Designation: E 2008 – 04

Standard Test Method for Volatility Rate by Thermogravimetry[1]

This standard is issued under the fixed designation E 2008; 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 covers procedures for assessing the volatility of solids and liquids at given temperatures using thermogravimetry under prescribed experimental conditions. Results of this test method are obtained as volatility rates expressed as mass per unit time. Rates $\geq$ 5 μg/min are achievable with this test method.

1.2 Temperatures typical for this test method are within the range from 25°C to 500°C. This temperature range may differ depending upon the instrumentation used.

1.3 This test method is intended to provide a value for the volatility rate of a sample using a thermogravimetric analysis measurement on a single representative specimen. It is the responsibility of the user of this test method to determine the need for and the number of repetitive measurements on fresh specimens necessary to satisfy end use requirements.

1.4 Computer- or electronic-based instruments, techniques, or data treatment equivalent to this test method may also be used.

NOTE 1—Users of this test method are expressly advised that all such instruments or techniques may not be equivalent. It is the responsibility of the user of this test method to determine the necessary equivalency prior to use.

1.5 The values stated in SI units are to be regarded as the 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 test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
E 473 Terminology Related to Thermal Analysis
E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
E 1142 Terminology Relating to Thermophysical Properties
E 1582 Practice for Calibration of Temperature Scale for Thermogravimetry
E 1860 Test Method for Elapsed Time Calibration of Thermal Analyzers
E 2040 Test Method for Mass Scale Calibration of Thermogravimetric Analyzers

3. Terminology

3.1 *Definitions*:

3.1.1 The following terms are applicable to this test method and can be found in Terminologies E 473 and E 1142:

3.1.1.1 *thermogravimetric analysis (TGA),*

3.1.1.2 *thermogravimetry (TG),*

3.1.1.3 *volatility.*

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *volatility rate*—the rate of conversion of a solid or liquid substance into the vapor state at a given temperature; mass per unit time.

4. Summary of Test Method

4.1 A solid or liquid specimen is confined in an appropriate container with a pinhole opening between 0.33 and 0.38 mm. The confined specimen is heated within a thermogravimetric analyzer either to a temperature and held constant at that temperature for a fixed interval of time (Method A, Fig. 1) or at a slow constant heating rate between temperature limits (Method B, Fig. 2). The mass of the specimen is measured continuously and it or its rate of change is displayed as a function of time or temperature. The volatility rate at any temperature is reported either as the average rate of mass loss per unit time from Method A or as the instantaneous rate of mass loss (first derivative) per unit time from Method B.

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[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 Test Methods and Recommended Practices.

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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.

