Designation: E1131 – 08 (Reapproved 2014)

Standard Test Method for Compositional Analysis by Thermogravimetry[1]

This standard is issued under the fixed designation E1131; 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 provides a general technique incorporating thermogravimetry to determine the amount of highly volatile matter, medium volatile matter, combustible material, and ash content of compounds. This test method will be useful in performing a compositional analysis in cases where agreed upon by interested parties.

1.2 This test method is applicable to solids and liquids.

1.3 The temperature range of test is typically room temperature to 1000°C. Composition between 1 and 100 weight % of individual components may be determined.

1.4 This test method utilizes an inert and reactive gas environment.

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

1.6 This standard is related ISO 11358 but is more detailed and specific.

1.7 *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:*[2]

D3172 Practice for Proximate Analysis of Coal and Coke

E473 Terminology Relating to Thermal Analysis and Rheology

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E1142 Terminology Relating to Thermophysical Properties

E1582 Practice for Calibration of Temperature Scale for Thermogravimetry

E2040 Test Method for Mass Scale Calibration of Thermogravimetric Analyzers

2.2 *ISO Standards:*[3]

ISO 11358 Plastics-Thermogravimetry (TG) of Polymers — General Principles

3. Terminology

3.1 *Definitions:*

3.1.1 Many of the technical terms used in this test method are defined in Terminologies E473 and E1142.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *highly volatile matter*—moisture, plasticizer, residual solvent or other low boiling (200°C or less) components.

3.2.2 *medium volatile matter*—medium volatility materials such as oil and polymer degradation products. In general, these materials degrade or volatilize in the temperature range 200 to 750°C.

3.2.3 *combustible material*—oxidizable material not volatile (in the unoxidized form) at 750°C, or some stipulated temperature dependent on material. Carbon is an example of such a material.

3.2.4 *ash*—nonvolatile residues in an oxidizing atmosphere which may include metal components, filler content or inert reinforcing materials.

3.2.5 *mass loss plateau*—a region of a thermogravimetric curve with a relatively constant mass.

4. Summary of Test Method

4.1 This test method is an empirical technique using thermogravimetry in which the mass of a substance, heated at a controlled rate in an appropriate environment, is recorded as a function of time or temperature. Mass loss over specific temperature ranges and in a specific atmosphere provide a compositional analysis of that substance.

5. Significance and Use

5.1 This test method is intended for use in quality control, material screening, and related problem solving where a

---

[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.

Current edition approved March 15, 2014. Published April 2014. Originally approved in 1986. Last previous edition approved in 2008 as E1131 – 08. DOI: 10.1520/E1131-08R14.

[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] Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, CP 56, CH-1211 Geneva 20, Switzerland, http://www.iso.org.

compositional analysis is desired or a comparison can be made with a known material of the same type.

5.2 The parameters described should be considered as guidelines. They may be altered to suit a particular analysis, provided the changes are noted in the report.

5.3 The proportion of the determined components in a given mixture or blend may indicate specific quality or end use performance characteristics. Particular examples include the following:

5.3.1 Increasing soot (carbon) content of used diesel lubricating oils indicates decreasing effectiveness.

5.3.2 Specific carbon-to-polymer ratio ranges are required in some elastomeric and plastic parts in order to achieve desired mechanical strength and stability.

5.3.3 Some filled elastomeric and plastic products require specific inert content (for example, ash, filler, reinforcing agent, etc.) to meet performance specifications.

5.3.4 The volatile matter, fixed carbon, and ash content of coal and coke are important parameters. The "ranking" of coal increases with increasing carbon content and decreasing volatile and hydrocarbon, (medium volatility) content.

6. Interferences

6.1 This test method depends upon distinctive thermostability ranges of the determined components as a principle of the test. For this reason, materials which have no well-defined thermostable range, or whose thermostabilities are the same as other components, may create interferences. Particular examples include the following:

6.1.1 Oil-filled elastomers have such high molecular weight oils and such low molecular weight polymer content that the oil and polymer may not be separated based upon temperature stability.

6.1.2 Ash content materials (metals) are slowly oxidized at high temperatures and in an air atmosphere, so that their mass increases (or decreases) with time. Under such conditions, a specific temperature or time region must be identified for the measurement of that component.

