), satisfactory for this test method which include:

7.4 *A specimen chamber* (sample chamber) that is capable of holding and heating a small (milligram sized) specimen in a continuous flow of purge gas.

7.5 *Temperature controller*, capable of executing a temperature program that changes the specimen chamber temperature between ambient and 1123 K at a rate that is constant to within 5 % of the nominal value in the range 0.2-2 K/s.

7.6 *A means of purging the specimen chamber environment* with a constant flow of inert (for example, nitrogen) or reactive (nitrogen/oxygen mixture) gas at a rate of 50-100 cm^3/min with an accuracy of ±1 %.

7.7 *A temperature sensor*, to provide an indication of the specimen temperature to ±0.5 K.

7.8 *A mixing chamber*, where the specimen and purge gases are mixed with sufficient oxygen to effect complete oxidation of the specimen gases in the combustion chamber.

7.9 *A means of introducing oxygen into the mixing section* at a constant flow rate of 0-50 cm^3/min, such that the concentration of oxygen is between 20-50 % (±0.1 %) by volume entering the combustion chamber.

7.10 *A combustor* (combustion chamber) capable of maintaining a constant temperature in the range of 1073-1273K (800-1000°C). Typically, the residence time of the specimen

---

[3] The boldface numbers in parentheses refer to a list of references at the end of this standard.

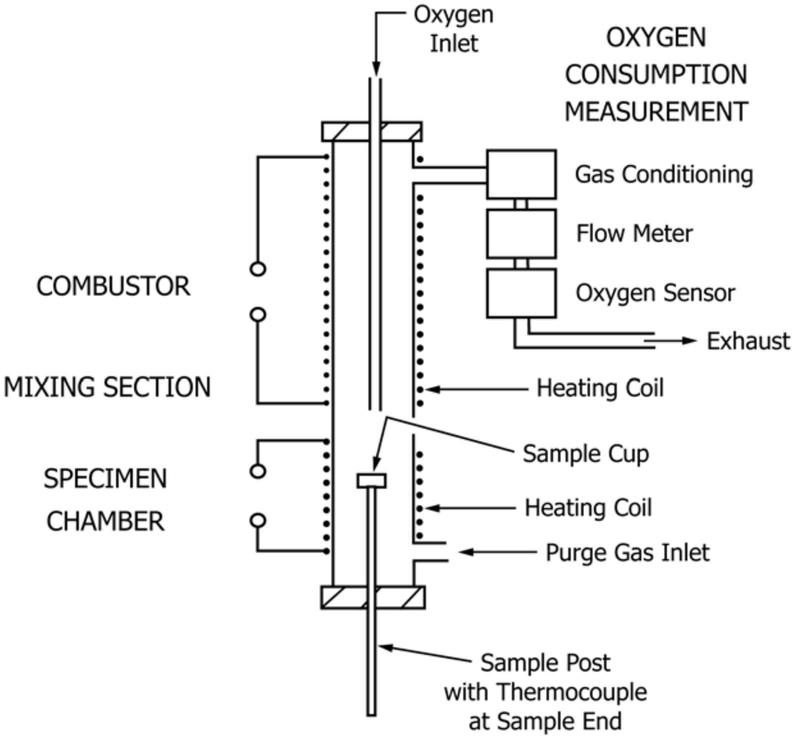

FIG. 1 Schematic Diagram of Apparatus

gases in the combustor is 10 seconds and the combustor temperature is 1173K (900°C) in accordance with Ref. (5).

7.11 *An in-line drier* to remove moisture and acid gases from the combustion stream to a dew point of 273K. Solid desiccant when used to dry the combustion stream shall be of an indicating type for visual observation of effectiveness. Anhydrous calcium sulfate has been found suitable

7.12 *A flow meter* capable of measuring gas flow rates of 50-200 cm^3/min with a response time of <0.1 s, sensitivity of 0.1 % of full scale, repeatability to ±0.2 % of full scale, and accuracy of ±1 % of the full scale.

7.13 *An oxygen analyzer* capable of measuring oxygen concentration in the range 0-100 % by volume (v/v) with a response time of <6 s for 90 % deflection, a sensitivity of <0.1 % O_2 (v/v), and a linearity of ±1 % of full scale at constant temperature and pressure.

7.14 *Recording device*, that is either digital or analog and capable of recording and displaying any portion of the heat release rate on the ordinate as a function of time or temperature on the abscissa.

