INTERNATIONAL STANDARD

ISO
11358

Plastics — Thermogravimetry (TG) of polymers — General principles

Plastiques — Thermogravimétrie (TG) des polymères — Principes généraux

Foreword

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International Standard ISO 11358 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

Annex A of this International Standard is for information only.

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Plastics — Thermogravimetry (TG) of polymers — General principles

1 Scope

1.1 This International Standard specifies the general conditions for the analysis of polymers using thermogravimetric techniques.

1.2 It is applicable to liquids or solids. Solid materials may be in the form of pellets, granules or powders. Fabricated shapes reduced to appropriate specimen size may also be analysed by this method.

1.3 Thermogravimetry can be used to determine the temperature(s) and rate(s) of decomposition of polymers, and to measure at the same time the amounts of volatile matter, additives and/or fillers they contain.

1.4 The thermogravimetric measurements may be carried out in a dynamic mode (mass change versus temperature or time under programmed conditions) or an isothermal mode (mass change versus time at constant temperature).

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 291:—[1]), *Plastics — Standard atmospheres for conditioning and testing.*

3 Definitions

For the purposes of this International Standard, the following definitions apply:

3.1 thermogravimetry (TG): A technique in which the mass of a test specimen is measured as a function of temperature or time, while the test specimen is subjected to a controlled temperature programme.

3.2 dynamic mass-change determination: A technique for obtaining a record of the variation of the mass of a test specimen with temperature T which is changing at a programmed rate.

3.3 isothermal mass-change determination: A technique for obtaining a record of the variation of the mass of a test specimen with time t at constant temperature T.

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1) To be published. (Revision of ISO 291:1977)

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3.4 TG curve: A curve drawn in thermogravimetry by plotting the mass of a test specimen as the ordinate (y-axis) and the temperature T, or time t, as the abscissa (x-axis).

3.5 differential scanning calorimetry (DSC): A technique in which the difference in heat flux (power) into a test specimen and a reference specimen is measured as a function of temperature and/or time while the test specimen and the reference specimen are subjected to a controlled temperature programme.

3.6 differential thermal analysis (DTA): A technique in which the difference in temperature between a test specimen and a reference specimen is measured as a function of temperature and/or time while the test specimen and the reference specimen are subjected to a controlled temperature programme.

3.7 Curie temperature: The temperature at which a ferromagnetic material passes from the ferromagnetic state to the paramagnetic state or *vice versa*.

3.8 sample: A small part or portion of a bulk material or batch of products intended to be representative of the whole.

3.9 test specimen: A complete product or single piece taken from a sample and used to carry out a test. In the case of bulk materials such as pellets, powders and granules: a portion taken from a sample and used to carry out a test.

4 Principle

4.1 A test specimen is heated at a constant rate with a controlled temperature programme, and the change in mass is measured as a function of temperature. Alternatively, the specimen is kept at a given constant temperature and the change in mass is measured as a function of time over a given period.

4.2 The change in mass of a material as a function of temperature and the extent of this change are indicators of the thermal stability of the material. TG data can therefore be used to evaluate the relative thermal stability of polymers of the same generic family and polymer-polymer or polymer-additive interactions, using measurements made under the same test conditions.

4.3 TG data may be used for process control, process development and material evaluation. Long-term thermal stability is a complex function of service and environmental conditions. TG data alone will not describe the long-term thermal stability of a polymer.

5 Apparatus

A number of commercial instruments suitable for thermogravimetric measurements are available. The basic apparatus components consist of the following:

5.1 Thermobalance, of the null or deflection type. Where the mass of the test specimen is less than 50 mg, the thermobalance shall be capable of measuring the mass with an accuracy of ± 0,020 mg. The thermobalance shall be constructed so that gas flows around the test specimen and permits heat transfer to it at a constant rate.

5.2 Furnace, with a housing of low thermal mass to allow rapid or slow heating and cooling (generally at least 50 °C/min) over a temperature range of ambient to about 1 000 °C.

5.3 Temperature sensor, capable of measuring the temperature of the test specimen. It shall be located as close as possible to the test specimen.

