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Plastics — Thermogravimetry (TG) of polymers —

Part 1:
General principles

Plastiques — Thermogravimétrie (TG) des polymères —

Partie 1: Principes généraux

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical chemical properties,* in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 249, *Plastics,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 11358-1:2014), which has been technically revised. The main changes compared to the previous edition are as follows:

- a normative reference to ISO 472 has been added;
- definitions specified in ISO 472 have been removed;
- measurement under reactive atmosphere has been added;
- the apparatus specifications have been changed;
- the calibration procedures have been revised;
- buoyancy correction has been added;
- use of a differential thermogravimetric curve has been added.

A list of all parts in the ISO 11358 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Plastics — Thermogravimetry (TG) of polymers —

Part 1:
General principles

1 Scope

This document specifies general conditions for the analysis of polymers using thermogravimetric techniques. It is applicable to liquids or solids. Solid materials can be in the form of pellets, granules or powders. Fabricated shapes reduced to appropriate specimen size can also be analysed by this method.

This document establishes methods for the investigation of physical effects and chemical reactions that are associated with changes of mass.

This document 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.

This document is applicable to measurements in dynamic mode (mass change versus temperature or time under programmed temperature conditions) or isothermal mode (mass change versus time at constant temperature).

This document is applicable to measurements at different testing atmospheres, such as separation of decomposition in an inert atmosphere from oxidative degradation.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 291, *Plastics — Standard atmospheres for conditioning and testing*

ISO 472, *Plastics — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472 and the following apply:

ISO and IEC maintain terminological databases for use in standardisation at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

3.1
dynamic mass-change determination
technique for recording the variation of the mass of a test specimen with temperature, T, which is changing at a programmed rate

3.2
isothermal mass-change determination
technique for recording the variation of the mass of a test specimen with time t at constant temperature T

3.3
Curie temperature

temperature at which a ferromagnetic material passes from the ferromagnetic state to the paramagnetic state or vice versa

4 Principle

A test specimen is heated at specified rates with a controlled temperature programme, and the change in mass is measured as a function of temperature (dynamic mass-change determination). 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 (isothermal mass-change determination).

During measurement, the test specimen is held in a controlled inert, oxidising or otherwise reactive atmosphere.

In general, the reactions which cause the mass of a test specimen to change are decomposition or oxidation reactions or the volatilisation of a component. In some cases, measurements with special reaction gases may also be carried out.

The change in mass vs. temperature and/or time is recorded as a thermogravimetric (TG) curve.

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 may 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.

NOTE TG data can 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 cannot be able to 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 consists of the following.

5.1 Thermobalance, meeting the following requirements:

- capability to generate constant heating and cooling rates suitable for intended measurements;
- capability to maintain the test temperature constant (to within ±0,3 K or less for the duration of measurement);
- capability to maintain a constant purge gas flow rate controllable to within ±10 % over the range of flow rates (e.g. 10 ml/min to 150 ml/min) required for intended measurements;
- temperature and mass range in line with experimental requirements;
- recording device capable of automatically recording the measured curve of mass versus temperature and time;

NOTE Some instruments can also display differential thermogravimetric curves (DTG curves) for improved evaluation of results.

- measurement of temperature signals with an accuracy of ±1 % of the absolute temperature measured in K or better;
- measurement of time with an accuracy of ±1 s or better;
- measurement of mass with an accuracy of ±20 µg or better.

5.2 Purge gas, dry air or oxygen (oxidizing conditions) or a suitable inert gas with an oxygen content of 0,001 % by volume or less (non-oxidizing conditions). In either case, the water content of the purge gas shall be less than 0,001 % by mass.

6 Test specimen preparation

6.1 General

Test specimens may be liquids or solids. Solids 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.

6.2 Test specimens from finished products

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

NOTE Test specimen size and shape are generally dependent on the sample holder. Surface area affects 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.

6.3 Test specimen conditioning

Unless otherwise specified in a material specification or product standard, test specimens shall be conditioned, prior to measurement, at one of the standard atmospheres specified in ISO 291, or by any other method specified by agreement between the interested parties.

6.4 Test specimen mass

The mass of the test specimen shall conform with the intended purpose of measurements and shall match the mass range of the thermobalance.

7 Calibration

7.1 Mass calibration

Calibrate the thermobalance using static purge gas conditions (to prevent any disturbance through buoyancy related to gas flow) as follows, using calibrated masses in the intended range of measurements.

Record the temperature at which the mass calibration was carried out.