7.15 *Pressurized gas sources*, capable of sustaining a regulated gas pressure of inert and reactive (oxygen) gas to the apparatus. The gas sources shall be greater than 99.5 % purity.

7.16 *Containers*, (pans, crucibles, vials, cups, etc.) which are inert to the specimen and suitable in shape and structural integrity to contain the specimen throughout the test in accordance with the specifications of this test method.

7.17 *Balance*, with a capacity of 250 mg or greater and a sensitivity of ±0.01 mg, to weigh specimens or containers, or both.

8. Calibration and Standardization

8.1 The transit time of the gas stream between the specimen chamber and the oxygen analyzer shall be determined in order to synchronize the sample temperature with the specific heat release.

8.1.1 Calibrate the time delay between the specimen chamber and the oxygen sensor by recording the time between a perturbation in the purge gas flow rate and the oxygen sensor response.

8.1.2 After making an initial calibration determination, recalibration is required only when changes to the system that might affect the transit time, that is, the flow volume, or gas flow rate of the instrument, or both, are changed.

8.2 Perform a temperature calibration to correct for temperature differences between the sample and the sensor caused by thermal lag during transient heating. This is similar to the procedure used in Test Method E967.

8.2.1 Place 10-20 mg of a high purity (≥99.99 %) calibration material with a known melting temperature in the center of a clean ceramic sample cup. The sample cup shall be identical to that used for testing.

8.2.1.1 The materials shown Table 1 have been shown to be suitable for the temperature calibration.

8.2.1.2 Use a different sample cup for each calibration material.

NOTE 3—If the same sample cup is used for two calibration materials, it is possible that contamination of the calibration materials (including alloying) will occur and that the melting temperatures will be affected.

8.2.2 Insert the sample cup and calibration material into the pyrolyzer and remove the air by purging with nitrogen as instructed in 4.2 (Method A) for a minimum of five minutes.

TABLE 1 Melting Temperatures of Calibration Materials

Calibration Material	Abbreviation	Melting Temperature	
		(°C)	(K)
Indium	In	157	430
Tin	Sn	232	505
Bismuth	Bi	271	545
Lead	Pb	328	601
Zinc	Zn	420	693
Antimony	Sb	631	904
Aluminum	Al	660	934
Sodium Chloride	NaCl	801	1074
Silver	Ag	962	1235

NOTE 4—Removal of the air is intended to prevent oxidation of the calibration materials during the heating program.

8.2.3 Increase the pyrolyzer temperature from a starting temperature of approximately 75°C to the maximum pyrolyzer temperature (namely in the range 850-900°C) at the heating rate β that will be used for testing in accordance with 4.2 (Method A). Note that typically the value of β is 1K/s. Record and store the data.

8.2.4 Perform the temperature calibration flowing purge gas under the same conditions that will be used to test the actual test specimens (Section 9).

NOTE 5—The heating rate, type of specimen holder, purge gas and the purge gas flow rate can affect the temperature calibration.

8.2.5 Record the temperature sensor reading at the melting temperature for a minimum of two calibration materials, one of which shall have a melting temperature below the temperature range of interest and one of which shall have a melting temperature above the temperature range of interest.

8.2.6 During the calibration, the temperature at which melting of the calibration material begins (onset of melting) shall be equated to the melting temperature of the calibration material. See Fig. X1.1 in Appendix for an example of a temperature calibration using zinc as the calibration material.

NOTE 6—When heat is absorbed during melting it causes a negative deviation of the heating rate and the temperature history from the programmed values over the melting temperature range. The initial deviation of the heating rate or the sensor temperature history from the programmed values occurs at the onset of melting (melting temperature).

8.2.7 Plot the melting temperature of the reference material on the ordinate (*y*-axis) versus the temperature sensor reading at the onset of melting on the abscissa (*x*-axis) and fit a straight line to the data using least squares regression as illustrated by the example shown in Fig. X1.2. In all subsequent tests, the specimen temperature, *T*, is calculated from the temperature sensor reading, the *y*-axis intercept and the slope of the best-fit line using the relationship shown below:

$$T = \text{Intercept} + (\text{Slope} \times \text{Temperature Sensor Reading})$$

8.3 Perform a system performance test in accordance with 4.2 (Method A) by measuring the flammability parameters of a reference material.