5.4 Temperature programmer, capable of providing a linear rate of scanning over a predetermined temperature range.

5.5 Recording device, capable of recording the specimen mass and temperature and/or time in a way that the relation between mass loss and temperature or time is illustrated. An X-Y recorder is suitable for this purpose.

5.6 Specimen holder, of shape and dimensions sufficient for a mass of at least 5 mg and made of a material capable of withstanding the maximum temperature to be used.

5.7 Purge gas: dry air or oxygen (oxidizing conditions) or a suitable inert gas with an oxygen content of 0,001 % (V/V) or less (non-oxidizing conditions). In either case, the water content of the purge gas shall be less than 0,001 % (m/m).

5.8 Flowmeter, capable of measuring gas-flow rates of 50 ml/min to 150 ml/min.

5.9 Balance, capable of measuring the initial mass of the specimen with an accuracy of 0,01 mg.

6 Test specimen preparation

Test specimens may be liquids or solids. The latter may be in the form of powders, pellets, granules or cut pieces. For finished products, the test specimen shall be in the form normally found in use.

6.1 Test specimens from finished products

Cut the test specimen to an appropriate size for the specimen holder. Microtomes or razor blades are suitable for this purpose.

NOTE — Test specimen size and shape will generally be dependent on the sample holder. Surface area will affect the overall results. For instance, in comparing a test specimen of large surface area with a test specimen of smaller surface area, both having the same mass, the smaller surface area test specimen normally changes at a slower rate.

6.2 Test specimen conditioning

Unless otherwise specified, test specimens shall be conditioned, prior to measurement, at 23 °C ± 2 °C and (50 ± 5) % relative humidity in accordance with ISO 291, or by any other method specified by agreement between the interested parties.

6.3 Test specimen mass

The mass of the test specimen shall be greater than 10 mg unless only smaller quantities of material are available.

7 Calibration

7.1 Mass calibration

Without any gas flow through the thermobalance (to prevent any disturbance through buoyancy and/or convection effects), calibrate the thermobalance as follows, using calibrated weights in the range 10 mg to 100 mg:

Zero the thermobalance. Place the calibration weight on the thermobalance and measure the corresponding mass change. If necessary, adjust the thermobalance so that the measured mass is equal to the mass of the calibration weight.

7.2 Temperature calibration

Position the temperature sensor, usually a thermocouple, to provide the most accurate reading of the test specimen temperature. This position may differ for each instrument.

Carry out the temperature calibration using the same atmosphere, rate of gas flow and heating rate as will be used in the actual determination (see clause 8).

If the thermobalance is used alone, use the following procedure:

a) Choose two or more standard reference materials from the set of five standards comprising GM761, selecting reference materials with a Curie temperature near the temperature range to be examined. If possible, choose the reference materials in such a way that the temperature range to be examined lies between the Curie temperatures of two of them.

b) Start heating at the same heating rate as will be used in the actual determination and carry out a calibration based on the start temperature T_A, mid-point temperature T_C and end temperature T_B for the Curie temperature transition.

NOTE — GM761 is specified as a range of Curie (magnetic transition) temperature standards by the International Confederation for Thermal Analysis (ICTA) and the National Institute of Standards and Technology (NIST) (see annex A).

Nickel of 99,99 % or higher purity can also be used for the calibration.

If the thermobalance is combined with a DSC or DTA detector, it is recommended that the thermobalance is temperature-calibrated using standard reference materials (NIST or ICTA) developed for DSC or DTA calibration. See annex A for a list of some of the standard calibration materials.

NOTES

1 The melting point of a standard reference material is defined as the intercept of the extrapolated baseline and the tangent to the slope of the endotherm at the point of inflection of the curve (the so-called onset temperature).

2 Calibration is the most critical stage in obtaining reliable thermogravimetry data; the relationship between the temperature sensor, specimen geometry and type of atmosphere, including the rate of gas flow, will affect the calibration of the measurement system.

