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An overview of differential scanning calorimetry

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In differential scanning calorimetry (DSC) the difference in power (ΔP, in mW) required to heat a sample (S) and an inert reference (R) is determined as a function of temperature (T). There are many commercially available DSC instruments, the designs of which usually vary only in terms of furnace arrangement and/or the number and positioning of thermocouples. Early instrument designs plotted the difference in temperature between S and R (differential thermal analysis, DTA) but this term is no longer in common use. DSC instruments are compact, with a footprint typically no larger than 0.5 × 0.5 m^2.

DSC is one of a group of techniques that make measurements at controlled temperature. Collectively these are known by the term thermoanalytical and the field is termed thermal analysis (TA).[1] The International Confederation of Thermal Analysis and Calorimetry (ICTAC) defines the nomenclature and calibration methods used throughout the TA field.

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DSC has widespread application in many diverse fields because it does not require the sample material to possess any specific functional or chemical property, save that it changes its heat content when undergoing a phase change. The small size of the sample pans limits the sample mass to ca. 5–10 mg and so solids are usually studied. Large volume instruments are available for solutions. The instrument can detect thermally-driven phase transitions (such as melting, crystallisation and glass transitions) as well as the loss of volatile components. It is possible to purchase DSC instruments capable of studying solutions, but these have larger cells and operate at slower heating rates, and so are not considered in this report.

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All DSC instruments control temperature (T) with respect to time (t). The heating rate (b) can be:

- Linear (dT/dt = b)
- Modulated (e.g. dT/dt = sin b)
- Stepped (e.g. a number of isothermal periods at discrete temperatures)
- Sample-controlled (e.g. the sample response governs b).

All DSC instruments use a heater (termed a furnace) to supply power to the sample and reference materials. Where a common (or single) furnace is used to heat S and R, the instrument is of a heat-*flux* design and where separate furnaces are used to heat S and R, the instrument is of a power-compensation design. Knowledge of the arrangement is important. Heat-flux instruments tend to have a greater thermal mass and so usually have lower maximum heating rates (typically up to ca. 200 °C min^{-1}). Power-compensation instruments, having smaller thermal mass furnaces, can achieve faster heating rates (typically up to ca. 750 °C min^{-1}). Solid-state (i.e. etched silicon chip) calorimeters, possessing very little thermal mass, can achieve heating rates of the order of 10^6 °C s^{-1}. Similarly, measurements may be performed at defined cooling rates. The cooling rates achievable will be dependent upon the cooling system (typically either a refrigerated cooling system (RCS) or a liquid-nitrogen circulator). Again, the maximum rates attainable will be fastest for solid-state systems and slowest for heat-flux instruments. A power-compensation instrument equipped with an RCS would typically cool to −60 °C at −100 °C min^{-1}.

[illegible]

Sample and reference materials are sealed in pans (or crucibles) and placed in the instrument before being heated (or cooled) in accordance with a user-defined programme. Pans are typically made of pressed aluminium (for experiments up to 600 °C) or aluminium oxide or gold (if higher experimental temperatures are required). Stainless steel, gold-plated stainless steel high-pressure crucibles and/or sealed glass crucibles are used for decomposition studies at high temperatures.

[illegible]-fl[illegible]. In heat-flux DSC, a common furnace heats the sample and reference pans and the temperature difference (ΔT) between them is recorded, usually with thermocouples placed close to, but not in contact with, the pans. The number and positioning of the thermocouples will vary between instrument designs. The power change occurring in the sample is directly proportional to the temperature difference and is calculated by multiplying the data by a constant of proportionality, determined by calibration with a certified reference material (CRM).

[illegible]. In power-compensation DSC, separate furnaces heat the sample and reference materials. The instrument varies the power supplied by the two furnaces to maintain the temperature difference between the sample and reference at a constant value (usually close, but not equal to, zero). The power difference (ΔP) between the sample and reference is thus measured directly.