8.3.1 Use general purpose, crystal-clear, additive-free, food grade polystyrene (CAS # 9003-53- 6) as the reference material for the system performance test. The flammability characteristics of this material are: $h_c = 40.2 \pm 0.6$ kJ/g; $\eta_c = 1080 \pm 45$ J/g-K; $T_p = 445 \pm 2°C$; and $Y_p = 0 \pm 0.01$ g/g.

8.3.2 If all systems and components of the instrumentation have been properly calibrated and are performing correctly, the flammability characteristics of the reference material shall fall within the ranges shown in 8.3.1.

NOTE 7—The system calibration is intended to show that the specimen temperature, gas flow rates and oxygen concentration are correct and that the data acquisition system is functioning properly. Further information can be found in references (**12**) and (**13**).

9. Test Specimens

9.1 The specimens shall be taken from a sample that is representative of the material.

9.2 Specimens shall be free of residual solvents and moisture.

9.3 Specimens shall be in any form (film, fiber, powder, pellet, droplet). If liquids are tested the boiling point shall be above the starting temperature of the sample chamber.

9.4 Specimen mass shall be in the range of 1-10 mg. Specimen mass is subject to the constraint that oxidation of the specimen gases consumes less than one half of the available oxygen in the combustion gas stream at any time during the test and at the heating rate used in the test. Typical specimen mass is 2-5 mg.

10. Test Parameters

10.1 The heat release capacity (η_c) is independent of the test parameters provided test parameters are chosen that remain within certain constraints (see Annex A1).

10.1.1 The specimen temperature range shall provide for complete degradation of the test specimen.

10.1.1.1 *Specimen temperature range*—The specimen temperature shall range from ambient to 1123K (850°C) or from 200K below, to 200K above, the decomposition temperature range of the specimen. The temperature range for solid plastics is typically 348-1123K (75-850°C).

10.1.2 The heating rate of the specimen shall provide for uniform specimen temperature at all times during the test.

10.1.2.1 *Heating Rate*—Heating rates are normally in the range 0.2-2 K/s depending on the specimen size. Typical heating rate is 1 K/s. To minimize temperature gradients within the sample the heating rate β (K/s) for a sample of mass m_o (mg) shall be in accordance with Ref. (**14**). For example, at the typical heating rate β = 1K/s, the maximum sample mass shall be 5 mg if the error in $Q_{\max}$ is to be less than the average reproducibility error in Table 2.

TABLE 2 Peak Heat Release Rate (W per g)

Material	Average[A]	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	s_r	s_R	r	R
Acrylic	468.6	8.3	28.9	23.3	80.9
PP	1083.6	22.8	89.3	64.0	250.1
HIPS	714.9	23.4	64.7	65.6	181.1
PC	526.9	25.0	54.1	70.0	151.4
PPSU	205.2	6.6	19.0	18.5	53.3

[A] The average of the laboratories' calculated averages.

10.1.3 The total flow rate and oxygen concentration shall provide sufficient residence time and oxygen for the mixed gases in the combustor to completely oxidize during the entire test.

10.1.3.1 *Gas Flow Rates*—shall be such that the combined flow rate of the purge gas and oxygen is 50-200 cm^3/min and the baseline oxygen concentration is 20-50 % O_2 (v/v). Typically, the combined flow rate is 100 cm^3/min and the oxygen concentration in the combustor is 20 % O_2 v/v.

10.1.4 *Combustor Temperature*—shall be set to completely oxidize the specimen gases in the time they are in the combustor. Typically the combustor temperature shall be set to 1173K (900°C).

11. Procedure

11.1 Turn on the purge gas and oxygen and allow the flow rate and oxygen signals to stabilize at the baseline values.

11.2 Set the combustor temperature to a temperature sufficient to completely oxidize the specimen gases. Allow the combustor to equilibrate at the set-point temperature until temperature changes are no greater than ±5K/hour.

11.3 Prepare the drier for use. Inspect and, if necessary, change the drying medium at the start of each test.

11.4 Program the specimen heating rate and the starting and ending temperatures for the heating range into the controls.

11.5 Program the oxygen concentration and total flow rate into the controls.

11.6 Weigh the specimen cup to an accuracy of 0.01 mg and record the tare mass.

11.7 Place the specimen into the specimen cup and weigh the specimen and cup to 0.01 mg.

11.8 Record the specimen mass m_o obtained by subtracting the tare from the mass of the specimen and cup.

11.9 Load the specimen cup containing the specimen onto the specimen platform making sure that there is good thermal contact between the specimen cup and the temperature sensor.