3 The rate of mass loss is dependent upon the rate of oxidation of the test specimen, and therefore dependent in part upon the atmosphere and rate of gas flow to which it is exposed. It is therefore important to use the same atmosphere and rate of gas flow in the calibration as in the actual determination.

8 Procedure

The procedure has to be adapted to the instrument that is used and to the test conditions. Two modes can be used: temperature scanning (see 8.1) and isothermal (see 8.2).

NOTE — A change in buoyancy and convection occurs in the thermobalance when the gas flow is operating. Even if there is no actual change in mass, an apparent change in mass is observed and the accuracy of mass measurement is reduced. It is recommended that a preliminary run without the test specimen is carried out at the same heating rate and gas-flow rate as in the actual test in order to observe the apparent change in mass. The precision of the mass measurement cannot be better than that obtained from the preliminary test.

8.1 Temperature-scanning mode

8.1.1 Weigh the test specimen.

8.1.2 Adjust the zero point of the thermobalance.

8.1.3 Place the sample holder containing the test specimen on the thermobalance. Select the gas-flow rate, start the gas flow and record the initial mass, unless the following paragraph applies:

For investigations under a strictly inert atmosphere, either evacuate the thermobalance with a vacuum pump and then fill with inert gas or flush with inert gas of a high flow rate for a long period before recording the mass.

8.1.4 Set the temperature programme to be followed, which shall be as specified by the referring standard, if applicable.

The programme shall include the initial and final temperatures, the isothermal levels at these temperatures, and the rates of heating between programmed temperatures.

8.1.5 Start the temperature programme and record the thermogravimetric curve.

NOTE — A change of gas is possible during the determination. In this case, it will be necessary to use the same flow rate. In addition, it is recommended that gases with similar densities are used in order to obtain a similar buoyancy effect. If gases of similar densities cannot be used, it may be necessary to make a buoyancy correction.

8.2 Isothermal mode

Carry out the operations specified in 8.1.1, 8.1.2 and 8.1.3. Then start the instrument, operating it at its maximum heating rate (for example 100 °C/min or greater) in order to reach the specified temperature as quickly as possible.

NOTE — A change of gas is possible during the determination. In this case, it will be necessary to use the same flow rate. In addition, it is recommended that gases with similar densities are used in order to obtain a similar buoyancy effect. If gases of similar densities cannot be used, it may be necessary to make a buoyancy correction.

9 Expression of results

9.1 Graphical presentation

Present the thermogravimetry data obtained in the form of a mass change or percentage mass change versus time or temperature curve. Determine specific temperatures and masses from the TG curve using the following procedures:

9.2 Determination of increase in mass

Determine the maximum mass m_{max} from the curve (a typical curve is shown in figure 1).

Calculate the mass gain M_G, expressed as a percentage, using the equation

$$M_G = \frac{m_{max} - m_s}{m_s} \times 100$$

where

m_{max} is the maximum mass, in milligrams;

m_s is the mass, in milligrams, before heating.

9.3 Determination of loss in mass in the case of a single-stage decrease in mass (see figure 2)

From the TG curve, determine points A, B and C where

A is the starting point — the point of intersection of the starting-mass line and the tangent to the TG curve at the point of maximum gradient;

B is the end point — the point of intersection of the final-mass line and the tangent to the TG curve at the point of maximum gradient;

C is the mid-point — the point of intersection of the TG curve and the line drawn parallel to the x-axis at the mid-point between A and B.