Set the thermobalance to zero. Place the calibration weight on the thermobalance and measure the corresponding mass change. In order to span a broader range, several different calibration weights may be used. If necessary, adjust the thermobalance so that the measured mass is equal to the calibration mass.

If mass calibration is done by procedures included in the instrument control software or by external service providers a valid calibration certificate may be acceptable to demonstrate adequate mass calibration.

7.2 Temperature calibration

Carry out the temperature calibration using the same atmosphere, rate of gas flow and heating rate as shall be used in the procedure specified in Clause 8.

If the thermobalance is not coupled with another thermoanalytical method, use the following procedure[1],[2].

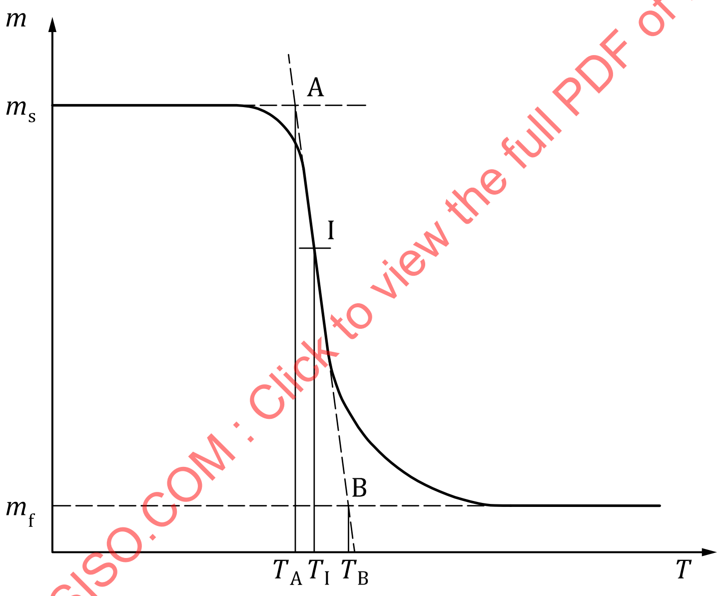
a) Choose two or more calibration materials with a Curie temperature near the temperature range to be examined. If possible, choose the calibration materials in such a way that the temperature range to be examined lies between the Curie temperatures of two of them.

b) Place a suitable magnet above or below the sample as required for the individual thermobalance used. As the strength of the magnetic field can influence the measurement of the Curie temperature, it is recommended to use a low magnetic field strength.

c) Put between 20 mg and 30 mg of calibration material in the sample crucible.

d) Start heating at the same heating rate, same type and material of crucible, and same type and flow of purge gas as will be used in the procedure specified in Clause 8 and carry out a calibration based on the start temperature T_A, inflection-point temperature T_i and end temperature T_B for the Curie temperature transition.

e) Determine the measured Curie temperature from the apparent mass change as shown in Figure 1. If necessary, adjust the thermobalance so that the measured temperature is equal to the declared Curie temperature.



Key

m	mass	A	extrapolated starting point
m_s, m_f	mass of starting point or end point, respectively	B	extrapolated end point
T	temperature	I	inflection point
T_A, T_B, T_I	temperatures of extrapolated starting point (A), extrapolated end point (B) or inflection point (I), respectively		

Figure 1 — Example of Curie temperature calibration

NOTE 1 The Curie point is the temperature at which a ferromagnetic material becomes paramagnetic on heating. The effect is reversible. Applying a magnetic field by placing a magnet below or above the sample exerts a downward or upward force on the ferromagnetic sample. This creates an apparent increase or decrease of weight which is lost upon heating the sample above its Curie temperature. More detailed information on evaluation of the apparent mass change occurring at the Curie point can be found in the literature[3],[4].

Certified calibration materials traceable to metrology laboratories should preferably be used. Suitable calibration materials can be available via instrument manufacturers or National Metrology Institutes. Examples of suitable magnetic calibration materials are given in Annex A.

If the thermobalance is combined with a single sensor differential thermal analysis (SS-DTA) [5],[6] differential thermal analysis (DTA) or differential scanning calorimetry (DSC) detector, it is recommended that the thermobalance is temperature-calibrated using procedures specified in corresponding standards, such as ISO 11357-1[7] for DSC.

NOTE 2 The single sensor differential Thermal analysis (SS-DTA) approach is based on the possibility to obtain a DTA signal by comparing the experimental sample temperature with a calculated reference temperature.

NOTE 3 The melting point of a calibration 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 extrapolated onset temperature).

