Designation: E2958 – 14

Standard Test Methods for Kinetic Parameters by Factor Jump/Modulated Thermogravimetry[1]

This standard is issued under the fixed designation E2958; 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 These test methods describe the model-free determination of Arrhenius activation energy by thermogravimetry using the factor jump (**1**)[2] (Method A) or modulated thermogravimetry (**2**) (Method B) techniques. With the assumption of a first-order kinetic model, the pre-exponential factor is additionally determined.

1.2 These test methods are applicable to materials with well-defined decomposition profiles, namely, a smooth, continuous mass change.

1.3 These test methods are applicable to decomposition occurring in the range from 400 K to 1200 K (nominally 100°C to 900°C). The temperature range may be extended depending on the instrumentation and material used.

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 There is no ISO standard similar to 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:*[3]

E473 Terminology Relating to Thermal Analysis and Rheology

E1142 Terminology Relating to Thermophysical Properties

E1582 Practice for Calibration of Temperature Scale for Thermogravimetry

E1641 Test Method for Decomposition Kinetics by Thermogravimetry Using the Ozawa/Flynn/Wall Method

E1877 Practice for Calculating Thermal Endurance of Materials from Thermogravimetric Decomposition Data

E1970 Practice for Statistical Treatment of Thermoanalytical Data

E2040 Test Method for Mass Scale Calibration of Thermogravimetric Analyzers

E2550 Test Method for Thermal Stability by Thermogravimetry

3. Terminology

3.1 *Definitions*—Technical terms used in this test method defined in Terminologies E473 and E1142 include *Arrhenius equation, activation energy, Celsius, failure criterion, pre-exponential factor, reaction order*, and *thermogravimetric analysis*.

4. Summary of Test Method

4.1 These test methods consist of heating a test specimen weighing a few milligrams at a heating rate of about 1 K/min with a superimposed step-and-hold (factor jump) or sinusoidal (modulated) temperature program through the decomposition temperature region. The specimen mass rate-of-change is continuously calculated and recorded as a function of temperature. The activation energy is then determined from the mass rate-of-change at two (or more) closely spaced temperature regions. The activation energy thus determined is based on no assumed reaction model or mechanism and thus is model free.

4.2 Assuming a first-order reaction model (n = 1), the additional reaction parameter logarithm-of-the-pre-exponential-factor (ln[Z]) is additionally determined.

4.3 Activation energy and logarithm-of-the-pre-exponential-factor may be displayed as a function of average temperature or conversion to provide additional information about the constancy of the decomposition reaction relative to these experimental parameters.

5. Significance and Use

5.1 The activation energy may be used to calculate thermal endurance and an estimate of the lifetime of the material at specified temperatures using Test Method E1877.

[1] These test methods are 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] The boldface numbers in parentheses refer to a list of references at the end of this standard.

[3] 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.

5.2 The kinetic parameters determine by this test method may be used in quality assurance, research and development.

5.3 The kinetic parameters of activation energy and logarithm of the pre-exponential factor determined by this method have little intrinsic value in themselves. Most practical applications of this information, such as lifetime estimation (see Test Method E1877), also require an estimation of the precision of the respective values. Determination of that precision by replicated determination is a non-manditory part of this standard.

6. Apparatus

6.1 The essential equipment required to provide minimum thermogravimetric analytical capability of this test method include:

6.1.1 A *thermobalance*, composed of (*a*) a *furnace* to provide uniform controlled heating of a specimen at a constant rate up to 100 K/min within the temperature range from ambient to 1200 K; (*b*) a *temperature* sensor to provide an indication of the specimen/furnace temperature to within ±0.1 K; (*c*) an *electrobalance* to continuously measure the specimen mass with a minimum capacity of 20 mg and a sensitivity of ±50 µg; and (*d*) a means of sustaining the specimen/container under *atmospheric control* of an inert or reactive purge gas of 99.99 % purity at a rate of 20 mL/min to 50 mL/min ± 5 mL/min.

6.1.2 A *temperature controller*, capable of executing a specific temperature program by operating the furnace between selected temperature limits at a rate of temperature change of 1 K/min to 100 K/min constant to within ±1 % or an isothermal temperature which is maintained constant to within ±0.05 K.

6.1.3 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 this test method are mass, mass rate-of-change, temperature, and time.

6.1.4 Auxiliary instrumentation or data analysis capability considered useful in conducting this method includes:

6.1.4.1 For Method B, the ability to apply a sinusoidal temperature program of a 100 s to 300 s period and ±0 K to 6 K amplitude upon the underlying linear temperature program or isothermal conditions.

6.1.4.2 For Method B, the capability to continuously calculate activation energy and logarithm of the pre-exponential factor.

NOTE 1—Alternative capabilities are described in Refs (**3-7**).

6.2 *Containers* (pans, crucibles, and so forth) that are inert to the specimen and that will remain dimensionally stable over the temperature range from ambient to 1200 K.

6.3 *High-Purity (99.99 %) Nitrogen Supply*, for purge gas.

NOTE 2—Other atmospheres may be used but shall be reported.

6.4 *Cryogenic Mill* capable of grinding up to 4 mg of material at a temperature less than 173 K (–100°C).

7. Sampling, Test Specimens, and Test Units

7.1 Since milligram quantities of specimens are used, it is essential that the specimens be representative of the samples from which they are taken. All specimens should be thoroughly mixed prior to sampling and should be sampled by removing portions form various parts of the sample. These portions should in turn be combined and mixed well to ensure a representative specimen for the determination.

7.2 Powdered or granular specimens that have a high surface-to-volume ratio, are preferred, although films, fibers, and fabric may be used providing that care is taken to ensure that all specimens are uniform in size and shape. Where the sample is a part or is in the form of pellets, the specimen may be prepared by filling, rasping or cryogenic milling.

NOTE 3—The specimen size and surface-to-volume ratio are known to affect the results of this test. A narrow range of specimen sizes should be used as noted in 10.1 and 12.1. Uniformity in particle size can be achieved, without the loss of volatiles, by using a cryoscopy (liquid nitrogen) mill to grind the sample to a powder. To prevent the condensation of moisture, the mill should be opened only after returning to ambient temperature, or the operation should be performed in a glove box filled with dry gas.

7.3 In the absence of other information, the samples are assumed to be analyze as-received except for the mechanical treatment noted in 7.2. If some heat treatment, such as drying, is applied to the sample prior to analysis, this treatment and any resulting mass loss shall be reported.

7.4 Some materials may require more sophisticated conditioning, such as maintaining the sample in a specified temperature and relative humidity for an extended period of times. Such conditioning may be conducted, but procedural details shall be included in the report.

8. Preparation of Apparatus and Experimental Conditions

8.1 Prepare the thermogravimetric analyzer using the procedures described in the manufacturer's operations manual.

8.2 Identify the weight loss to be used as the failure criterion. Report this value.

NOTE 4—The value of 5 % mass loss of the specific decomposition step is commonly used in thermogravimetry and accelerated lifetime testing as the failure criteria (see Test Method E1641).

9. Calibration and Standardization

9.1 Calibrate the temperature scale of the thermogravimetric analyzer at 1 K/min using Practice E1582.

9.2 Calibrate the mass loss scale of the thermogravimetric analyzer using Test Method E2040.

METHOD A
FACTOR JUMP METHOD

10. Procedure

10.1 Place 2 mg to 4 mg of the specimen into a clean, tared instrument specimen container.

NOTE 5—Other specimen size may be used but shall be reported.

NOTE 6—Powdered or granular specimens should be distributed evenly