[illegible]

DSC measurements comprise contributions from two sources; heat capacity (C_p) effects and any other processes (phase transformations or chemical reactions) that the sample might undergo (represented by the generic term f(T,t)).

$$\frac{d/}{d} = {}_{p}\frac{d}{d} + (\ ,\ ) \qquad (1)$$

If the sample undergoes a phase change or chemical process, or there is a change in heat capacity, there will be a concomitant event in the DSC data. Typical DSC data, in this case an endotherm resulting from melting of a pure compound, are shown in Fig. 1. It should be noted that endotherms may be plotted positive or negative depending upon whether the instrument calculates ΔP as S–R or R–S. The convention varies between manufacturers and so the direction should be indicated on the y-axis. Several parameters may be determined, including the heat of fusion (ΔH_{fus}

proceed in the forward direction only and so are termed non-reversing. Since the kinetic response follows a sine function it should be 90° out of phase with the heat capacity term.

The utility of MTDSC comes in being able to deconvolute the overall heat-flow signal into these two components. Deconvolution requires calculation of the underlying heat flow signal (which is the average of the modulated response – equivalent to the heat flow signal that would be recorded for a normal DSC experiment performed at the same underlying linear heating rate). This can be considered equal to:

$$\text{Underlying heat flow} = {}_{\text{p}}\text{b} + {}'(\, , \,) \qquad (4)$$

Heat capacity reflects the rise in temperature for a given input of heat and so can be determined by comparing the amplitude of the modulated heat-flow (A_{mhf}) with the amplitude of the modulated heating rate (A_{mhr}):

$${}_{\text{p}} = \frac{\text{mhf}}{\text{mhr}} \qquad (5)$$

The amplitudes are determined using a Fourier Transform. From eqn (4) and (5) it can be seen that the heat capacity (reversing) component of the underlying heat flow is given by:

$$\text{Reversing heat flow} = \text{b}\frac{\text{mhf}}{\text{mhr}} \qquad (6)$$

Hence the kinetic response (non-reversing) component of the heat flow can be determined by difference:

$$\text{Non-reversing heat-flow} = \text{Underlying heat flow} - \text{b}\frac{\text{mhf}}{\text{mhr}} \qquad (7)$$

Heat flow data recorded with MTDSC thus allows separation of processes into reversing or non-reversing events. This aids both identification and isolation (if multiple events occur at the same temperature) of processes, although being a mathematical routine it is possible to introduce artifacts into the reversing and non-reversing data if the modulation parameters are not selected carefully.

[illegible]

[illegible]. Pans comprise a base and a lid. The seal between pan and lid can be hermetic (air-tight) or non-hermetic and correct selection is important. If the sample contains water that will evaporate into the headspace of the pan, different responses will be seen in hermetic and non-hermetic pans (the headspace of a hermetic pan will become saturated and evaporation will stop). Similarly, if there is a large expansion in volume of a sample (as it melts for instance) the increase in pressure inside a hermetic pan can cause the seal to fail (although hermetically sealed high-pressure pans can cope with up to 250 MPa pressure). For this reason, some pans have a pinhole in the lid to prevent a build up of pressure. In all cases, the sample and reference pans should be as closely matched in weight as possible.

[illegible]. The most important parameter is the heating rate. DSC heating rates typically range between 2–200 °C min^{-1}. Varying heating rate can help identify whether thermal transitions are thermodynamic or kinetic in nature, because kinetic events show a dependence on heating rate. It is thus good practice to repeat measurements at two heating rates, an order of magnitude apart (2 and 20 or 20 and 200 °C min^{-1} for instance). It is also advisable to cool the sample after the first heating run and then reheat it using the same parameters. This will identify events that are thermally reversible.

Most DSC instruments purge the air space around the sample and reference pans with a gas (typically nitrogen or helium). The purge gas serves many functions. Firstly, if the instrument is operated at sub-ambient temperatures, the gas, being dry, prevents condensation or freezing of water. It serves as a heat-transfer medium to ensure the pan and contents are at a temperature as close as possible to the heating block (if greater heat transfer is needed, helium is used as the purge gas). Finally, if any gaseous degradation products are emitted from the pan, the purge gas ensures they are carried out to waste and do not condense on the instrument.