11.10 Raise the specimen cup into the center of the specimen chamber making sure that a gas-tight seal is obtained.

11.11 Allow the flow rate and oxygen signals to re-stabilize at the baseline values.

11.12 Initiate the constant rate heating of the specimen from the starting temperature to the final temperature of the temperature range. Record flow rate and oxygen data as required to perform calculations.

11.13 Decrease the specimen temperature to the starting temperature and remove the specimen cup.

11.14 Weigh the specimen cup including any specimen residue remaining after the test and subtract the tare mass to obtain the residual mass m_p or m_c after thermal or thermal oxidative decomposition, respectively.

12. Calculation or Interpretation of Results

12.1 Calculate the specific heat release rate, *Q(t)* (W/g) at time *t* during the heating program as follows:

$$Q(t) = \frac{E\rho F}{m_o}\Delta[O_2] \tag{1}$$

12.2 For Method A only:

12.2.1 Calculate the heat release capacity η_c (J/g-K) as follows:

$$\eta_c = \frac{Q_{max}}{\beta} \tag{2}$$

where:

Q_{max} = the maximum value of *Q(t)* in the test, W/g.
β = average heating rate over the measurement range.

12.2.2 Calculate the heat release temperature, T_{max} (K) as the temperature at which $Q(t) = Q_{max}$.

12.2.3 Calculate the specific heat release, h_c (J/g) as the integral of (area under) the *Q(t)* versus *t* curve once baseline is re-established following a controlled thermal decomposition experiment.

12.2.4 Calculate the pyrolysis residue Y_p (g/g) as follows:

$$Y_p = \frac{m_p}{m_o} \tag{3}$$

12.2.5 Calculate the specific heat of combustion of the specimen gases (J/g) as follows:

$$h_{c,\,gas} = \frac{h_c}{1 - Y_p} \tag{4}$$

12.3 For Method B only:

12.3.1 Calculate the combustion temperature, $T_{max}{}^{0}$ as the temperature at which the specific combustion rate is a maximum, that is, $Q(t) = Q_{max}{}^{0}$

12.3.2 Calculate the combustion residue Y_c (g/g) as follows:

$$Y_c = \frac{m_c}{m_o} \tag{5}$$

12.3.3 Calculate the net calorific value, $h_c{}^{0}$ (J/g) as the integral of (area under) the *Q(t)* versus *t* curve once baseline is re-established following a controlled thermal oxidative decomposition test.

13. Report

13.1 Report the following information unless specified otherwise in the relevant material or performance standard. Clearly state the units for all measurements in the report. Certain units convenient for reporting are suggested in parentheses.

13.1.1 Specimen identification code or number

13.1.2 Manufacturer or submitter

13.1.3 Test Laboratory

13.1.4 Test Method (A or B)

13.1.5 Date of test

13.1.6 Operator

13.1.7 Composition, physical form (for example, film, fiber, powder, etc.) or generic identification of specimen

13.1.8 Specimen mass (mg)

13.1.9 Details of specimen preparation

13.1.10 Temperature range of test (K)

13.1.11 Heating rate (test average) β (K/s)

13.1.12 Number of replicate specimens tested under these conditions

13.1.13 For Method A only

13.1.13.1 Heat release capacity, η_c (J/g-K)

13.1.13.2 Maximum specific heat release, Q_{max} (W/g)

13.1.13.3 Heat release temperature, T_{max} (K)

13.1.13.4 Specific heat release, h_c (J/g)

13.1.13.5 Yield of pyrolysis residue, Y_p (g/g)

13.1.13.6 Specific heat of combustion of fuel gases, $h_{c,\ gas}$ (J/g)

13.1.14 For Method B only

13.1.14.1 Net calorific value, h_c^o (J/g)

13.1.14.2 Maximum specific combustion rate, $Q_{max}{}^o$ (W/g)

13.1.14.3 Combustion temperature, $T_{max}{}^o$ (K)

13.1.14.4 Yield of combustion residue Y_c (g/g)

14. Precision and Bias[4]

14.1 *Precision*—The precision of this test method is based on an interlaboratory study of this test method, which was conducted in 2010. A total of twelve laboratories participated in this study, analyzing five different solid materials for a total of five parameters. Each "test result" reported represents an individual determination, and all participants reported triplicate test results for each material/parameter combination. Practice E691 was followed for the design and analysis of the data.

