

5.2 Thermal analysis

5.2.1 Thermal analysis

Techniques in which a physical property of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme.

In addition to being more accurate, this definition has the advantage that it can be adapted to define any thermoanalytical technique by alteration of only a few words in each instance. It follows from the above definition that some techniques, such as X-ray diffraction or IR spectroscopy, can, when used in a specific manner, yield thermoanalytical information: these individual cases are not discussed further.

5.2.2 Individual thermoanalytical techniques

Classification

In the light of the new definition some one hundred techniques known to the Committee have been assessed and those previously defined, those that have come into prominence in the interim and those showing prospect of future development were classified to bring out interrelationships. The arrangement finally adopted for the defined techniques (Table 5.1) incorporate additional physical properties and/or techniques as necessary: various modes of certain techniques can also be distinguished.

TABLE 5.1. Classification of Thermoanalytical Techniques

Physical Property	Derived Technique(s)	Acceptable abbreviation
Mass	Thermogravimetry	TG
	Isobaric mass-change determination	
	Evolved gas detection	EGD
	Evolved gas analysis	EGA
	Emanation thermal analysis	
Temperature	Thermoparticulate analysis	
	Heating or cooling curve determination	
	Differential thermal analysis	DTA
Enthalpy	Differential scanning calorimetry*	DSC
Dimensions	Thermodilatometry	
Mechanical charcs.	Thermomechanical measurement	
	Dynamic thermomechanical measurement	
Acoustic charcs.	Thermosonimetry	

	Thermoacoustimetry
Optical charcs.	Thermoptometry
Electrical charcs.	Thermoelectrometry
Magnetic charcs.	Thermomagnetometry

*The confusion that has arisen about this term is resolved by separating two modes (Power-compensation DSC and Heat-flux DSC) as described in the definition given in the text.

The definitions and conventions of the individual techniques in the order introduced in Table 5.1 are given as follows.

Some relevant terms especially used at TG and the DTA techniques are also included.

Thermogravimetry (TG)

A technique in which the mass of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature programme.

The record is the *thermogravimetric or TG curve*; the mass should be plotted on the ordinate decreasing downwards and temperature (T) or time (t) on the abscissa increasing from left to right.

Thermobalance

A thermobalance is used for weighing a sample continuously while it is being heated or cooled.

Heating Rate

The heating rate is the rate of temperature increase, which is customarily quoted in degrees per minute (on the Celsius or Kelvin scales). The heating or cooling rate is said to be constant when the temperature/time curve is linear.

Plateau

A plateau (AB, Fig.5.1) is that part of the TG curve where the mass is essentially constant.

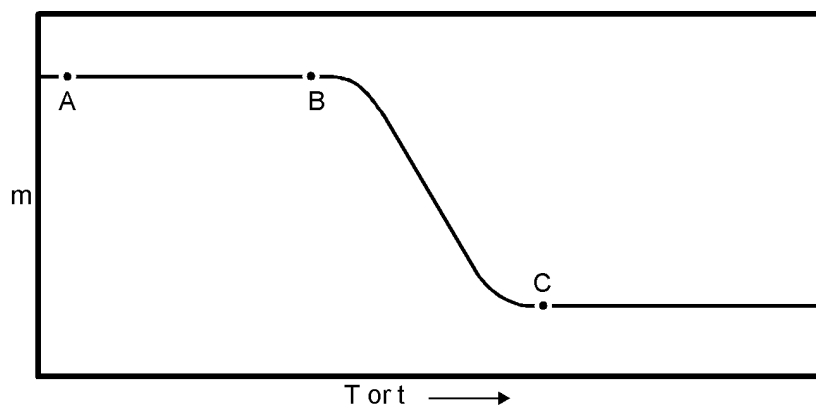


Fig. 5.1 Formalized TG Curve

Initial Temperature

The initial temperature, T_i , (B, Fig. 5.1) is that temperature (on the Celsius or Kelvin scale) at which the cumulative-mass change reaches a magnitude that the thermobalance can detect.

Final Temperature

The final temperature, T_f , (C, Fig. 5.1), is that temperature (on the Celsius or Kelvin scale) at which the cumulative mass change reaches a maximum.

Reaction Interval

The reaction interval is the temperature difference between T_f and T_i as defined above.

Isobaric Mass-change Determination

A technique in which the equilibrium mass of a substance at constant partial pressure of the volatile product(s) is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme.