NOTE 4 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. Without correction of time lag, the temperature calibration also depends on the heating rate. Some instruments can provide automatic correction of time lag and/or heating rate independent temperature calibration.

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 procedure specified in Clause 8.

8 Procedure

8.1 General

Depending on the measurement requirements, a suitable instrument setup has to be chosen. Three modes may be used:

- temperature scanning (see 8.2);
- isothermal (see 8.3); or
- a combination of both.

Select the gas flow rate.

Adjust the zero point of the thermobalance including sample holder using the same purge gas, crucible and flow rate as to be used for the sample measurement.

Place the sample holder containing the test specimen on the thermobalance. Start the purge 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 or purge with the inert gas to be used for measurement for at least 10 min at the same flow rate to be used for measurement before recording the mass.

If a change of purge gas is required during the determination, the same flow rate shall be used. In addition, it is recommended that gases with similar densities are selected in order to obtain a similar buoyancy effect. If gases of similar densities cannot be used, it can be necessary to perform buoyancy corrections for all purge gases involved.

When using multiple purge gases, the distances between the purge gas sources and the instrument shall be kept as short as possible to minimize the time lag due to line purging.

8.2 Temperature scanning mode

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 duration of the isothermals at these temperatures, and the rates of heating between programmed temperatures, and the purge gas(es) to be used for the different programme steps.

Start the measurement programme and record the thermogravimetric curve.

8.3 Isothermal mode

Start the instrument, running at its maximum heating rate in order to reach the specified isothermal temperature as quickly as possible and record the thermogravimetric curve.

If excessive overshoot is obtained prior to reach the specified isothermal temperature the applicable heating rate may be reduced adequately.

8.4 Buoyancy correction

For higher accuracy of mass measurements corrections can be required to compensate for changes in buoyancy and convection occurring in the thermobalance due to type and/or flow of purge gas. If this applies, a blank run shall be done using the same heating rate, type and material of crucible and type and flow of purge gas as for measurements. For this blank run either an empty crucible may be used, or the crucible may be filled with an inert material having a similar mass as the sample to be measured. Upon subtracting this blank curve from the measurement run, a buoyancy corrected TG-curve is obtained.

NOTE Some instruments provide the capability of automatic buoyancy correction which can improve the accuracy of results compared to measurements without buoyancy correction. However, the highest accuracy of results is obtained upon performing buoyancy correction as described in 8.4.

9 Expression of results

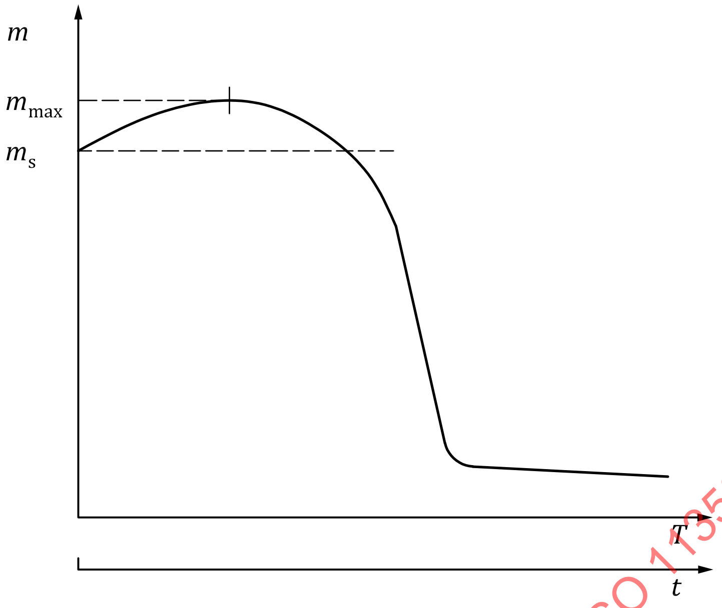
9.1 Graphical representation

Present the thermogravimetry data obtained in the form of a mass or mass change versus time or temperature curve. Determine specific temperatures and masses from the TG curve using the procedures specified in 9.2 and 9.3.

NOTE The determination of a mass change versus temperature or time curve can be favoured by instruments having the capability of calculating the first derivative of the mass curve. Such differential TG curves can facilitate the analysis of overlapping effects or determination of inflection points.

9.2 Determination of increase in mass

Determine the maximum mass, m_{max}, from the curve. A typical mass gain curve is shown in Figure 2.