6.1.3 Polymers, especially neoprene and acrylonitrile butadiene rubber (NBR), carbonize to a considerable extent, giving low values for the polymer and high values for the carbon. Approximate corrections can be made for this if the type of polymer is known.

6.1.4 Certain pigments used in rubber lose weight on heating. For example, some pigments exhibit water loss in the range 500 to 600°C, resulting in high polymer values. Others, such as calcium carbonate, release carbon dioxide (CO_2) upon decomposition at 825°C, that may result in high carbon values. The extent of interference is dependent upon the type and quantity of pigment present.

7. Apparatus

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

7.1.1 *A thermobalance,* composed of (*1*) a furnace to provide uniform controlled heating or a specimen to a constant temperature or at a constant rate within the 25 to 1000°C temperature range of this test method; (*2*) a temperature sensor to provide an indication of the specimen/furnace temperature to ±1°C; (*3*) an electrobalance to continuously measure the specimen mass with a minimum capacity of 30 mg and a sensitivity of ±1 µg; and (*4*) a means of sustaining the specimen/container under atmosphere control with a purge rate of 10 to 100 ± 5 mL/min.

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 between 10 and 100°C/min constant to within ±1 % for a minimum of 100 min.

7.1.3 *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 Thermogravimetric analyzers are mass, temperature, and time.

NOTE 1—The capability to display the first derivative of the signal may be useful in the measurement of obscure thermostability ranges.

7.1.4 *Containers (pans, crucibles, and so forth),* which are inert to the specimen and which will remain dimensionally stable within the temperature limits of this test method.

7.2 *Gas flow dontrol device,* with the capability of switching between inert and reactive gases.

8. Reagents and Materials

8.1 An inert compressed gas such as argon or nitrogen and a reactive compressed gas such as air or oxygen are required for this test method.

8.2 *Purity of Purge Gases:*

8.2.1 0.01 % maximum total impurity.

8.2.2 1.0 µg/g water impurity maximum.

8.2.3 1.0 µg/g hydrocarbon impurity maximum.

8.2.4 The inert purge gas must not contain more than 10 µg/g oxygen.

9. Test Specimen

9.1 Specimens are ordinarily measured as received. If some heat or mechanical treatment is applied to the specimen prior to test, this treatment shall be noted in the report.

9.2 Since the applicable samples may be mixtures or blends, take care to ensure that the analyzed specimen is representative of the sample from which it is taken. If the sample is a liquid, mixing prior to taking the specimen is sufficient to ensure this consideration. If the sample is a solid, take several specimens from different areas of the sample and either combine for a single determination, or each run separately with the final analysis representing an average of the determinations. Note the number of determinations in the report.

10. Calibration

10.1 Calibrate the mass signal from the apparatus according to Test Method E2040.

10.2 Calibrate the temperature signal from the apparatus according to Practice E1582.

11. Procedure

11.1 Establish the inert (nitrogen) and reactive (air or oxygen) gases at the desired flow rates. For most analyses, this rate will be in the range of 10 to 100 mL/min. Higher flow rates may be used for some analyses, particularly when utilizing high heating rates.

11.2 Switch the purge gas to the inert (nitrogen) gas.

11.3 Zero the mass signal *r* and tare the balance.

11.4 Open the apparatus to expose the specimen holder.

11.5 Prepare the specimen as outlined in 9.2 and carefully place it in the specimen holder. Typically, a sample mass of 10 to 30 mg shall be used (see Table 1).

NOTE 2—Specimens smaller than 10 mg may be used if larger specimens cause instrument fouling or poor reproducibility.

11.6 Position the specimen temperature sensor to the same location used in calibration. (See Section 10.)

11.7 Enclose the specimen holder.

11.8 Record the initial mass. If the apparatus in use has provisions for direct percentage measurements, adjust to read 100 %.

11.9 Initiate the heating program within the desired temperature range. See Table 1 for suggested heating rates and temperature ranges. Record the specimen mass change continuously over the temperature interval.

11.9.1 The mass loss profile may be expressed in either milligrams or mass percent of original specimen mass. Expanded scale operation may be useful over selected temperature ranges.