The record is the isobaric mass-change curve; the mass should be plotted on the ordinate decreasing downwards and temperature on the abscissa increasing from left to right.

Note: Throughout this section *substance* is to be understood in the sense of *substance and/or its reaction products*.

Evolved Gas Detection (EGD)

A technique in which the evolution of gas from a substance is detected as a function of temperature whilst the substance is subjected to a controlled temperature programme.

Evolved Gas Analysis (EGA)

A technique in which the nature and/or amount of volatile product(s) released by a substance are/is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme. The method of analysis should always be clearly stated.

Emanation Thermal Analysis

A technique in which the release of radio-active emanation from a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme.

Thermoparticulate Analysis

A technique in which the release of particulate matter from a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme.

Heating-curve Determination

A technique in which the temperature of a substance is measured as a function of the programmed temperature whilst the substance is subjected to a controlled temperature programme in the heating mode.

Sample temperature should be plotted on the ordinate increasing upwards and programmed temperature or time on the abscissa increasing from left to right.

Two *derivative curves*, heating-rate curves (for dT/dt against T or t) and inverse heating-rate curves (for dt/dT against T or t), can be obtained.

Differential Thermal Analysis (DTA)

A technique in which the temperature difference between a substance and a reference material is measured as a function of temperature whilst the substance and reference material are subjected to the same controlled temperature programme.

The record is the *differential thermal or DTA curve*; the temperature difference (ΔT) should be plotted on the ordinate with endothermic reactions downwards and temperature or time on the abscissa increasing from left to right.

The term *quantitative differential thermal analysis* (quantitative DTA) covers those uses of DTA where the equipment is designed to produce quantitative results in terms of energy and/or any other physical parameter.

Sample

The sample is the material investigated, whether diluted or undiluted.

Reference Material

The reference material is a known substance, usually inactive thermally over the temperature range of interest.

Specimens

The specimens are the *sample* and *reference material*.

Sample Holder

The sample holder is the container or support for the sample.

Reference Holder

The reference holder is the container or support for the *reference material*.

Specimen-holder Assembly

The specimen-holder assembly is the complete assembly in which the *specimens* are housed. Where the heating or cooling source is incorporated in one unit with the containers or supports for the sample and reference material, this would be regarded as part of the specimen-holder assembly.

Block

A block is a type of *specimen-holder assembly* in which a relatively large mass of material is in intimate contact with the *specimens* or specimen holders.

Record

The record is the differential thermal or DTA curve shown in Fig. 5.2. The temperature difference (ΔT) should be plotted on the ordinate with endothermic reactions downwards and temperature or time on the abscissa increasing from left to right. It must be remembered that although the ordinate is conventionally labelled ΔT , the output from the ΔT thermocouple will, in most instances, vary with temperature and the measurement recorded is normally the e.m.f. output, E - i.e., the conversion factor, b , in the equation $\Delta T = bE$ is not constant since $b = f(T)$. A similar situation occurs with other sensor systems.

All definitions refer to a single peak such as that shown in Fig. 5.2. Multiple peak systems, showing shoulders or more than one maximum or minimum, can be considered to result from superposition of single peaks.

Base Line

The base line (AB and DE, Fig. 5.2) corresponds to the portion or portions of the DTA curve for which ΔT is approximately zero.

Peak

A peak (BCD, Fig. 5.2) is that portion of the DTA curve which departs from and subsequently returns to the base line.

Endothermic Peak

An endothermic peak, or endotherm, is a peak where the temperature of the sample falls below that of the reference material, i.e., ΔT is negative.

Exothermic Peak

An exothermic peak, or exotherm, is a peak where the temperature of the sample rises above that of the reference material, i.e., ΔT is positive.

Peak Width

Peak width (B',D',Fig. 5.2) is the time or temperature interval between the points of departure from and return to the base line. There are several ways of interpolating the base

line, and that given in Fig. 5.2 is only an example. Location of points B and D (Fig. 5.2) depends on the method of interpolation of the base line.

Peak Height

Peak height (CF, Fig. 5.2) is the distance, vertical to the time or temperature axis, between the interpolated base line and the peak tip (C, Fig. 5.2). There are several ways of interpolating the base line, and that given in Fig. 5.2 is only an example. Location of points B and D (Fig. 5.2) depends on the method of interpolation of the base line.

Peak Area

Peak area (BCDB, Fig. 5.2) is the area enclosed between the peak and the interpolated base line.