Key

m	mass
T	temperature
t	time

Figure 2 — Example of a TG curve showing an increase in mass

Calculate the mass gain, m_g, expressed as a percentage, using Formula (1):

$$m_g = \frac{m_{max} - m_s}{m_s} \times 100 \qquad (1)$$

where

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

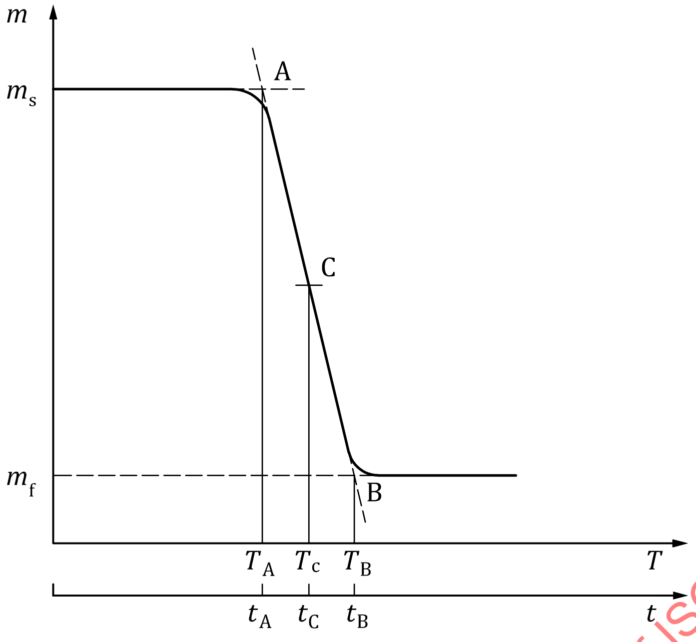
m_s is the mass at the starting temperature, in milligrams.

NOTE An increase in mass according to 9.2 is observed in exceptional cases only where absorption of purge gas components occurs. It can also occur upon chemical reactions with special purge gases.

9.3 Determination of loss in mass

9.3.1 Single-stage decrease in mass

See Figure 3.



Key

m	mass
T	temperature
t	time
T_A, T_B, T_C	temperature of starting point, end point or mid-point, respectively
t_A, t_B, t_C	time of starting point, end point or mid-point, respectively
A	starting point
B	end point
C	mid-point

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

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

- A is the starting point — the point of intersection of the starting-mass baseline 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 baseline 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 with the temperature at which both baselines are equidistant.

Determine masses m_s and m_f and temperatures T_A, T_B and T_C or times t_A, t_B and t_C corresponding to points A, B and C.

Calculate the mass loss m_l, expressed as a percentage, using Formula (2):

$$m_l = \frac{m_s - m_f}{m_s} \times 100 \qquad (2)$$

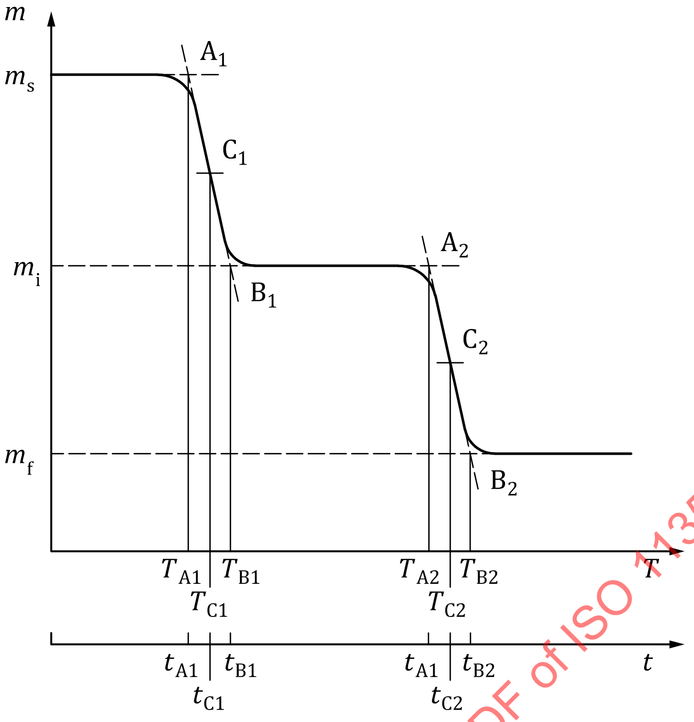
where

m_f is the mass, in milligrams, at the end point B;

m_s is the mass, in milligrams, at the starting point A.

9.3.2 Multi-stage decrease in mass

See Figure 4.