Determine masses m_s and m_f and temperatures T_A, T_B and T_C corresponding to points A, B and C.
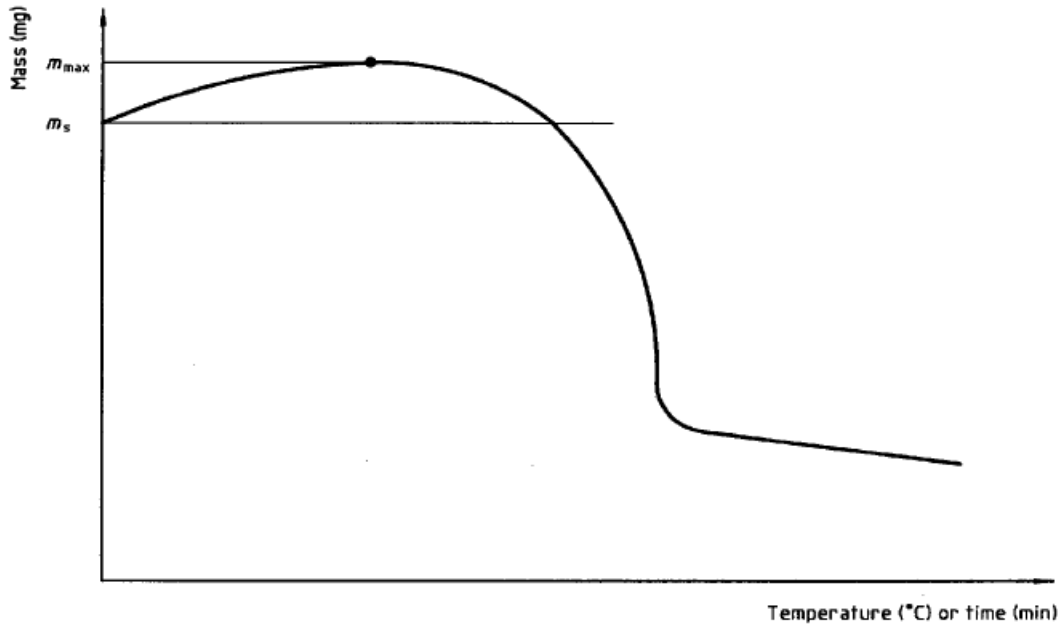

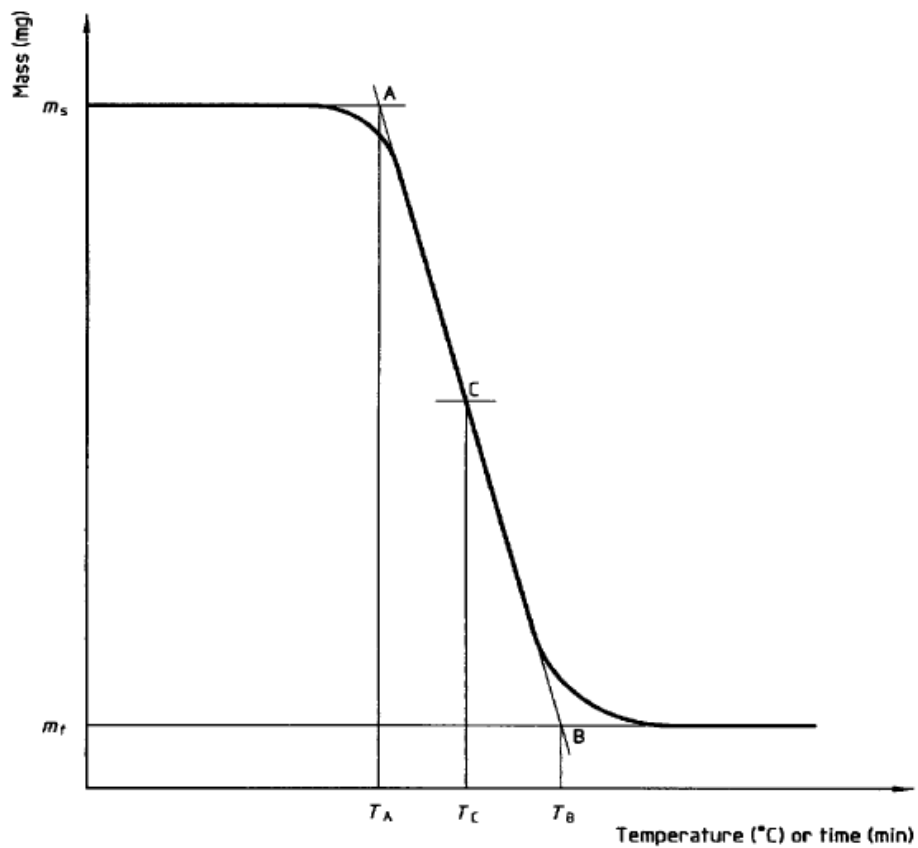Figure 1 — Example of a TG curve showing an increase in mass