11.9.2 If only one or two components of the compositional analysis are desired, specific, more limited temperature ranges may be used. Similarly, several heating rates may be used during analysis in those regions of greater or lesser interest. Isothermal periods may be necessary for some materials. See Table 1 for suggested parameters.

11.10 Once a mass loss plateau is established in the range 600 to 950°C, depending on the material, switch from inert to reactive (air or oxygen) environment.

11.10.1 If a distinct plateau is not observed in this range, the atmosphere change is made based on the zero slope indication of the recorded first derivative or upon some agreed upon temperature. Suggested temperatures for this region are given in Table 1.

11.10.2 The resolution of this region may be enhanced, where carbon is present in large quantities or of special interest, by maintaining the specimen at constant temperature for several minutes after switching environments.

11.11 The analysis is complete upon the establishment of a mass loss plateau following the introduction of the reactive gas.

11.12 Switch to the inert purge gas.

11.13 Calculate and report the sample composition.

12. Calculation

12.1 Highly volatile matter is represented by a mass loss measured between the starting temperature and Temperature *X* (see Fig. 1). Temperature *X* should be taken in the center of the first mass loss plateau or, if no resolvable plateau exists, at an agreed upon temperature value. Suggested values for Temperature *X* are given in Table 2.

12.1.1 Highly volatile matter content may be determined by the following equation:

$$V = \frac{W - R}{W} \times 100\,\% \tag{1}$$

where:

V = highly volatile matter content, as received basis (%),
W = original specimen mass (mg), and
R = mass measured at Temperature X (mg).

12.2 Medium volatile matter is represented by the mass loss measured from Temperature *X* to Temperature *Y* (see Fig. 1). Temperature *Y* should correspond to the mass loss plateau used for switching atmospheres.

12.2.1 Medium volatile matter content can be determined using the following equation:

$$O = \frac{R - S}{W} \times 100\,\% \tag{2}$$

where:

O = medium volatile matter content, as-received basis, %,
R = mass measured at Temperature X, (mg),
S = mass measured at Temperature Y, (mg), and
W = original specimen mass, (mg).

12.3 Combustible material content is represented by the mass loss measured from Temperature *Y* to Temperature *Z* (see Fig. 1). This region corresponds to the mass loss as a result of the oxidation of carbon to carbon dioxide.

12.3.1 Combustible material content may be calculated by the following equation:

$$C = \frac{S - T}{W} \times 100\,\% \tag{3}$$

TABLE 1 Suggested Compositional Analysis Parameters

Material	Sample Size mg	Flow Rate mL/min[A]	Purge Time Min	Temperature				Heating Rate °C/min	Gas Switchover °C
				Initial	X	Y	Z[B]		
coal	20	50	5	ambient	110	900	900	10 to 150	900
elastomers	20	50	2	ambient	325	550	750	10	600
thermoplastics	20	50	2	ambient	200	600	750	10	600
lubricants	20	40 to 500	1	50	150	600	750	10 to 100	600
thermosets	20	50	2	ambient	200	550	750	10	600

[A] May differ depending upon instrument design.
[B] *Z* is not necessarily the final temperature.