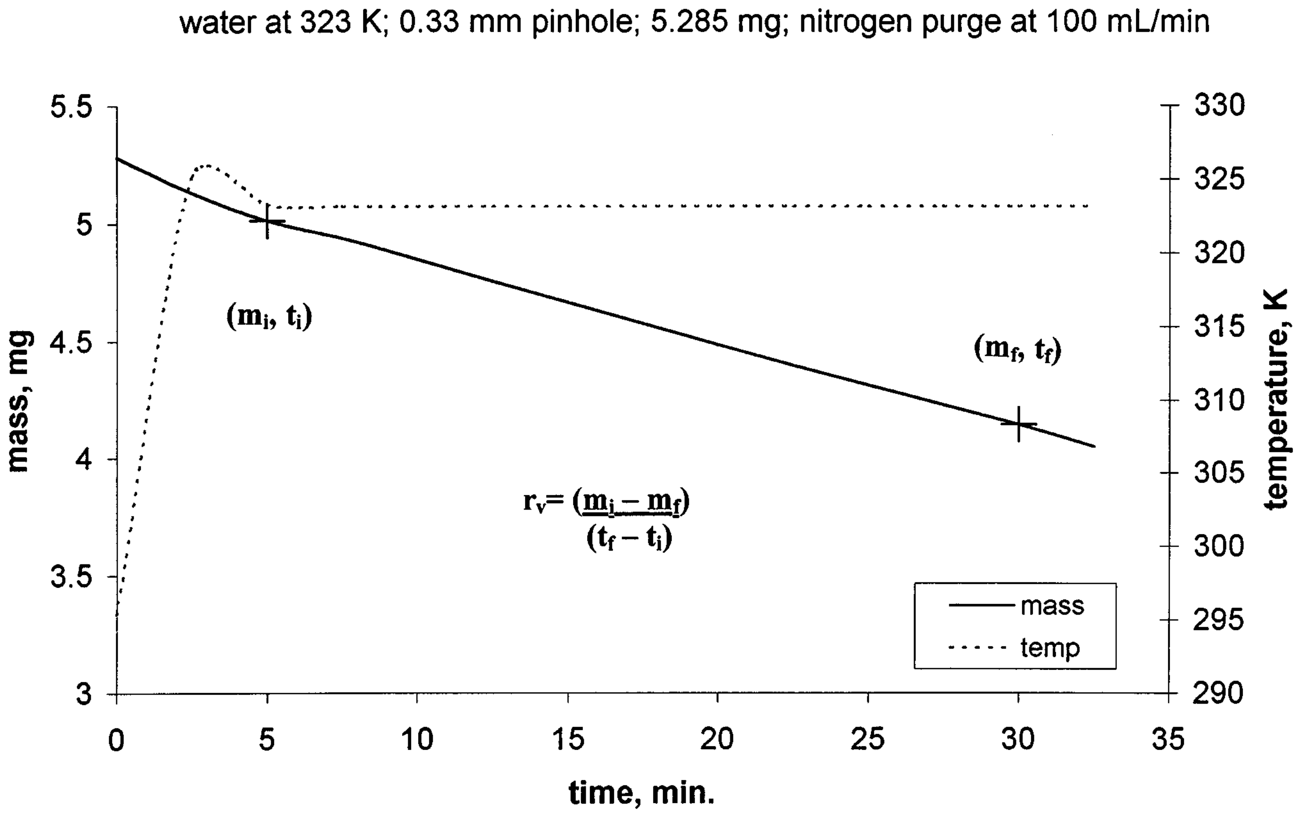

FIG. 1 Method A: R_v= Average Volatility Rate

5. Significance and Use

5.1 Volatility of a material is not an equilibrium thermodynamic property but is a characteristic of a material related to a thermodynamic property which is vapor pressure. It is influenced by such factors as surface area, temperature, particle size, and purge gas flow rate; that is, it is diffusion controlled.

5.2 The extent of containment achieved for specimens in this test method by means of a pinhole opening between 0.33 to 0.38 mm allows for measurement circumstances that are relatively insensitive to experimental variables other than temperature. Decreasing the extent of containment by use of pinholes larger than 0.38 mm will increase the magnitude of the observed rate of mass loss but will also reduce the measurement precision by increasing the sensitivity to variations in other experimental variables.

5.3 Results obtained by this test method are not strictly equivalent to those experienced in processing or handling conditions but may be used to rank materials for their volatility in such circumstances. Therefore, the volatility rates determined by this test method should be considered as index values only.

5.4 The volatility rate may be used to estimate such quantifiable values as drying interval or the extent of volatile release from a process.

6. Interferences

6.1 Specimens that consist of a mixture of two or more volatile components or that undergo decomposition during this test may exhibit curvature in the mass loss versus time plot of Method A (see Fig. 3). In such cases the volatility rate is not constant and shall not be reported as a singular value.

7. Apparatus

7.1 The essential instrumentation required to provide the minimum thermogravimetric analytical capability for this test method includes:

7.1.1 A *thermobalance*, composed of:

7.1.1.1 A *furnace*, to provide uniform controlled heating of a specimen at a constant temperature or at a constant rate within the applicable temperature range of this test method;

7.1.1.2 A *temperature sensor*, to provide an indication of the specimen/furnace temperature to ±1 K;

7.1.1.3 A continuously recording *balance*, to measure the specimen mass with a minimum capacity of 100 mg and a sensitivity of ±10 µg;

7.1.1.4 A means of sustaining the specimen/container under *atmospheric control* of inert gas (nitrogen, helium, and so forth) of 99.9 % purity at a purge rate of 50 to 100 mL/min ±5 %.

