Designation: E487 – 14

Standard Test Method for Constant-Temperature Stability of Chemical Materials[1]

This standard is issued under the fixed designation E487; 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 describes the assessment of constant-temperature stability (CTS) of chemical materials that undergo exothermic reactions. The techniques and apparatus described may be used on solids, liquids, or slurries of chemical substances.

1.2 When a series of materials is tested by this test method, the results permit ordering the materials relative to each other with respect to their thermal stability.

1.3 *Limitations of Test:*

1.3.1 This test method is limited to ambient temperatures and above.

1.3.2 This test method determines neither a safe storage temperature nor a safe processing temperature.

NOTE 1—A safe storage or processing temperature requires that any heat produced by a reaction be removed as fast as generated and that proper consideration be given to hazards associated with reaction products.

1.3.3 When this test method is used to order the relative thermal stability of materials, the tests must be run under the same confinement condition (see 8.3).

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

1.5 *This standard should be used to measure and describe the properties of materials, products, or assemblies in response to heat and flame under controlled laboratory conditions and should not be used to describe or appraise the fire hazard or fire risk of materials, products, or assemblies under actual fire conditions. However, results of this test may be used as elements of a fire risk assessment which takes into account all of the factors which are pertinent to an assessment of the fire hazard of a particular end use.*

1.6 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses 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:*[2]

E473 Terminology Relating to Thermal Analysis and Rheology

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

E1860 Test Method for Elapsed Time Calibration of Thermal Analyzers

3. Terminology

3.1 *Definitions:*

3.1.1 *constant-temperature stability (CTS) value*—the maximum temperature at which a chemical compound or mixture may be held for a 120-min period under the conditions imposed in this test without exhibiting a measurable exothermic reaction.

3.2 The specialized terms in this standard are described in Terminologies E473 and E1445 including differential scanning calorimetry, differential thermal analysis, exotherm, and first-deviation-from-baseline.

4. Summary of Test Method

4.1 A sample of the chemical compound or mixture is placed in a glass or metal tube that is heated to a test temperature of interest. The sample temperature and heat flow or the difference between the sample temperature and the temperature of an inert reference material, are monitored over a 120-min period or until an exothermic reaction is recorded.

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[1] This test method is under the jurisdiction of ASTM Committee E27 on Hazard Potential of Chemicals and is the direct responsibility of E27.02 on Thermal Stability and Condensed Phases.

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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.

Test temperatures are decreased in 10°C intervals until no exothermic reaction is observed in the 120-min test period. The Constant Temperature Stability is determined and reported using either Method A or Method B.

NOTE 2—Test periods other than two 120-min periods may be used but shall be reported.

NOTE 3—The processing times in many industrial scale unit operations (for example, drying, distillations, and the like) normally significantly exceed the 120-min time period in this CTS test procedure. Therefore, for the effective application of the CTS data for industrial scale operations, the CTS time must be extended to be greater than the processing time in the actual operation.

5. Significance and Use

5.1 This test method is a useful adjunct to dynamic thermal tests that are performed under conditions in which the sample temperature is increased continuously at a programmed rate. Results obtained under dynamic test conditions present difficulties in determining the temperature at which an exotherm initiates because onset temperature is dependent on heating rate. The test method described in the present standard attempts to determine the onset temperature under isothermal conditions where the heating rate is zero.

6. Apparatus

6.1 The design and complexity of the apparatus required for this method depends upon the size of the sample to be used. In general, observance of an exothermic reaction in small samples (less than 50 mg) is best done using differential thermal analysis or differential scanning calorimetry equipment and techniques. Larger samples (up to 2 g) may be tested using a Kuhner Micro CTS apparatus.

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

6.2.1 A test chamber composed of:

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 the specimen/furnace temperature to ±0.1°C.

6.2.1.3 *Differential Sensor*, to detect a difference in heat flow or temperature between specimen and reference specimen equivalent to 1 mW or 40 mK.

NOTE 4—Sample temperature may be measured either absolutely or differentially. When differential temperature measurements are made, and a reference material is used, the reference material should match the physical state and heat capacity of the sample as closely as practical. Typical reference materials are calcined aluminum oxide, glass beads, silicone oils, and a combination of these.

NOTE 5—Commercially available differential thermal analysis or differential scanning calorimetry apparatus capable of operating in an isothermal mode may be used. Alternatively, the apparatus may be assembled or fabricated from commercially available components (see 12.1).

6.2.2 A temperature *Controller* capable of heating from ambient to 400°C at a rate of 1°C/min to 50°C/min and maintaining an isothermal temperature constant within that range to ±1°C for 120 min.

6.2.3 A *Data Collection 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 are heat flow, temperature and time.

6.2.4 *Containers* (pans, crucibles, vials, test tubes, etc.) which are inert to the specimen and reference material and which are of suitable structure, shape, and integrity to contain the specimen and reference in accordance with the temperature and specimen mass requirements described in this section.

6.3 A *Balance* with a capacity of 100 mg or more to weigh specimens and/or containers (pans, crucibles, vials, and the like) to ±0.1 mg (see Note 6).

7. Hazards

7.1 Dynamic thermal tests are normally carried out on small samples before the present test is undertaken. Therefore, the experimenter should have some knowledge of the magnitude of hazard associated with the material. Larger samples should be used only after due consideration is given to the potential for hazardous reaction. Thermodynamic calculations also can be used to determine the potential hazard.

7.2 Special precautions should be taken to protect personnel and equipment when the apparatus in use requires the insertion of samples into a heated block or furnace. These should include adequate shielding and ventilation of equipment, and face and hand protection.