Instruments should be calibrated for temperature and enthalpy upon installation and then performance verified on a daily or weekly basis (recalibration being required if the verification test indicates it). Calibration is performed with a certified reference material (CRM). Typically, CRMs for DSC are highly pure materials with well-established melting points and heats of fusion. IUPAC recommends a number of CRMs for DSC calibration (Table 1). Of these, indium is the most widely used material, although calibration with at least two CRMs, possessing melting points over the range at which measurements are to be performed, is advised. CRMs should be used under an inert gas and disposed of after use (the exception is indium, which can be reused if not heated above 180 °C). Gallium will react with aluminium and indium will alloy with gold and so care is needed when selecting pan material. As a general point, uncertainty of heat of fusion measurements will be determined by the uncertainty of the balance used to weigh the sample material.

MTDSC requires selection of additional experimental parameters (underlying heating rate and frequency and amplitude of oscillation). Proper selection is vital to ensure artifacts are not introduced to the data post-deconvolution. In particular, MTDSC assumes that the response of the sample varies linearly

Table 1 ICTAC CRMs for calibration of DSC instruments

CRM	Melting temperature (°C)	Enthalpy of fusion (J g^{-1})
Cyclopentane	−93.4	8.63
Gallium	29.8	79.9
Benzoic acid	123.0	148.0
Indium	156.6	28.6
Tin	231.9	60.4
Zinc	419.53	107.50
Aluminium	660.3	398.0

with the modulation in temperature. It also assumes that any changes in the underlying heat flow are slow relative to the time scale of the modulation (this allows averaging of the data, required to recover the underlying heat flow). This means there must be many modulations over the course of a transition (a minimum of six is usually recommended). If these conditions cannot be met then deconvolution cannot be achieved. Melting of a pure material is an example where deconvolution usually fails, because as a material melts its temperature will not rise until melting has finished; thus, during melting the temperature of the sample cannot be modulated. Selection of the modulation parameters therefore requires some prior knowledge of the transitions through which the sample will progress and it may be that several experiments will need to be performed with varying parameters to optimise the data. Typical starting values are an underlying heating rate of 2 °C min^{-1}, frequency 30–60 s and amplitude 0.5–1 °C.

Selection criteria for DSC instruments

Table 2 summarises key features of DSC instrumentation and includes criteria to be considered when purchasing DSC equipment. It also provides some guidance on instrumental requirements for different applications, for example measurements above or below ambient temperature.

References

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Table 2 Selection criteria for DSC instruments

Feature	Definition of feature and guidance for assessment	Reasoning
1 [illegible]		
( ) [illegible]	DSC instruments are available in two designs and the configuration affects the performance envelope Determine whether the instrument is of heat-flux or power-compensation design. Consider the types of sample to be studied and the maximum heating rates that might be used	The furnace arrangement defines the maximum heating and cooling rates that can be achieved
(i) Heat-flux instrument	A single furnace is used to heat both the sample and reference materials Determine the maximum heating and cooling rates the instrument can achieve	The furnace has a large thermal mass and so maximum heating and cooling rates likely to be reduced, although the instrument will probably be more robust
(ii) Power-compensation instrument	Individual furnaces are used to heat the sample and reference materials Determine the maximum heating and cooling rates the instrument can achieve	The furnaces have smaller thermal masses, so maximum heating and cooling rates likely to be increased
( ) [illegible]		
(i) Ease of dismantling	The user may be able to perform a cleaning routine if the instrument is easily disassembled Determine the ease with which the furnace lid can be removed and the DSC assembly reached	Volatile samples or materials that sublime can leave deposits on the DSC assembly and cover. If these areas are easy to reach, the user can remove these deposits manually, improving instrument performance and lifetime
(ii) Thermocouple arrangement	Thermocouples measure temperature. Multiple thermocouples wired in series form a thermopile Determine the number and location of thermocouples under the sample and reference pans	A greater number of thermocouples will reduce the need for exact positioning of pans.
(iii) Purge gas	The purge gas flows over the sample and reference pans, improving thermal contact with the instrument and removing volatile components Determine if one (or more) purge gases can be used and	Nitrogen is typically used but helium will increase thermal contact, improving resolution of events that occur at similar temperatures. May require cylinders of both gasses.