14.1.1 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the *r* value for that material; *r* is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

14.1.1.1 Repeatability limits are listed in Tables 2-6.

14.1.2 *Reproducibility Limit (R)*—Two test results shall be judged not equivalent if they differ by more than the *R* value for that material; *R* is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

14.1.2.1 Reproducibility limits are listed in Tables 2-6.

14.1.3 The terms *repeatability limit* and *reproducibility limit* are used as specified in Practice E177.

14.1.4 Any judgment in accordance with statements 14.1.1 and 14.1.2 would have an approximate 95 % probability of being correct.

14.2 *Bias*—At the time of the study, there was no accepted reference material suitable for determining the bias for this test method, therefore no statement on bias is being made.

14.3 The precision statement was determined through statistical examination of 882 test results, submitted by twelve laboratories, reporting five parameters, for five solid materials.

14.4 To judge the equivalency of two test results, it is recommended to choose the material that is closest in characteristics to the test material.

15. Keywords

15.1 calorimetry; carbon dioxide; combustion; controlled heating; heat release; heat release rate; heat release capacity; oxidative thermal decomposition; oxygen consumption calorimetry; pyrolysis; thermal analysis; thermal decomposition

TABLE 3 Heat Release Capacity (J per g-K)

Material	Average[A]	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	s_r	s_R	r	R
Acrylic	471.0	9.0	26.7	25.1	74.7
PP	1095.3	32.5	86.4	91.0	242.0
HIPS	715.0	23.0	59.1	64.5	165.5
PC	529.5	25.3	48.2	70.9	134.9
PPSU	208.8	7.4	18.0	20.8	50.5

[A] The average of the laboratories' calculated averages.

---

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D20-1254.

TABLE 4 Total Heat Release (kJ per g)

Material	Average[A]	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	s_r	s_R	r	R
Acrylic	23.5	0.2	1.4	0.6	3.8
PP	41.5	0.8	2.3	2.3	6.4
HIPS	34.2	0.3	1.7	0.9	4.7
PC	21.0	0.3	1.3	0.8	3.6
PPSU	11.9	0.3	1.0	0.7	2.8

[A] The average of the laboratories' calculated averages.

TABLE 5 Peak Heat Release Temperature (°C)

Material	Average[A]	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	s_r	s_R	r	R
Acrylic	390.4	2.1	8.2	5.9	23.0
PP	481.1	2.0	9.8	5.7	27.5
HIPS	456.0	2.2	8.4	6.1	23.6
PC	525.3	2.4	11.4	6.6	31.8
PPSU	606.6	1.8	15.1	5.1	42.3

[A] The average of the laboratories' calculated averages.

TABLE 6 Char Yield (%)

Material	Average[A]	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	s_r	s_R	r	R
Acrylic	0.18	0.23	0.32	0.64	0.91
PP	0.21	0.19	0.34	0.53	0.96
HIPS	8.22	0.90	1.24	2.53	3.46
PC	19.38	0.91	1.62	2.54	4.52
PPSU	41.25	1.36	2.54	3.80	7.12

[A] The average of the laboratories' calculated averages.

ANNEX

(Mandatory Information)

A1. ANNEX

A1.1 The equipment used in this test method shall consist of a specimen chamber, mixing section, and combustor as separate components, Refs. (**1**, **3**, **9**, **11**) or combined into a single tube and individually heated by electrical resistance wire connected to separate power supplies as illustrated in Fig. 1, Ref. (**5**).

A1.2 Alternative constructions have been found suitable in which the specimen chamber is a commercial thermogravimetric analyzer, Ref. (**11**) or a pyrolysis probe, Refs. (**1**, **3**, **8**) thermally connected to a combustor, Refs. (**1**, **9**) or mass spectrometer, Refs. (**8**, **10**).

A1.3 *Specimen Chamber.* The volume of a cylindrical specimen chamber having length l_s (cm) and internal diameter d_s (cm) is fixed by the requirement that the residence time τ (s) of the sample gases in the specimen chamber through which the purge gas flows at volumetric flow rate F_s (cm^3/s) is less than 10 % of the time interval over which pyrolysis takes place during the test. This condition ensures that the sample gases exit the sample chamber as they are produced during the test and are therefore synchronized with the mass loss of the sample. At the gas flow rates used in this test the flow is laminar and fully developed for $l_s / d_s > 10$, under which conditions the time-averaged exit fraction of sample gases approaches unity. The temperature interval ΔT over which plastics thermally decompose at constant heating rate β is typically 50K and is independent of β. The specimen chamber volume shall therefore satisfy:

$$\tau = \frac{V_s}{F_s} << \frac{50\ K}{\beta} \equiv (0.10)\frac{50\ K}{\beta} \tag{A1.1}$$

