



# Standard Test Method for Reaction Induction Time by Thermal Analysis<sup>1</sup>

This standard is issued under the fixed designation E2046; 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

## 1. Scope

1.1 This test method describes the measurement of Reaction Induction Time (RIT) of chemical materials that undergo exothermic reactions with an induction period. The techniques and apparatus described may be used for solids, liquids, or slurries of chemical substances. The temperature range covered by this test method is typically from ambient to 400°C. This range may be extended depending upon the apparatus used.

1.2 The RIT is a relative index value, not an absolute thermodynamic property. As an index value, the RIT value may change depending upon experimental conditions. A comparison of RIT values may be made only for materials tested under similar conditions of apparatus, specimen size, and so forth. Furthermore, the RIT value may not predict behavior of large quantities of material.

1.3 The RIT shall not be used by itself to establish a safe operating temperature. It may be used in conjunction with other test methods (for example, E487, E537, and E1981) as part of a hazard analysis of a particular operation.

1.4 This test method may be used for RIT values greater than 15 min (as relative imprecision increases at shorter periods).

1.5 This test method is used to study catalytic, autocatalytic, and accelerating reactions. These reactions depend upon time as well as temperature. Such reactions are often studied by fixing one experimental parameter (that is, time or temperature) and then measuring the other parameter (that is, temperature or time). This test method measures time to reaction onset detection under isothermal conditions. It is related to Test Method E487 that measures detected reaction onset temperature under constant time conditions

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

1.7 There is no ISO standard equivalent to this test method.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee E27 on Hazard Potential of Chemicals and is the direct responsibility of Subcommittee E27.02 on Thermal Stability and Condensed Phases.

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1.8 *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 consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- D3350 Specification for Polyethylene Plastics Pipe and Fittings Materials
- D3895 Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry
- D4565 Test Methods for Physical and Environmental Performance Properties of Insulations and Jackets for Telecommunications Wire and Cable
- D5483 Test Method for Oxidation Induction Time of Lubricating Greases by Pressure Differential Scanning Calorimetry
- D6186 Test Method for Oxidation Induction Time of Lubricating Oils by Pressure Differential Scanning Calorimetry (PDSC)
- E473 Terminology Relating to Thermal Analysis and Rheology
- E487 Test Method for Constant-Temperature Stability of Chemical Materials
- E537 Test Method for The Thermal Stability of Chemicals by Differential Scanning Calorimetry
- E967 Test Method for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers
- E968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters
- E1445 Terminology Relating to Hazard Potential of Chemicals
- E1858 Test Method for Determining Oxidation Induction Time of Hydrocarbons by Differential Scanning Calorimetry
- E1860 Test Method for Elapsed Time Calibration of Thermal Analyzers

<sup>2</sup> 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.

**E1981** Guide for Assessing Thermal Stability of Materials by Methods of Accelerating Rate Calorimetry

**E2070** Test Method for Kinetic Parameters by Differential Scanning Calorimetry Using Isothermal Methods

### 3. Terminology

3.1 The specialized terms used in this test method are described in Terminologies **E473** and **E1445**, including *differential scanning calorimetry*, *differential thermal analysis*, *extrapolated onset value*, *first-deviation-from-baseline*, *onset value*, *isothermal*, and *reaction*.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *constant temperature stability (CTS) value, n*—the maximum temperature at which a chemical compound or mixture may be held for a minimum of two hours without exhibiting a measurable exothermic reaction. (See Test Method **E487**.)

3.2.2 *reaction induction time (RIT) value, n*—the time a chemical compound or mixture may be held under isothermal conditions until it exhibits a specified exothermic reaction.

### 4. Summary of Test Method

4.1 A specimen of the chemical compound or mixture is placed in an inert container that is then heated to an operator-selected test temperature of interest. The specimen temperature and the difference in heat flow or temperature between the test specimen and an inert reference are monitored until an exothermic reaction is recorded. The time from the attainment of the isothermal test temperature until the extrapolated onset to the exothermic reaction is taken as the Reaction Induction Time.

