This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

Designation: E698 – 23

Standard Test Method for Kinetic Parameters for Thermally Unstable Materials Using Differential Scanning Calorimetry and the Flynn/Wall/Ozawa Method[1]

This standard is issued under the fixed designation E698; 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.

INTRODUCTION

The kinetics of exothermic reactions are important in assessing the potential of materials and systems for thermal explosion. This test method provides a means for determining Arrhenius activation energies and pre-exponential factors using differential thermal methods. This test method is to be used in conjunction with other tests to characterize the hazard potential of chemicals.

1. Scope

1.1 This test method covers the determination of the overall kinetic parameters for exothermic reactions using the Flynn/Wall/Ozawa method and differential scanning calorimetry.

1.2 This technique is applicable to reactions whose behavior can be described by the Arrhenius equation and the general rate law.

1.3 *Limitations*—There are cases where this technique is not applicable. Limitations may be indicated by curves departing from a straight line (see 11.2) or the isothermal aging test not closely agreeing with the results predicted by the calculated kinetic values. In particular, this test method is not applicable to reactions that are partially inhibited. The technique may not work with reactions that include simultaneous or consecutive reaction steps. This test method may not apply to materials that undergo phase transitions if the reaction rate is significant at the transition temperature.

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 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E473 Terminology Relating to Thermal Analysis and Rheology

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

E968 Practice for Heat Flow Calibration of Differential Scanning Calorimeters (Withdrawn 2023)[3]

E1142 Terminology Relating to Thermophysical Properties

E1231 Practice for Calculation of Hazard Potential Figures of Merit for Thermally Unstable Materials

E1445 Terminology Relating to Hazard Potential of Chemicals

E1860 Test Method for Elapsed Time Calibration of Thermal Analyzers

E1970 Practice for Statistical Treatment of Thermoanalytical Data

E2781 Practice for Evaluation of Methods for Determination of Kinetic Parameters by Calorimetry and Differential Scanning Calorimetry

[1] This test method is 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] 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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

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E2890 Test Method for Determination of Kinetic Parameters and Reaction Order for Thermally Unstable Materials by Differential Scanning Calorimetry Using the Kissinger and Farjas Methods
E3142 Test Method for Thermal Lag of Thermal Analysis Apparatus

3. Terminology

3.1 Technical terms used in this test method are defined in Terminologies E473, E1142, and E1445 including *activation energy, Arrhenius equation, Celsius, differential scanning calorimetry, enthalpy, general rate law, Kelvin, kinetics, peak value, pre-exponential factor, reaction, reaction order,* and *temperature*.

4. Summary of Test Method

4.1 A specimen is placed in a suitable container and positioned in a differential scanning calorimeter (*DSC*).

4.2 The temperature surrounding the specimen is increased at a linear rate and any exothermic reaction peaks recorded.

4.3 Steps 4.1 and 4.2 are repeated for several heating rates in the range from 1 K min^{-1} to 10 K min^{-1}.

4.4 Temperatures at which the reaction peak maxima occur are plotted as a function of their respective heating rates.

4.5 Kinetic values calculated from the peak temperature-heating rate relationship are used to predict a reaction half-life at a selected temperature.

4.6 A specimen is aged at the selected temperature for the predicted half-life time.

4.7 The aged specimen is temperature programmed in a differential scanning calorimeter and its reaction peak area compared with that for an unaged sample run under the same conditions.

4.8 If the normalized area for the aged specimen is approximately half that for the unaged sample, the kinetic values are confirmed for the temperature selected.

5. Significance and Use

5.1 The kinetic parameters combined with the general rate law and the reaction enthalpy can be used for the determination of thermal hazard using Practice E1231 (**1**).[4]

6. Apparatus

6.1 *General*—The equipment used in this test method should be capable of displaying quantitative changes of enthalpy as a function of time (t) or temperature (T), should be linearly programmable and have the capabilities of subjecting the sample cell to different atmospheres. The heat sensing element should be external to the sample.

6.2 *Differential Scanning Calorimeter (DSC):*

6.2.1 A test chamber composed of:

6.2.1.1 *A furnace,* to provide uniform controlled heating (cooling) of a specimen and reference to a constant temperature or at a constant rate within the applicable temperature range of this test method.

6.2.1.2 *A temperature sensor,* to provide an indication of the specimen/furnace temperature readable to ±0.1 K.

6.2.1.3 *A differential sensor,* to detect a difference in heat flow between the specimen and reference equivalent to 10 µW.

6.2.1.4 A means of sustaining a *test chamber environment*, of an inert purge gas at a rate of 10 mL⁄min to 50 mL⁄min.

NOTE 1—Typically, 99+ % pure nitrogen, argon, or helium are employed when oxidation in air is a concern. Unless effects of moisture are to be studied, use of dry purge gas is recommended; especially for operation at subambient temperature.

6.2.2 *A temperature controller,* capable of executing a specific temperature program by operating the furnace(s) between selected temperature limits at a rate of temperature change between 0.5 K/min and 10 K⁄min constant to ±0.1 K⁄min or at an isothermal temperature constant to ±0.1 K.

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.

6.3 *Containers (pans, crucibles, vials, etc.),* which are inert to the specimen and reference materials and which are suitable structural shape and integrity to contain the specimen and reference in accordance with the specific requirements of this test method.

6.4 *A balance,* with a capacity of at least 100 mg, to weigh specimens or containers (pans, crucibles, vials, etc.) to within 10 µg.

6.5 Auxiliary equipment useful for conducting this test method below ambient temperature.

6.5.1 *A coolant system,* which can be directly coupled with the controller to the furnace to hasten its recovery from elevated temperatures, to provide constant cooling rates, or to sustain an isothermal subambient temperature, or a combination thereof.

7. Safety Precautions

7.1 The use of this test method on materials whose potential hazards are unknown requires that precaution be taken during sample preparation and testing.

7.2 Where particle size reduction by grinding is necessary, the user of this test method should presume that the material is dangerous.

7.3 Toxic or corrosive effluents, or both, may be released when heating the material and could be harmful to the personnel or the apparatus. Use of an exhaust system to remove such effluents is recommended.

8. Sampling

8.1 Specimen size is kept small to minimize temperature gradients within the sample. In general, a sample mass resulting in a maximum heat generation of less than 8 mJ⁄s (8 mW) is satisfactory.

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