NOTE 2—Excessive purge rates should be avoided as this may introduce interferences due to turbulence effects and temperature gradients.

7.1.2 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 to 2 K/min constant to within ±0.1 K/min or to rapidly heat a specimen at a minimum of 50 K/min to an isothermal temperature that is maintained constant to ±1 K for a minimum of 30 min.

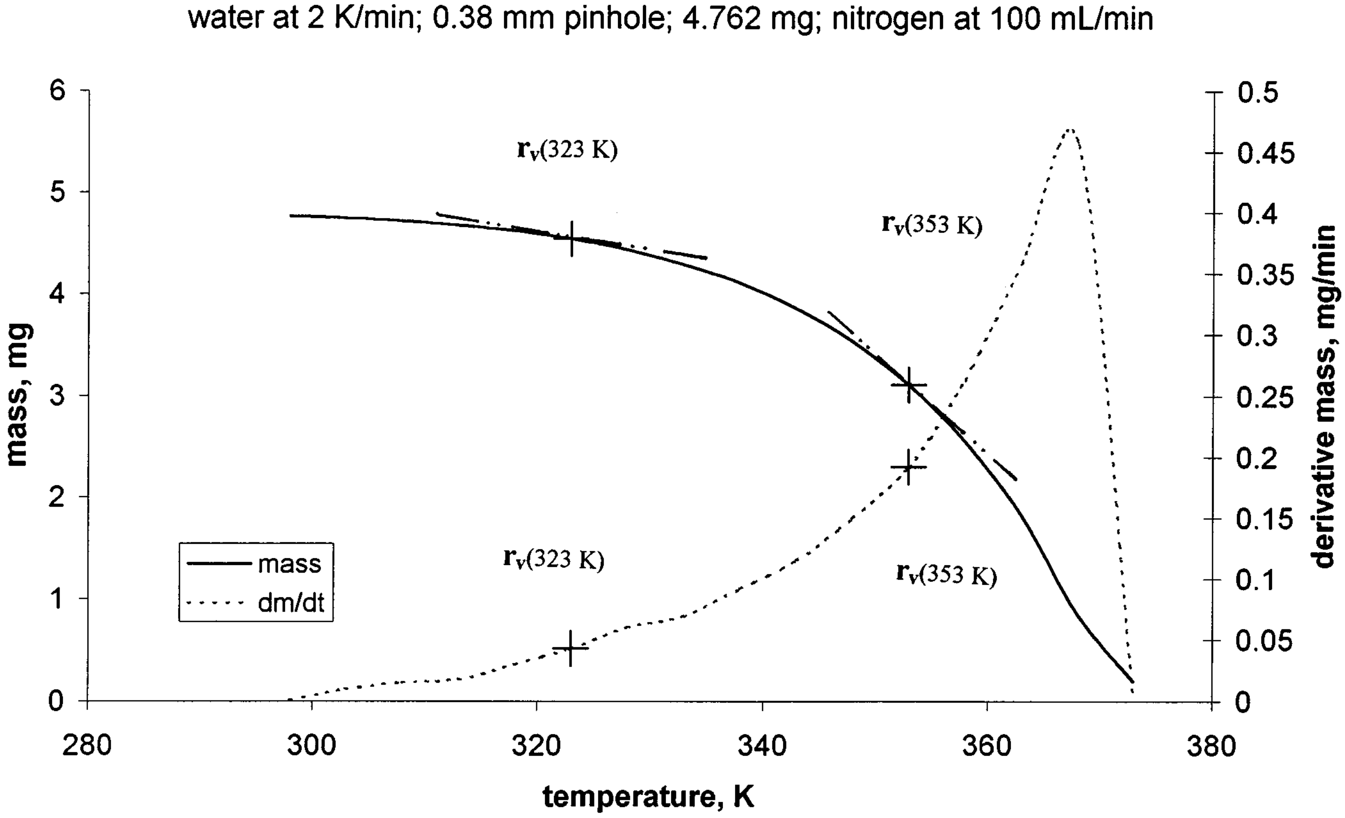

FIG. 2 Method B: R_v= Instantaneous Volatility Rate

7.1.3 A *recording device,* either analog or digital, capable of recording and displaying any fraction of the specimen mass signal (TGA curve), including the signal noise versus time or temperature.