4.2 Using fresh specimens measurements at more than one isothermal test temperature may be made.

4.3 The RIT is expressed as time at a specific test temperature. For example:

$$\text{RIT} = 120 \text{ min at } 100^{\circ}\text{C}$$

### 5. Significance and Use

5.1 This test method measures the time to extrapolated onset of an exothermic reaction under constant temperature (isothermal) conditions for reactions which have an induction period, for example, those which are catalytic, autocatalytic, or accelerating in nature or which contain reaction inhibitors.

5.2 The RIT determined by this test method is an index measurement that is useful for comparing one material to another at the test temperature of interest and in the same apparatus type only.

5.3 This test method is a useful adjunct to dynamic thermal tests, such as Test Method **E537**, which are performed under conditions in which the sample temperature is increased continuously at constant rate. Results obtained under dynamic test conditions may result in higher estimates of temperature at which an exothermic reaction initiates because the detected onset temperature is dependent upon the heating rate and because dynamic methods allow insufficient time for autocatalytic reactions to measurably affect the onset temperature.

5.4 RIT values determined under a series of isothermal test conditions may be plotted as their logarithm versus the reciprocal of the absolute temperature to produce a plot, the slope of which is proportional to the activation energy of the reaction as described in Test Method **E2070**.

5.5 This test method may be used in research and development, manufacturing, process and quality control, and regulatory compliance.

5.6 This test method is similar to that for Oxidation Induction Time (OIT) (for example, Specification **D3350** and Test Methods **D3895**, **D4565**, **D5483**, **D6186**, and **E1858**) where the time to the oxidation reaction under isothermal test conditions is measured. The OIT test method measures the presence of antioxidant packages and is a relative measurement of a material's resistance to oxidation.

### 6. Apparatus

6.1 The design and complexity of the apparatus required for this test method depends upon the size of the specimen to be used. In general, observation of an exothermic reaction in small specimens (less than 50 mg) is performed using differential scanning calorimetry or differential thermal analysis equipment and techniques. Large samples (up to 2 g) may be tested using devices such as the Kuhner Micro CTS apparatus.

6.2 The following items are required to obtain the appropriate experimental data.

NOTE 1—Commercially available differential scanning calorimetry apparatus may be used. Alternatively, the apparatus may be assembled or fabricated from commercially available components.

6.2.1 *Test Chamber*, composed of the following:

6.2.1.1 *Furnace(s)*, to provide uniform controlled heating of a specimen and reference to a constant temperature.

6.2.1.2 *Temperature Sensor*, to provide an indication of specimen/furnace temperature to  $\pm 0.1$  K.

6.2.1.3 *Differential Sensor*, to detect a difference in heat flow (or temperature) between the specimen and the reference specimen equivalent to 10  $\mu\text{W}$  or 0.01 mK.

NOTE 2—A reference material is used when differential heat flow or differential temperature measurements are made. The reference material should match the physical state and heat capacity of the specimen as closely as practical. Typical reference materials include calcined aluminum oxide, glass beads, silicone oil, or combinations thereof.

6.2.1.4 *Means of Sustaining a Test Chamber Environment*, through the use of an air purge gas at a rate of 10 to 100  $\pm 5$  mL/min.

NOTE 3—Typically, air or inert 99.9+ % pure nitrogen, argon, or helium is employed (when oxidation in air is a concern). Unless effects of moisture are to be studied, use of dry purge gas is recommended.

NOTE 4—For the Kuhner Micro CTS apparatus, the purge gas is provided by operation in a laboratory hood with the door(s) approximately 50 % closed.

6.2.2 *Temperature Controller*, capable of heating from ambient to 400°C at a rate of up to 20°C/min and maintaining an isothermal temperature constant within that range of  $\pm 0.4^{\circ}\text{C}$  for the duration of the test, or both.