For a cylindrical specimen chamber with fully developed laminar flow at l_s the dimensions shall satisfy:

$$\frac{\pi d_s^2 l_s/4}{F_s} = \frac{10\pi d_s^3 l_s/4}{F_s} = (0.10)\frac{50\ K}{\beta} \tag{A1.2}$$

For the stated performance requirements and under the nominal conditions of the test (Sections 9 – 11), $F_s = 1.33$ cm^3/s (80 cm^3/min), $\beta = 1$ K/s, the diameter of the specimen chamber is:

$$d_s \le \left(\frac{(2\ K)\ (F_s)}{\pi\beta} \right)^{\frac{1}{3}} = 1\ cm \qquad (A1.3)$$

For these same conditions the specimen chamber length is, $l_s \ge 10\ d_s = 10$ cm. Materials of construction include high temperature, corrosion resistant metals (Inconel) and ceramics (99.8 % alumina, mullite). The specimen chamber shall be heated by a suitable means capable of raising the sample temperature from 20°C/ambient to 900°C at a rate of up to 2 K/s. Electrical resistance heating using nickel-chromium or iron-chromium-aluminum alloys is suitable for this purpose.

A1.4 *Mixing Section.* The fuel and purge gases mix with oxygen at the inlet of the mixing section. To ensure complete mixing of fuel gases and oxygen and fully developed flow entering the combustor the length/diameter ratio of the mixing section shall be $l_m / d_m \ge 10$. For the geometry of Fig. 1 with $d_m = d_s = 1$ cm, the mixing section length shall be $l_m \ge 10$. The temperature of the mixing section shall be between the temperature of the sample chamber and the combustor at all times during the test to prevent the delay or loss of sample gases entering the combustor due to condensation on the walls of the mixing section.

A1.5 *Combustor.* The volume of the cylindrical combustor having length l_c (cm) and diameter d_c (cm) is fixed by the requirement that the residence time τ_c of the purge gas, sample gas, and oxygen at their combined volumetric flow rate F (cm^3/s) entering the combustion chamber is greater than or equal to 10 seconds at the typical operating temperature of 900°C so as to effect complete oxidation of the sample gases. The combustion chamber dimensions shall therefore satisfy:

$$\tau_c = \frac{V_c}{F} = \frac{\pi d_c^2 l_s / 4}{F} \ge 10\ s \qquad (A1.4)$$

For a combustion chamber diameter, $d_c = d_s = 1$ cm, the length of the combustion chamber required to effect complete oxidation of the sample gases for the geometry of Fig. 1 and under normal conditions of the test, $\tau_c = 10$ s at 900°C, F = 1.67 cm^3/s (100 cm^3/min),

$$l_c \ge \frac{4\tau_c F}{\pi d_s^2} = 21\ cm \qquad (A1.5)$$

Materials of construction suitable for the combustor include high temperature (1200°C), corrosion resistant metals such as Inconel and ceramics such as 99.8 % alumina and mullite. The combustor shall be thermally insulated and heated by a suitable means capable of maintaining an internal temperature of 1000°C. Electrical resistance heating using nickel-chromium or iron-chromium-aluminum alloys has been found suitable.

APPENDIX

(Nonmandatory Information)

X1. APPENDIX

X1.1 See Table X1.1 and Table X1.2.

X1.2 Fig. X1.1 is an example of the temperature deviation observed during the heating of zinc calibration material (**13**). Fig. X1.2 is an example of the relationship between melting temperature and sensor reading at the initial temperature deviation for high purity calibration materials (**13**).

TABLE X1.1 Flammability Characteristics for 14 Commercial Plastics Obtained by Method A