7.1.4 *Sealable containers* (pans, crucibles, and so forth), that are inert to the specimen, that will remain gravimetrically stable within the temperature limits of this test method, and that contain a pinhole in the lid of diameter between 0.33 and 0.38 mm.[3]

NOTE 3—The most critical parameters for containers suitable for use with this test method are the pinhole diameter and the lid thickness. Sealable containers of volumes (25 to 50 µL) and wall thicknesses (80 to 150 µm) commercially available from Mettler-Toledo, Perkin-Elmer Corporation, and TA Instruments, Inc. have been found suitable for this purpose.

7.2 Auxiliary equipment necessary or useful in conducting this test method includes:

7.2.1 While not required, it is convenient to have a data analysis device that will continuously calculate and display the first derivative of mass with respect to time (in mass/min) capable of detecting 0.05 µg/min.

7.2.2 Device to encapsulate the specimen in sealable containers.

7.2.3 Micropipette or syringe to deliver liquid specimens of 1 to 30 µL into the containers.

8. Sampling

8.1 Samples are ordinarily measured as received. If a pretreatment is applied to any specimen, this treatment shall be noted in the report.

8.2 Since the applicable samples may be mixtures or blends, care shall be taken to ensure that the analyzed specimen is representative of the sample from which it is taken. If the sample is liquid, mixing prior to taking the specimen is sufficient to ensure this consideration. If the sample is solid, take several samplings from different areas and either combine into a single specimen or run as a separate specimen with the final analysis representing an average of these determinations. Include the number of determinations in the report.

9. Calibration

9.1 Perform temperature calibration in accordance with Practice E 1582 using the same purge gas conditions and container type to be used for the subsequent measurements at a heating rate of 2 K/min. Do not disturb the temperature sensor position after this calibration.

9.2 Perform mass calibration in accordance with Test Method E 2040.

9.3 Perform time scale calibration in accordance with Test Method E 1860.

10. Procedure

10.1 *Method A—Isothermal Test*:

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[3] The sole source of supply of the 0.33 to 0.38-mm diameter pinhole lids known to the committee at this time is Kalbsey Corporation, 2725 W. CR1500 N., Carbon, IN 47837. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