6.2.3 *A Data Recording Device*, to provide a means of acquiring, storing, and displaying measured or calculated

signals, or both. The minimum output signals required for differential scanning calorimetry or differential thermal analysis are heatflow (or differential temperature), temperature, and time.

6.2.4 *Containers* (pans, crucibles, vials, test tubes, and so forth, and lids), which are inert to the specimen and reference materials at the maximum temperature used and which are of suitable structure, shape, and integrity to contain the specimen and reference in accordance with the temperature and mass requirements as described in this section.

6.3 *Balance*, with a capacity of 100 mg or more to weigh specimens or containers to  $\pm 0.1$  mg.

NOTE 5—A balance capacity of 10 g or more with a readability to  $\pm 0.1$  g is required for use with the Kuhner Micro CTS device.

## 7. Hazards

7.1 Dynamic thermal tests, utilizing milligram quantities of materials, such as Test Method E537, are normally conducted on specimens before the present test is undertaken. The experimenter shall have sufficient knowledge of the magnitude of hazard associated with the material. Larger specimens shall be used only after due consideration is given to the potential for hazardous reaction. Thermodynamic calculations also may be used to determine the potential hazard.

7.2 Special precautions shall be taken to protect personnel and equipment when the apparatus in use requires the insertion of specimens into a heated block or furnace. These shall include adequate shielding and ventilation of equipment, and face and hand protection (see Note 8).

## 8. Sampling

8.1 Specimens shall be representative of the material being studied and shall be prepared to achieve good thermal contact between the specimen and the container.

8.2 Specimen size depends upon the sensitivity of the available apparatus.

NOTE 6—Specimen size of 1 to 7 mg is typically used in thermal analysis apparatus. Specimen size of 1 to 2 g is typically used with the Kuhner Micro CTS apparatus.

8.3 Specimens may be run in an unconfined or in a sealed container, depending upon which condition has the more relevance for the end use of the data.

## 9. Calibration

9.1 Apparatus temperature calibration shall be performed in accordance with Practice E967 at a heating rate of  $1^\circ\text{C}/\text{min}$ .

9.2 Apparatus heat flow calibration may be performed in accordance with Practice E968.

9.3 Apparatus elapsed time shall be verified to be better than  $\pm 1\%$  by Test Method E1860.

## 10. Procedure

10.1 Weigh 1 to 7 mg with a precision of  $\pm 1$  mg of the test specimen into a clean specimen container. Seal the container, if desired.

NOTE 7—The Kuhner Micro CTS device uses up to 2-g specimens. For

specimens of a size greater than 1 g, record mass to  $\pm 0.1$  g.

10.2 Place the test specimen into the apparatus onto the sample position, at ambient temperature conditions. Place a specimen container containing 1 to 7 mg of inert reference material (1 to 2 g for the Kuhner Micro CTS) in the reference position.

10.3 Heat the test specimen and reference material from ambient to the isothermal temperature of test at  $20^\circ\text{C}/\text{min}$  with no more than  $1^\circ\text{C}$  overshoot. Zero time is recorded when the specimen test temperature reaches the isothermal test temperature  $\pm 1^\circ\text{C}$ . Record the thermal curve.

NOTE 8—In some apparatus, it may be possible to load the specimen and reference into the furnace preheated to the isothermal test temperature. Appropriate provisions shall be made to ensure the safety of the operator.

NOTE 9—A dynamic test method, such as Test Method E537 may be used to estimate potential isothermal test temperatures.

10.4 Record the sample temperature 5 min into the experiment.

10.5 Terminate the experiment when the peak of the reaction exotherm is observed or when no exotherm is observed or after an operator-selected time. (In the absence of other information, after 200 min). The reaction is exothermic if it results in a measurable increase in specimen temperature or heat flow above baseline.

10.6 Display the thermal curve with differential heat flow or differential temperature on the Y-axis and time on the X-axis. Extend the recorded baseline beyond the reaction exotherm. Construct a tangent at the point of the most rapid rate of increase in heat flow and extrapolate it to intersect with the constructed baseline. The time at the intersection of these two lines is the reaction induction time. (See Fig. 1.)