Figure 2 — Example of a TG curve showing a single-stage decrease in mass

Calculate the mass loss M_L, expressed as a percentage, using the equation

$$M_L = \frac{m_s - m_f}{m_s} \times 100$$

where

    m_f is the mass, in milligrams, at the final temperature;

    m_s is the mass, in milligrams, before heating.

9.4 Determination of loss in mass in the case of a multi-stage decrease in mass (see figure 3)

Determine points A_1, B_1, C_1, A_2, B_2, C_2, and so on (if there are more than two stages) as described in 9.3.

Determine masses m_s, m_i and m_f and temperatures T_{A1}, T_{B1}, T_{C1}, T_{A2}, T_{B2}, T_{C2}, and so on, corresponding to these points.
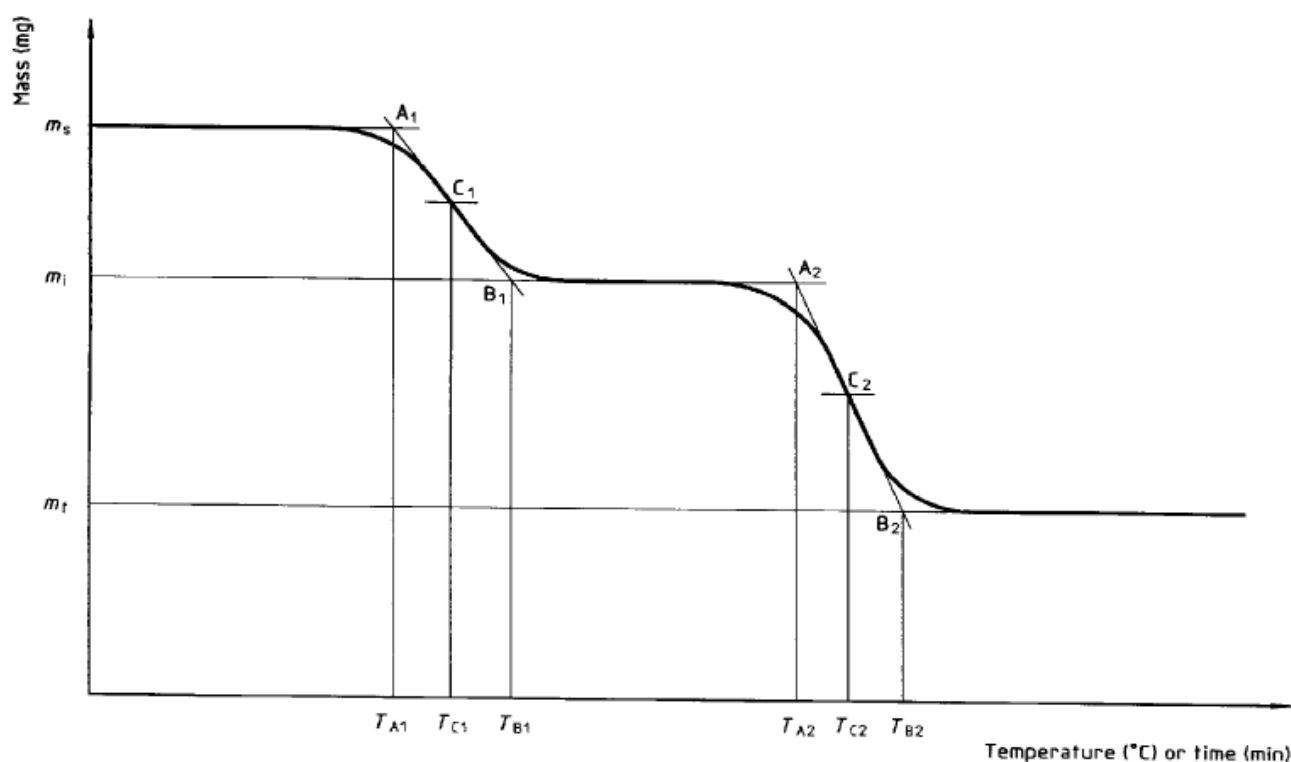