Key

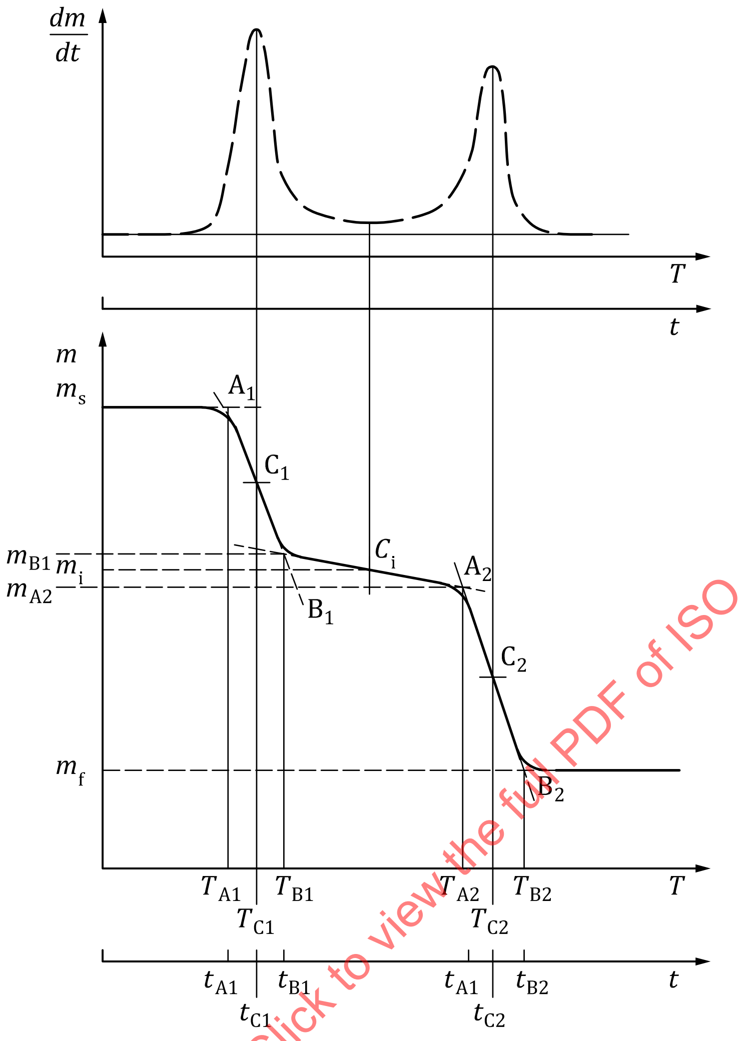
m	mass
T	temperature
t	time
T_{An}, T_{Bn}, T_{Cn}	temperature of starting point, end point or mid-point, respectively
t_{An}, t_{Bn}, t_{Cn}	time of starting point, end point or mid-point, respectively
A_n, B_n, C_n	starting point, end point or mid-point of step *n*, respectively

Figure 4 — Example of a TG curve showing a multi-stage decrease in mass

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 9.3.1.

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

If the TG curve does not indicate constant mass in the part of the curve between the primary and secondary stage (see Figure 5), 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 of the first stage 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 of the second stage A_2. The mass m_i shall be taken at the mid-point (C_i) between m_{B1} and m_{A2}.



Key

m	mass
$\frac{\mathrm{d}m}{\mathrm{d}t}$	first derivative of mass over time (DTG curve)
T	temperature
t	time
$T_{\mathrm{A}n}$, $T_{\mathrm{B}n}$, $T_{\mathrm{C}n}$	temperature of starting point, end point or mid-point, respectively
$t_{\mathrm{A}n}$, $t_{\mathrm{B}n}$, $t_{\mathrm{C}n}$	time of starting point, end point or mid-point, respectively
A_n, B_n, C_n	starting point, end point or mid-point of step *n*, respectively
C_i	mid-point between mass-loss steps

Figure 5 — Example of a TG and DTG curve showing a multi-stage decrease in mass

A differential TG curve (DTG curve) may be used to facilitate evaluation of results. As the minimum and maximum gradients of the differential thermogravimetric curve reflect the inflection points, they can deviate from the mid-points of the mass loss stages (C_1, C_2) and mid-points between those stages (C_i).

Calculate the first loss in mass, $m_{\mathrm{l}1}$, expressed as a percentage, using Formula (3):

$$m_{\mathrm{l}1} = \frac{m_\mathrm{s} - m_\mathrm{i}}{m_\mathrm{s}} \times 100 \qquad (3)$$

where m_i is the mass, in milligrams, at the first end temperature.