NOTE 10—The precision of this test method is a constant value (see Section 12) and does not depend upon the measured value. For this reason, this test method is applicable to RIT values greater than 15 min. If RIT values of less than 15 min are observed, the test temperature may be lowered to obtain longer RIT values.

NOTE 11—In some cases, where agreed upon by the parties involved, the time at the first deviation from baseline may be taken as the RIT values. This alternative shall be included in the report.

10.7 Report the RIT (from 10.6) and the isothermal test temperature (from 10.4) as follows:

$$\text{RIT} = 120 \text{ min at } 200^\circ\text{C}$$

NOTE 12—If no reaction is observed, then the RIT may be reported as greater than the condition tested. For example: RIT > 200 min at  $200^\circ\text{C}$ .

NOTE 13—For materials with high activation energies, the RIT will vary significantly over a small temperature range.

## 11. Report

11.1 Report the following information:

11.1.1 Full identification of the sample (for example, process stream, date and time of acquisition, lot number, and so forth).

11.1.2 Specimen mass.

11.1.3 Description of the apparatus, including the material and type of specimen containers.

11.1.4 Test conditions including atmosphere and degree of confinement.

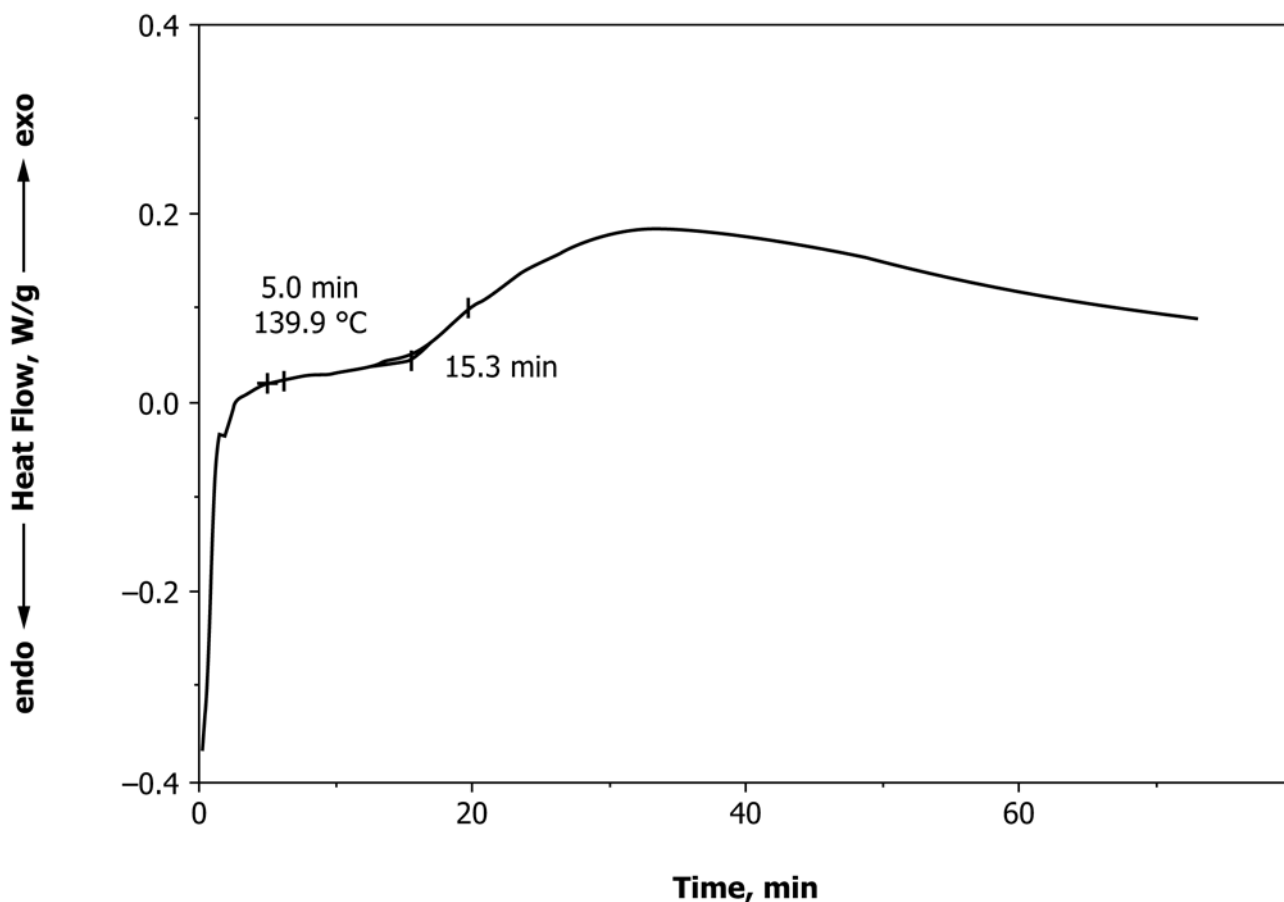


FIG. 1 Reaction Induction Time Measurement for *p*-nitrosodiphenylamine

11.1.5 RIT value (min) and indicator (that is, extrapolated onset or first-deviation from baseline).

11.1.6 Isothermal test temperature (°C).

11.1.7 Copy of the original thermal curve.

11.1.8 The dated version of this test method.

## 12. Precision and Bias

12.1 An interlaboratory test program was conducted in 2003 to determine the precision and bias of this standard using phenyltetrazolthiol as a test material.<sup>3</sup> The results from 10 laboratories, using 5 replicates (that is, 36 degrees of experimental freedom) are used to provide the information below. Seven instrument models from 3 manufacturers were used in this study.

### 12.2 Precision:

12.2.1 Within laboratory variability may be described using the repeatability value (*r*) obtained by multiplying the standard deviation by 2.8. The repeatability value estimates the 95 % confidence limit. That is, two results obtained in the same laboratory should be considered suspect (at the 95 % confidence level) if they differ by more than the repeatability value *r*.