Figure 3 — Example of a TG curve showing a multi-stage decrease in mass

If the TG curve does not indicate constant mass in the part of the curve between the primary and secondary stage (see figure 4), the point of intersection of the tangent to this part of the curve at the point of minimum gradient and the tangent to the first-stage part of the curve at the point of maximum gradient shall be taken as end point B_1 and the point of intersection of this minimum-gradient tangent and the maximum-gradient tangent to the second-stage part of the curve shall be taken as starting point A_2. The mass m_i shall be taken as the mid-point between m_{B1} and m_{A2}.
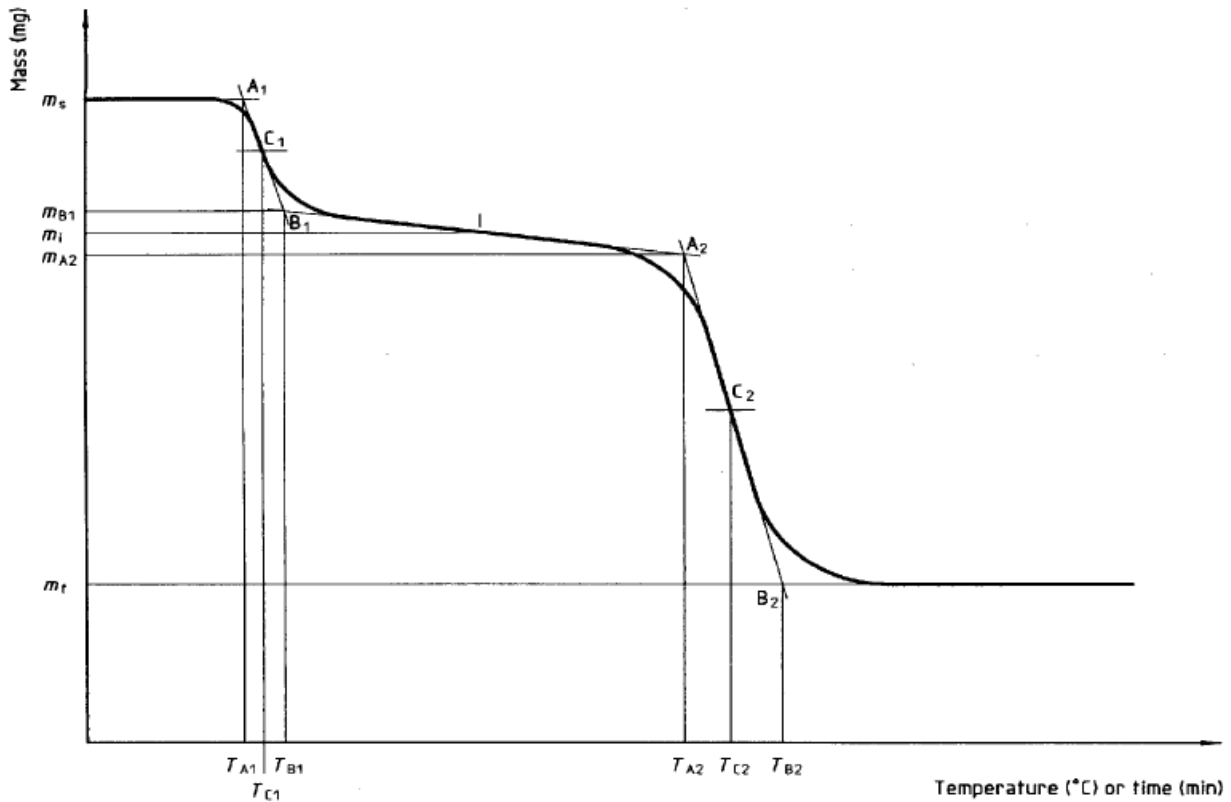
Figure 4 — Example of a TG curve showing a multi-stage decrease in mass where constant mass is not reached between reactions

Calculate the first loss in mass M_{L1}, expressed as a percentage, using the equation

$$M_{L1} = \frac{m_s - m_i}{m_s} \times 100$$

where

m_i is the mass, in milligrams, at the first end temperature;

m_s is the mass, in milligrams, before heating.