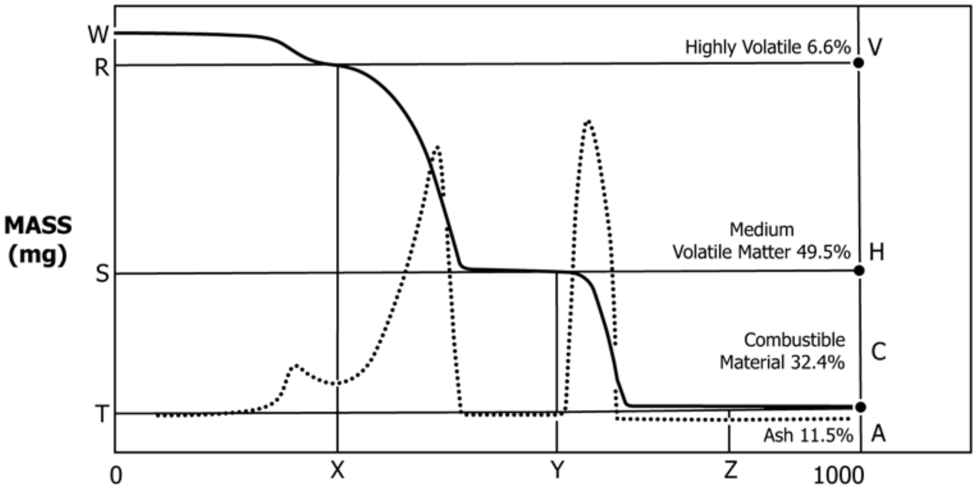

FIG. 1 Sample Thermogravimetric Curve

Sample:	Rubber, lot 63, approximately 30 % carbon fill	
Pretreatment:	None	
Apparatus:	TG (Model XX)	
Temperature Range:	Ambient to 1000°C at 10°C/min	
Purge Gas:	Ambient to 600°C-Nitrogen 99.99 % 600°C to 1000°C-Air, Zero Grade Flow-50 mL/min	
Preanalysis Purge Time	10 min	
Determinations:	Duplicate	
Composition in Weight Percent	Highly Volatile	6.6 %
	Medium Volatile	49.5 %
	Combustible	32.4 %
	Ash	11.5 %

FIG. 2 Example Report

where:

C = combustible material content, as-received basis, (%),
S = mass measured at Temperature Y, (mg),
T = mass measured at Temperature Z, (mg) and
W = original specimen mass, (mg).

12.4 The residual weight remaining after the evolution of carbon dioxide is taken as ash content. This component is measured at Temperature Z. This temperature is not necessarily the final temperature. Suggested values for Temperature Z are given in Table 1.

12.4.1 The ash components of some materials may slowly oxidize and subsequently gain or lose weight at high temperatures. In such materials, a value for Temperature Z must be chosen prior to such transitions.

12.4.2 The ash content may be calculated using the following equation:

$$A = \frac{T}{W} \times 100\,\% \qquad (4)$$

where:

A = ash content, as received basis, (%),
T = mass measured at Temperature Z, (mg) and
W = original specimen mass.

NOTE 3—The use of the recorded first derivative may be useful in locating the value of X, Y, and Z by examining areas of the curve where the derivative returns to, or approaches the baseline (see Fig. 1).

NOTE 4—When performing the calculations, retain all available decimal places in the measured values. Rounding of the values to the appropriate significant figures should only occur in the final result.

TABLE 2 Compositional Analysis Interlaboratory Test Parameters

Test Parameters by Material

Material	Sample Mass^A (mg)	Purge Gas Flow (mL/min)	Preanalysis Purge (min)
Coal	20	50	1
Lubricant	10	100	1
Polyethylene	20	50	1
Calcium Oxalate	10	50	1

Test Parameters by Component

Component	Start Temperature °C	Rate °C/min	Final Temperature °C	Hold (min)	Gas
Coal^A					
Highly Volatile^B	50	50	110 (X)	5	N_2
Medium Volatile	110	100	950 (Y)	15	N_2
Combustible	950	0	950	10	Air
Ash	950	0	950 (Z)	0	Air
Lubricant					
Highly Volatile	50	20	150 (X)	2	N_2
Medium Volatile	150	100	650 (Y)	5	N_2
Combustible	650	20	750	0	Air
Ash	750	0	750 (Z)	1	Air
Polyethylene					
Highly Volatile	Ambient	10	150 (X)	0	N_2
Medium Volatile	150	10	600 (Y)	0	N_2
Combustible	600	10	750	1	Air
Ash	750	10	800 (Z)	0	Air
Calcium Oxalate Monohydrate^C					
Highly Volatile	Ambient	10	200 (X)	0	N_2
Medium Volatile	200	10	600 (Y)	0	N_2
Combustible	600	10	800	0	Air
Ash	800	10	800 (Z)	0	Air

[A] Smaller sample sizes may be used to avoid instrument fouling.

[B] Coal is determined on a dry basis therefore the highly volatile component will not be measured. The initial mass should be measured at 110°C after the 5 min hold. If direct percentage measurements are being made, reset balance to 100 %. Temperature (X) = 110°C, Mass (W) = Mass (R).

[C] For calcium oxalate, the component's nomenclature refers to mass loss plateaus rather than the definitions of the test method.