12.2.2 The within laboratory repeatability standard deviation for Reaction Induction Time indicated by the first-deviation-from-baseline time and the extrapolated onset time were found to be 1.98 and 1.86 min, respectively. The standard deviation does not appear to be a function of the absolute value of the measurement.

NOTE 14—There is some experimental information suggesting that metal sample containers may catalyze the decomposition measurement of the phenyltetrazolthiol sample used in this interlaboratory test. Nonetheless, Intralaboratory testing on other test specimens confirms the within laboratory repeatability values indicated above.

12.2.3 Between laboratory variability may be described using the reproducibility value (*R*) obtained by multiplying the standard deviation by 2.8. The reproducibility value estimates the 95 % confidence limits. That is, two results obtained in different laboratories, should be considered suspect (at the 95 % confidence level) if they differ by more than the reproducibility value *R*.

12.2.4 The between laboratory reproducibility standard deviation for first-deviation-from-baseline time and the extrapolated onset time were found to be 7.3 and 5.2 min, respectively. The standard deviation does not appear to be a function of the absolute value of the measurement

12.3 Bias—Bias is the difference between the value obtained and that of a reference material. There is no known reference material for Reaction Induction Time nor are there

<sup>3</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E27-1005. Contact ASTM Customer Service at service@astm.org.

known RIT values for phenyltetrazolthiol. Therefore bias is unable to be estimated for this standard.

12.3.1 The mean values determined for first-deviation-from-baseline time and extrapolated onset time for phenyltetrazolthiol was found to be 28.0 and 54.4 minutes, respectively, at 120°C (see **Note 13**).

### **13. Keywords**

13.1 differential scanning calorimetry (DSC); differential thermal analysis (DTA); hazard potential; reaction induction time (RIT); reactions, thermal; thermal analysis (TA); thermal stability

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