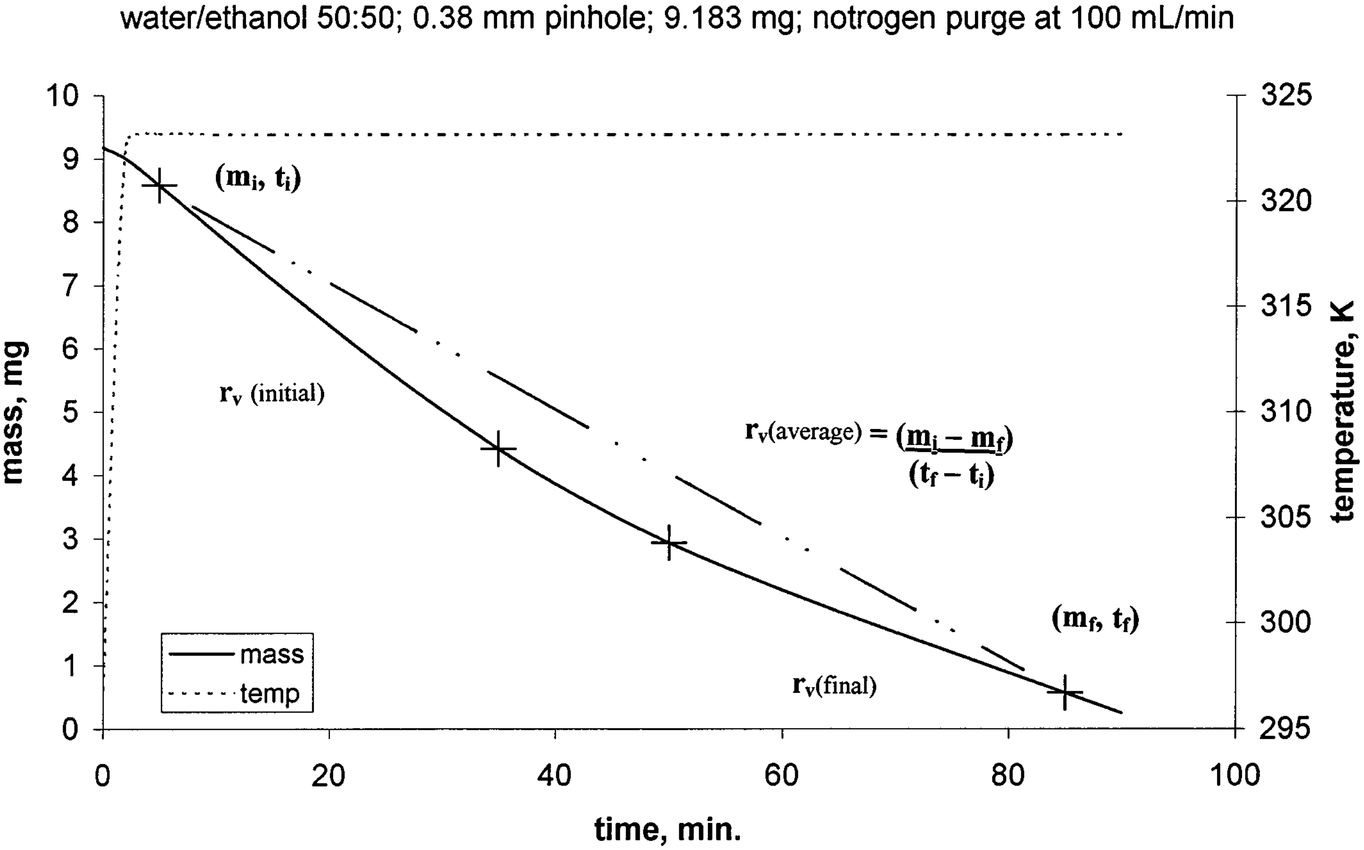

FIG. 3 Method A- Two Component Mixture

10.1.1 Initiate a purge gas flow through the thermobalance between 50 to 100 mL/min ±5 %.

10.1.2 Equilibrate the furnace, gas purge, and so forth at room temperature, and tare the balance.

NOTE 4—If the balance is tarred with the crucible and lid in place, then the mass of the test specimen may be recorded directly

10.1.3 Encapsulate a specimen in an appropriate container with the specified pinhole. Specimen sizes between 1 and 30 mg are typical for this test method, with the larger mass being used for more volatile specimens.

NOTE 5—**Caution:** Volatile materials may pose a respiratory hazard. Avoid unnecessary exposure to vapors.

10.1.4 Place the encapsulated specimen in the thermogravimetric analyzer, close the furnace, and allow the temperature, purge, and so forth, to become stable within ±1 % of settings.

NOTE 6—For highly volatile substances, a significant mass fraction of the specimen could be lost during this period of equilibration. Any large discrepancy between the specimen mass as delivered and subsequently recorded by the thermobalance should be noted in the report.

10.1.5 Heat the specimen rapidly at 50 K/min to the desired isothermal temperature, and thereafter, maintain the isothermal temperature to ±1 K for 30 min. Record the specimen mass in mg or µg continually during this heating program versus time. The specimen temperature may also be recorded during the heating program

NOTE 7—If the specimen is exhausted before 30 min have elapsed, it is recommended that the test be repeated with a larger specimen mass. If excessively large specimen mass is required to complete a 30-min test time, a shorter time interval or a lower isothermal temperature may be used and shall be reported.

NOTE 8—The initial rapid heating to the desired isothermal temperature may result in a momentary overshoot in the furnace temperature. Overshoot in itself does not create a measurement question provided the data in 10.1.7 is taken only from the region where the isothermal temperature is stable and provided that not all of the specimen has been exhausted.

10.1.6 Restore the furnace to ambient temperature, and remove the specimen container.

10.1.7 Calculate the volatility rate in accordance with11.2.

10.1.8 Repeat 10.1.2-10.1.7 for additional samples.

10.2 *Method B—Constant Heating Rate Test*:

10.2.1 Follow the instructions given in 10.1.1-10.1.4.

10.2.2 Heat the specimen at a constant heating rate of 2 ±0.1 K/min between ambient temperature and the desired limit temperature. Record the specimen mass in mg or µg continually during this heating program versus temperature, and calculate and display the first derivative (with respect to time) of the mass loss in µg/min during heating.