Extrapolated Onset

The extrapolated onset (G, Fig 5.2) is the point of intersection of the tangent drawn at the point of greatest slope on the leading edge of the peak (BC, Fig. 5.2) with the extrapolated base line (BG, Fig. 5.2).

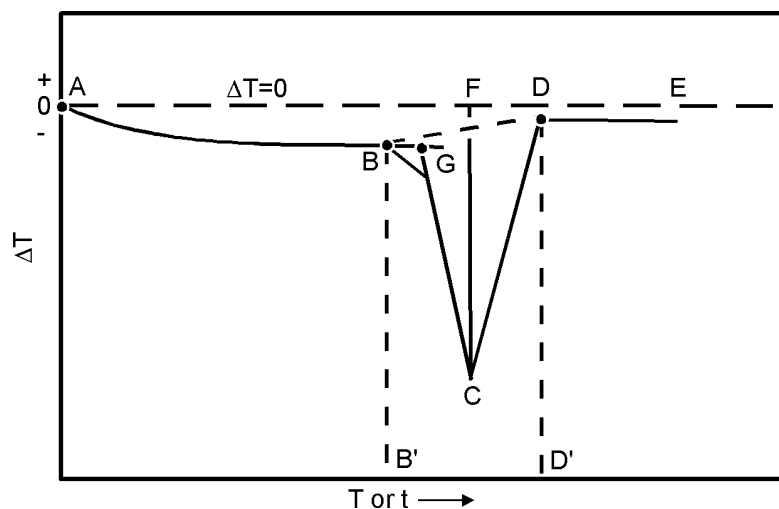


Fig. 5.2 Formalized DTA Curve

Differential Scanning Calorimetry (DSC)

A technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature whilst the substance and reference

material are subjected to a controlled temperature programme.

Two modes, *power-compensation differential scanning calorimetry (power-compensation DSC)* and *heat-flux differential scanning calorimetry (heat-flux DSC)*, can be distinguished depending on the method of measurement used.

Note: A system with multiple sensors (e.g. Calvet-type arrangement) or with a controlled heat leak (Boersma-type arrangement) would be *heat-flux DSC*, whereas systems without these or equivalent arrangements would be *quantitative DTA*.

Thermodilatometry

A technique in which a dimension of a substance under negligible load is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme.

The record is the *thermodilatometric curve*; the dimension should be plotted on the ordinate increasing upwards and temperature or time on the abscissa increasing from left to right. *Linear thermodilatometry* and *volume thermodilatometry* are distinguished on the basis of the dimensions measured.

Thermomechanical Measurement

A technique in which the deformation of a substance under non-oscillatory load is measured as a function of temperature while the substance is subjected to a controlled temperature program.

The mode, as determined by the type of stress applied (compression, tension, flexure or torsion), should always be stated.

Dynamic Thermomechanical Measurement

A technique in which the dynamic modulus and/or damping of a substance under oscillatory load is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme.

Torsional braid measurement is a particular case of dynamic thermomechanometry in which the material is supported on a braid.

Thermosonimetry

A technique in which the sound emitted by a substance is measured as a function of

temperature whilst the substance is subjected to a controlled temperature programme.

Thermoacoustimetry

A technique in which the characteristics of imposed acoustic waves are measured as a function of temperature after passing through a substance whilst the substance is subjected to a controlled temperature programme.

Thermoptometry

A technique in which an optical characteristic of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme. Measurement of total light, light of specific wavelength(s), refractive index and luminescence lead to *thermophotometry*, *thermorefractometry* and *thermoluminescence*, respectively. Observation under the microscope leads to *thermomicroscopy*. Other terms may have to be added.

Thermoelectrometry

A technique in which an electrical characteristic of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme. The most common measurements are of resistance, conductance or capacitance.

Thermomagnetometry

A technique in which the magnetic susceptibility of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme.

5.2.3 Multiple techniques

Simultaneous Techniques

This term covers the application of two or more techniques to the same sample at the same time, e.g. simultaneous thermogravimetry and differential thermal analysis.

Coupled Simultaneous Techniques

This term covers the application of two or more techniques to the same sample when the two instruments involved are connected through an interface, e.g., simultaneous differential thermal analysis and mass spectrometry.

Discontinuous Simultaneous Techniques

This term covers the application of coupled techniques to the same sample when sampling for the second technique is discontinuous, e.g., discontinuous simultaneous differential thermal analysis and gas chromatography, when discrete portions of evolved volatile products are collected from the sample compartment in the instrument used for the first technique.