8. Sampling

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

8.2 Specimen size depends upon the sensitivity of the available apparatus (see 12.1).

NOTE 6—Specimen size of 4–7 mg is typically used in thermal analysis apparatus. The Kuhner Micro CTS uses up to 2 g of sample. For test specimen size greater than 1 g, record mass to ±0.1 g.

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

8.4 In selecting the material of construction of the specimen container, consideration should be given to possible interaction with the specimen.

9. Calibration

9.1 Apparatus temperature calibration shall be performed according to Practice E967 at a heating rate of 1°C/min.

9.2 Apparatus heat flow calibration shall be performed according to Practice E968 for differential scanning calorimeters. Differential thermal and Kuhner Micro CTS apparatus shall be calibrated according to the manufacturers' instructions.

9.3 Apparatus elapsed time shall be calibrated according to Test Method E1860.

10. Procedure

10.1 Bring the sample holder of the apparatus to a temperature 10°C below that approximated as the onset temperature in a previous differential thermal analysis measurement. Maintain control at the set temperature at no more than ±1°C.

NOTE 7—The onset temperature may be determined using Practice E537.

10.2 Place the samples and containers in the heated sample holder at the control temperature. Note the starting time as the time of sample insertion and begin a temperature record versus time immediately.

NOTE 8—If the test apparatus allows the sample to be brought to the test temperature in less than 10 min with not more than 1°C overshoot, then place the sample and reference in the heating unit at ambient temperature.

10.3 Maintain the sample temperature for 120 min or until an exothermic reaction is observed. Reaction is indicated by an exothermic heat flow, departure of the temperature trace from the set heater temperature or from the reference temperature depending on the type apparatus used. The reaction is exothermic if it results in a measurable increase in sample temperature. Record the isothermal test temperature and the time interval from the start of the experiment to occurrence of an exotherm as measured by the first-deviation-from baseline.

NOTE 9—Other test periods may be used but shall be reported.

10.4 When an exothermic reaction is observed, decrease the experimental temperature by 10°C, and repeat the experiment with a new sample. Follow the procedure until no exothermic reaction is observed in a 120-min period.

10.5 Repeat 10.4 using a sample twice as large as that used in the initial determinations. If a significant change in time or temperature is noted repeat by again doubling the sample size.

10.6 A rectilinear plot of temperature versus time using the values obtained in 10.4 and 10.5 is helpful in minimizing the number of tests required and in predicting the limiting CTS value.

11. Calculations

11.1 *Method A:*

11.1.1 Report the highest temperature at which the first-deviation-from-baseline (taken to be the indication of a exothermic reaction) is observed at more than 120 min. Report this value as CTS (Method A) = yy°C at 120 min.

NOTE 10—The first-deviation-from-baseline is determined on a scale that permits the peak of the exotherm to be displayed.

11.2 *Method B:*

11.2.1 Create a rectilinear plot of the temperature versus time for the first-deviation-from-baseline (taken to be the indication of an exothermic reaction) using the values obtained in 10.4 and 10.5. Using this plot interpolate the time axis to 120 min and determine the corresponding temperature. Report this value as CTS (Method B = xx°C at 120 min.

12. Performance Criteria for Test Apparatus

12.1 The apparatus used for this test is considered adequate if a CTS value of 120°C to 140°C is obtained for 4–nitroso-N-phenylbenzeneamine (also known as 4–nitrosodiphenylamine) or a value of 210°C to 230°C for 3–methyl-4–nitrophenol.

13. Report

13.1 The report shall include the following:

13.1.1 Description of the sample,

13.1.2 Sample weight,

13.1.3 Description of apparatus including materials or construction of sampler container,

13.1.4 Test conditions including atmosphere and degree of confinement,

13.1.5 Temperatures investigated,

13.1.6 Whether an exothermic reaction took place at each temperature,

13.1.7 Time interval before each exotherm, and

13.1.8 The Constant Temperature Stability determined including Method, temperature and time. For example CTS (Method A) = 140°C.

14. Precision and Bias

14.1 *Precision:*

14.1.1 An interlaboratory test program was conducted in 2003 in which 13 laboratories, using 7 instrument models supplied by 4 vendors examined the Constant Temperature Stability of 1-phenyl-1H-tetrazole-5-thiol, known to decomposed autocatalytically.[3]

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

14.1.3 For Method A, within laboratory precision is defined by 10.4 of this test method requiring that the test specimen be tested only at 10°C intervals.

14.1.4 For Method B, the within laboratory repeatability standard deviation is 0.95°C.

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

14.1.6 6 For Method A, the between laboratory reproducibility standard deviation is 4.8°C.

14.1.7 For Method B, the between laboratory reproducibility standard deviation is 4.3°C.

14.2 *Bias:*

14.2.1 Bias is the difference between the value obtained by this standard and that of a reference material. There is no known Constant Temperature Stability reference material nor are CTS values known for phenyltetrazothiol, so bias may not be evaluated.

14.2.2 For Method A, the mean CTS value at 120 min for phenyltetrazolthiol was 103°C.

14.2.3 For Method B, the mean CTS value at 120 min for phenyltetrazolthiol was 108°C.

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[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E27-1006. Contact ASTM Customer Service at service@astm.org.

14.2.4 Phenyltetrazol was also evaluated in an intralaboratory test using the RADEX apparatus, an approach that is not yet an ASTM International standard. In this work, the RADEX value for "No reaction within 120 min" was found to be 104°C.

15. Keywords

15.1 constant temperature stability (CTS); differential scanning calorimetry (DSC); differential thermal analysis (DTA); hazard potential; reactions, thermal; thermal analysis; thermal hazard; thermal stability

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