13. Report

13.1 The report shall include the following (see Fig. 2 and Table 2):

13.1.1 Description of the material, including the name of the manufacturer and information on lot number and proposed chemical composition, when known, 13.1.2 Description of any sample pretreatment prior to analysis,

13.1.3 Description of the thermogravimetric analysis apparatus, including, where appropriate, the make and model of commercial equipment used.

13.1.4 Temperature range over which the various components are measured and the respective heating rates,

13.1.5 Purge gas, flow rate, and composition,

13.1.6 Pre-analysis purge time,

13.1.7 Number of determinations,

13.1.8 The weight percent highly volatile matter, medium volatile matter, combustible material, and ash content, and

13.1.9 Original (or photocopy) of the thermal curve.

13.1.10 The specific dated version of this test method used.

14. Precision and Bias

14.1 *Precision*—On the basis of an interlaboratory test[4] of this test method, in which nine laboratories tested four materials on two days close together, using the test parameters in Table 2, the test results in Table 4 were obtained.

NOTE 5—The precision values stated in Table 4 are based on four specific materials studied in this interlaboratory test. These precision values may vary with the type of material analyzed and the testing parameters selected.

14.2 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.

TABLE 3 Summary of Bias

	Compositional Analysis, %	Proximate Analysis, %	Theoretical, %
Coal			
medium volatile matter	40.4	. . .	. . .
combustible material	53.6	. . .	. . .
ash	6.1	6.2	. . .
volatiles	. . .	40.4	. . .
fixed carbon	. . .	53.9	. . .
Calcium Oxalate Monohydrate			
highly volatile matter	11.6	. . .	. . .
medium volatile matter	18.1	. . .	. . .
combustible material	30.8	. . .	. . .
ash	39.5	. . .	39.2
carbon monoxide	. . .	. . .	18.9
carbon dioxide	. . .	. . .	29.7
water	. . .	. . .	12.2

TABLE 4 Precision Test Values

NOTE 1—Where: *X* = average component concentration in weight percent, *r* = repeatability interval as defined by Practice E691, and *R* = reproducibility interval as defined by Practice E691.

NOTE 2—Three materials are reported here on a dry basis, with no highly volatile component. Polyethylene is reported on a dry ash-free basis.

	X	*r*	*R*
Highly Volatile Matter, %			
calcium oxalate monohydrate[A]	11.6	0.3	0.5
Medium Volatile Matter, %			
high volatility bituminous coal	40.4	1.6	3.3
used diesel lubricating oil	96.7	0.7	1.1
carbon filled polyethylene	97.3	0.4	0.5
calcium oxalate monohydrate	18.1	0.5	0.6
Combustible Matter, %			
high volatility bituminous coal	53.6	1.3	2.8
used diesel lubricating oil	2.5	0.4	0.5
carbon filled polyethylene	2.7	0.4	0.5
calcium oxalate monohydrate	30.8	0.6	1.1
Ash, %			
high volatility bituminous coal	6.1	1.1	2.2
used diesel lubricating oil[B]	0.8	0.7	1.2
calcium oxalate monohydrate	39.5	1.3	1.3

[A] Although the four components measured in calcium oxalate monohydrate do not strictly follow the definitions of this test method, their four well defined mass loss plateaus provide precision data indicative of a well behaved specimen.

[B] Although outside the scope of this test method, the ash component for lubricating oil is included to indicate the precision to be expected when measuring components below 1 %.

14.3 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 limit.

14.4 The interpretation of this data will produce individual precision statements for each material and component using the following as an example: two test results obtained by different laboratories on replicate samples of lubricating oil of about 2.5 % combustible material would not be expected to differ by more than 0.5 %.

14.5 *Bias*—No reference materials were selected for the interlaboratory testing of this test method; however, data was provided for coal using Practice D3172 for proximate analysis. In addition, the results from the calcium oxalate compositional analysis can be compared to calculated theoretical values for each mass loss plateau. The bias indicated for this test method is summarized in Table 3.

15. Keywords

15.1 ash; combustible material; composition; compositional analysis; highly volatile matter; medium volatile matter; thermogravimetry

---

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E37-1009. Contact ASTM Customer Service at service@astm.org.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/