Calculate the second loss in mass M_{L2}, expressed as a percentage, using the equation

$$M_{L2} = \frac{m_i - m_f}{m_s} \times 100$$

where

m_i is the mass, in milligrams, at the second starting temperature;

m_f is the mass, in milligrams, at the second end temperature;

m_s is the mass, in milligrams, before heating.

Calculate any further losses in mass in the same way.

9.5 Determination of residue

Calculate the mass R of the residue, expressed as a percentage, using the equation

$$R = \frac{m_f}{m_s} \times 100$$

where

m_f is the mass, in milligrams, at the last end temperature;

m_s is the mass, in milligrams, before heating.

10 Test report

The test report shall include the following information:

a)   a reference to this International Standard;

b)   all details necessary for complete identification of the material analysed;

c)   the form and dimensions (if applicable) of the test specimen;

d)   the mass of the test specimen;

e)   details of the conditioning of the test specimen prior to the test;

f)   the type of thermobalance used;

g)   the specimen holder size and material of construction;

h)   the type of temperature sensor used and the position (inside or outside the specimen holder);

i)   the atmosphere and gas-flow rate used;

j)   the rate of temperature increase (programmed heating) or isothermal temperature used;

k)   the standard reference material used for temperature calibration;

l)   the mass gain and/or mass loss(es) calculated in 9.2, 9.3 and 9.4;

m)   the residue calculated in 9.5;

n)   the mass change temperatures determined in 9.3 and 9.4;

o)   any observations regarding equipment, test conditions or test specimen behaviour;

p)   the date of the test.

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Annex A
(informative)

Standard reference materials for calibration purposes

Table A.1 — Magnetic-transition NIST GM761 reference materials used for simple TG instrument and combined instrument

Values in degrees Celsius

Reference material	T_A	T_C	T_B
Permanorm 3	253	259	267
Nickel	351	353	355
Mumetal	378	382	386
Permanorm 5	451	455	458
Trafoperm	749	750	751
NOTE — NIST is the US National Institute of Standards and Technology.			

Table A.2 — Transition or melting temperatures and enthalpies of fusion for various reference materials used for instruments combined with DSC or DTA

Reference material	Transition or melting point (equilibrium temp.) °C	Enthalpy of fusion $J \cdot g^{-1}$	NIST reference number
Cyclohexane (transition)	− 83 [1]		NIST GM757
Mercury (melting)	− 38,9	11,47	NIST SRM2225
1,2-Dichloroethane (melting)	− 32 [1]		NIST GM757
Cyclohexane (melting)	7 [1]		NIST GM757
Phenyl ether (melting)	30 [1]		NIST GM757
o-Terphenyl (melting)	58 [1]		NIST GM757
Biphenyl (melting)	69,2	120,2	NIST SRM2222
Potassium nitrate (transition)	127,7		NIST GM758
Indium (melting)	157	28,42	NIST GM758
Potassium perchlorate (transition)	299,5		NIST GM758, GM759
Tin (melting)	231,9	60,22	NIST SRM2220, GM758
Lead (melting)	327,5	23,16	
Zinc (melting)	419,6	107,38	NIST SRM2221a
Silver sulfate (transition)	430		NIST GM758, GM759
Quartz (transition)	573		NIST GM759, GM760
Potassium sulfate (transition)	583		NIST GM759, GM760
Potassium chromate (transition)	665		NIST GM759, GM760
Barium carbonate (transition)	810		NIST GM760
Strontium carbonate (transition)	925		NIST GM760
1) Peak temperature.			
NOTE — NIST is the US National Institute of Standards and Technology.			

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