NOTE 9—If the specimen is exhausted before reaching the desired limit temperature, repeat the test using a larger specimen mass. If excessively large specimen mass is required to reach the limit temperature, it may be necessary to terminate the test at a lower limit temperature, and this shall be noted in the report.

10.2.3 Restore the furnace to ambient temperature, and remove the specimen container.

10.2.4 Calculate the volatility rate in accordance with 11.3.

10.2.5 Repeat 10.2.1-10.2.4 for additional samples.

11. Calculation

11.1 Use all available decimals for each value in the calculations. Round the final volatility rate to the nearest 0.1 µg/min.

11.2 Using Method A, the volatility rate is obtained from the difference in mass at the initial time and the mass at the final time at the isothermal temperature divided by 30 min (or other elapsed time used, see Fig. 1):

$$\text{volatility rate, } r_v = (m_i – m_f)/(t_f – t_i) \text{ or } (m_i – m_f)/30 \qquad (1)$$

where:

m_i = mass at initial time (t_i), and

m_f = mass at final time (t_f).

NOTE 10—If the mass loss rate is not constant with time at the isothermal temperature, this calculation will result in an average value of volatility rate. Selecting shorter time segments, such as the first few minutes and the last few minutes, will result in different values that could demonstrate the range of volatility rate exhibited by the sample (see also Fig. 3).

11.3 Using Method B, the volatility rate is either the computed first derivative of the mass loss curve at any specific temperature(s) of interest or is the rate obtained by determining the slope of the mass loss curve over a 4 K (2 min) interval centered about the specific temperature of interest (see Fig. 2).

12. Report

12.1 Report the following information:

12.1.1 A complete identification and description of the material tested, including any pretreatment of a specimen.

12.1.2 A description of the instrumentation used.

12.1.3 Test conditions, including temperature program executed, purge gas composition and flow rate, initial specimen size, and pinhole size.

12.1.4 The mass loss curve or the first derivative with respect to time of mass loss, or both.

12.1.5 The volatility rate (µg/min) and the associated temperature (K or °C).

13. Precision and Bias

13.1 The precision and bias of this standard method were determined in an interlaboratory test (ILT) in 2003. Eight laboratories using thermogravimetric analyzers from three manufacturers and four instrument models participated in the ILT. The volatility rates for camphor at 333 K and squalane at 573 K were determined using the isothermal test. The constant heating rate test was used to determine the volatility rates for water at 323 and 353 K. Each laboratory reported the volatility rates in quintuplicate. The statistical analysis was conducted in accordance with Practice E 691. A research report describing the details of the ILT has been filed at ASTM Headquarters[4].

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

13.2.1 Between laboratory variability may be estimated using the reproducibility value (R) obtained by multiplying the reproducibility standard deviation (SR) by 2.8. The reproducibility value estimates the 95 % confidence limit. That is, two between laboratory results should be considered suspect if they differ by more than the reproducibility value (R).

13.2.2 The terms repeatability limit and reproducibility limit in Table 1 are used as specified in Practice E 177.

13.3 *Bias*—Bias is the difference between a test result and an accepted reference value. There is no accepted reference value for volatility rates for camphor, squalane and water. Therefore no bias information can be provided.

14. Keywords

14.1 mass loss; thermogravimetric analysis (TGA); thermogravimetry (TG); volatility; volatility rate

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[4] A Research Report is available from ASTM. Request RR:E37–1031

TABLE 1 Need Title

Material	T/K	Average Volatility Rate, mg min-1	Repeatability Standard Deviation, Sr	Reproducibility Standard Deviation,SR	Repeatability Limit, r	Reproducibility Limit, R
Camphor	333	2311	0.194	0.271	0.543	0.760
Squalane	573	112.9	24.2	49.3	67.8	138
Water	323	44.44	6.54	8.12	18.3	22.7
Water	353	204.87	23.9	36.6	67.0	102

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