PLASTIC (n = 3)	η_c (J/g-K)	$\pm\eta_c$ (J/g-K)	h_c (kJ/g)	$\pm h_c$ (kJ/g)	Y_p (%)	$\pm Y_p$ (%)	T_{max} (°K)	$\pm T_{max}$ (°K)
HDPE	1486	20	43.5	0.2	0.1	0.1	504	1
PP	1130	24	43.2	0.2	2.5	0.0	483	1
HIPS	859	4	37.8	0.1	0.0	0.2	452	1
PA66	623	34	29.4	0.1	1.0	0.1	475	2
ABS	581	14	37.0	0.2	6.2	0.3	454	1
PC 2	539	26	20.4	0.1	22.5	0.8	547	2
PC 1	484	13	20.4	0.1	23.2	0.2	545	3
PMMA	475	6	24.9	0.1	0.0	0.0	393	2
PET	357	16	16.8	0.7	12.6	1.5	459	3
PPS	248	27	15.7	0.1	44.0	0.6	535	1
POM	235	19	14.3	0.0	0.0	0.0	398	6
PEI	201	7	9.3	0.2	51.3	0.3	565	1
PVC	129	3	10.8	0.2	18.8	0.1	467	4
FEP	57	1	4.1	0.0	0.0	0.0	589	1
AVG. COV:	3.3 %		1.0%		3.9%		0.5%	

TABLE X1.2 Comparison of ASTM D5865 to Method B of Current Practice. Net Calorific Values are the Average of Three Tests

POLYMER	D5865 (kJ/g)	Method B (kJ/g)	Relative Deviation (%)
Polyethylene	43.3	44.1	1.8
Polystyrene	39.8	40.1	0.8
Polyetheretherketone	30.2	30.9	2.3
Phenolic Triazine	29.8	29.5	-1.0
Polycarbonate	29.8	29.1	-2.3
Polyaramide fiber	27.8	28.1	1.1
Polybutyleneterephthalate	26.7	26.3	-1.5
Polymethylmethacrylate	24.9	25.0	0.4
Polyethyleneterephthalate	21.8	23.2	6.4
Polyoxymethylene	15.9	15.0	-5.7

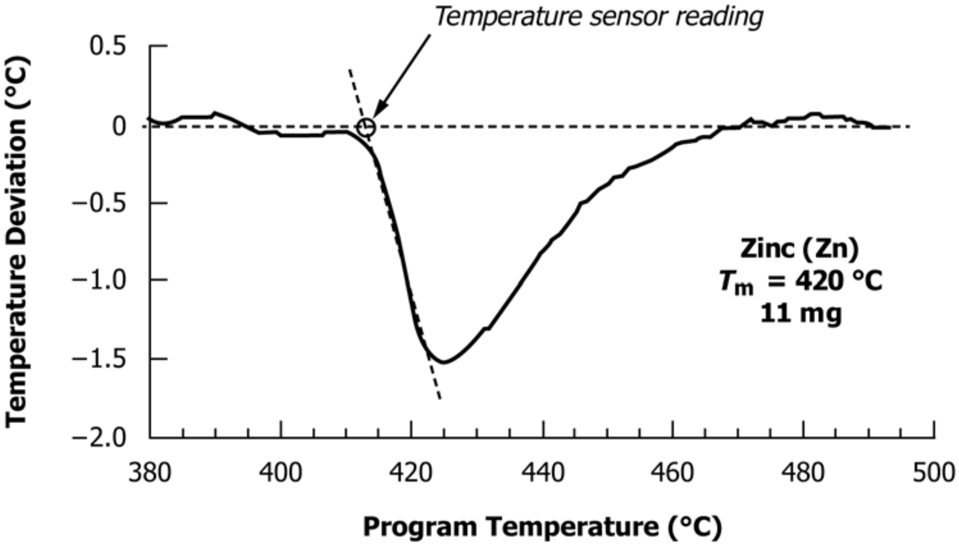

FIG. X1.1 Example of the Temperature Deviation Versus Program Temperature Measured During the Melting of Zinc Calibration Material

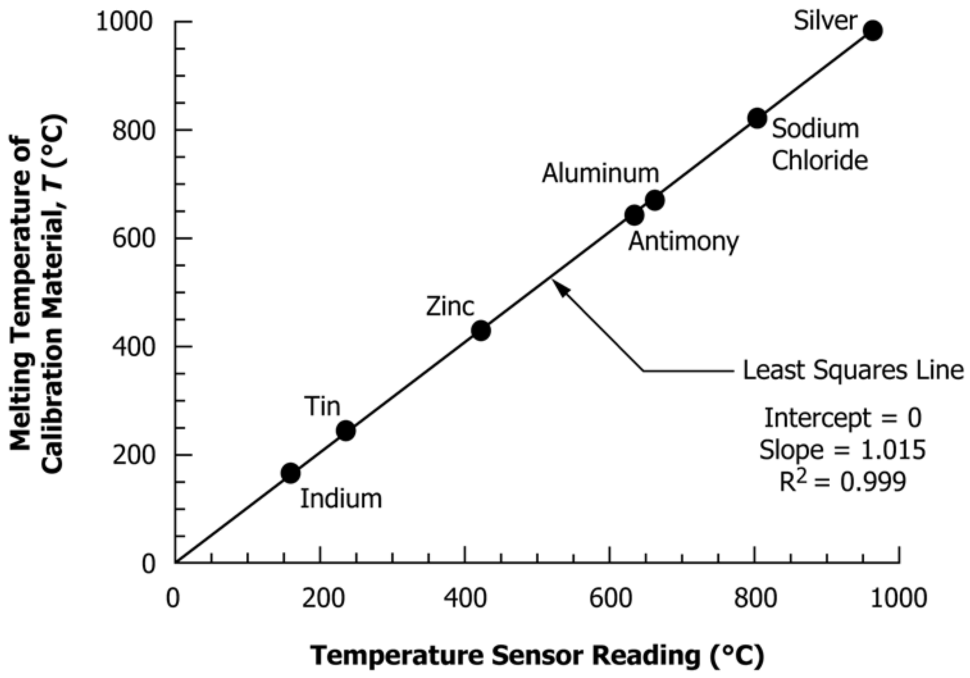

FIG. X1.2 Example of a Plot of Melting Temperature of Calibration Material Versus Temperature Sensor Reading

REFERENCES

(1) R.E. Lyon and R.N. Walters, "Pyrolysis Combustion Flow Calorimetry," *Journal of Analytical and Applied Pyrolysis*, 71(1), 2004, pp. 27-46.

(2) R.E. Lyon, "Solid State Thermochemistry of Flaming Combustion," in: *Fire Retardancy of Polymeric Materials*, A.F. Grand and C.A. Wilkie, (eds.), Marcel Dekker, Inc., NY, 2000, pp. 391-447.

(3) R.N. Walters and R.E. Lyon, "Molar Group Contributions to Polymer Flammability," *Journal of Applied Polymer Science*, 87, 2003, pp. 548-563

(4) R.E. Lyon, "Heat Release Kinetics," *Fire and Materials*, 24(4), 2000, pp.179-186.

(5) R.E. Lyon, R.N. Walters and S.I. Stoliarov, "A Thermal Analysis Method for Measuring Polymer Flammability," Journal of ASTM International, 3(4), 2006, pp. 1-18.

(6) R. E. Lyon and Marc Janssens, "Polymer Flammability," in the *Encyclopedia of Polymer Science & Engineering (On-line Edition)*, John Wiley & Sons, New York, NY, October 2005.

(7) R.E. Lyon, "Plastics and Rubber," in *Handbook of Building Materials for Fire Protection*, C. A. Harper, Ed., McGraw-Hill, New York, 2004, pp. 3.1-3.51.

(8) A. Schoemann, P.R. Westmoreland, H. Zhang, R.J. Farris, R.N. Walters, R.E. Lyon, "A Pyrolysis/GC-MS Method for Characterizing Flammability and Thermal Decomposition of Polymers," *Proc. 4th Joint Meeting of the U.S. Sections of the Combustion Institute*, Philadelphia, PA, March 21-23, 2005.

(9) R.E. Lyon and R.N. Walters, "A Microscale Combustion Calorimeter," Final Report DOT/FAA/AR-01/117, February 2002.

(10) T.V. Inguilizian, "Correlating Polymer Flammability Using Measured Pyrolysis Kinetics," Master of Science Thesis, University of Massachusetts, Amherst, January 1999.

(11) C.A. Wilkie, G. Chigwada, J.W. Gilman, and R.E. Lyon, "High-Throughput Techniques for the Evaluation of Fire Retardancy," *Journal of Materials Chemistry*, 16, 2023-2030 (2006)

(12) Howell, B.A., The Utilization of TG/GC/MS in the Establishment of the Mechanism of Polystyrene Degradation, , *Journal of Thermal Analysis and Calorimetry*, 89(2), pp. 393-398, 2007.

(13) Lyon, R.E., Walters, R.N. , Stoliarov, S.I., and Safronava, N., Principles and Practice of Microscale Combustion Calorimetry, *FAA Final Report DOT/FAA/TC-12/39*, April 2013.

(14) Lyon, R.E., Safronava, N., Senese , J., and Stoliarov, S.I., Thermokinetic Model of Sample Response in Nonisothermal Analysis, *Thermochimica Acta*, 545, 82-89 (2012).