Table 2 (Contd.)

Feature	Definition of feature and guidance for assessment	Reasoning
(ii) Maximum cooling rate	The fastest rate at which the sample can be cooled Determine the fastest cooling rate. Remember that the rate	Faster cooling rates allow quicker sample turnover as well as ability to match processing conditions

Table 2 (Contd.)

Feature	Definition of feature and guidance for assessment	Reasoning
(iii) Autosampler	An accessory that will automatically load and remove pans from the instrument Determine whether an autosampler is standard or available as an option	An autosampler ensures consistent positioning of pan on sensor as well as provides capacity to run experiments overnight. Need to ensure samples are stable to temperature and/or relative humidity while waiting to be loaded if autosampler does not control these
( ). [illegible]	Certified reference materials (CRM) used to calibrate temperature and enthalpy	
(i) Temperature	CRMs for calibration of temperature Determine whether CRMs are supplied with the instrument	Usually indium plus either tin or zinc. Available from various agencies if not supplied by the manufacturer
(ii) Enthalpy	CRMs for calibration of enthalpy Determine whether CRMs are supplied with the instrument	Usually indium. Available from various agencies if not supplied by the manufacturer
(iii) Calibration routine in software	A feature within the software to automate calibration Determine whether there is an automated calibration routine in the software	Ensures calibration is performed consistently and keeps a record of calibration files
( ) [illegible] ft [illegible]	How are data captured, analysed and/or exported?	
(i) Computer hardware	The computer system used to run the instrument Determine whether the instrument is run by a separate computer or by an on-board computer. If the former, determine whether the hardware specification is available	If a laboratory has multiple instruments, then the ability to run all the instruments from one computer reduces space requirement. On-board computer might become obsolete – difficult to update/upgrade
(ii) Data capture rate	The rate at which data are recorded by the software Determine the maximum data capture rate and whether it can be altered in the operating software	If the data capture rate is too slow, then there may be too few data points at fast heating rates and resolution of data will be affected
(iii) Instrument parameters	The variable settings that affect the experiment and instrument operation Determine whether the software gives full control over all instrument functions, settings and parameters. Pay particular attention to whether calibration adjustments can be made as instrument performance changes with time/use	Are all functions accessible through software or are there manual alternatives/overrides? Where data are being recorded for regulatory submission, limited control over settings may be preferable
(iv) Software	The software used to operate the instrument and process the data Determine the software package(s) supplied with the instrument. Is there a single licensed copy or can all users have their own copy of the software? Determine whether the software package includes the tools necessary to enable data analysis. Is there a separate analysis program? What is the default file extension?	A single license would mean that data files can only be opened on the instrument computer – might preclude data analysis on a separate computer unless data can be exported. Some data analysis routines can be automated (e.g. Peak finder, area integration, glass transition step height). Experimental data file might only be readable by manufacturer's software
(v) Data presentation	The method by which data are presented Determine whether the software can be used to export the data as a graphic file	Data are often needed for inclusion in a report or publication and may need to be formatted in a particular manner
(vi) Data format	The file formats in which data can be exported Determine the types of file formats in which the data can be exported	Data exported in an ASCII format can generally be imported into any generic analysis program
( ). [illegible]	Ability of the instrument to connect with other analyzers	
(i) Evolved gas analysis	The purge gas is directed into a connected mass spectrometer Determine whether an evolved gas analyser is supplied with the instrument or available as an accessory	Can identify molecular mass of volatile components, which aids interpretation of thermal events
(ii) Simultaneous spectrophotometric analysis	Some instrument designs allow a spectrophotometric probe to	

Table 2 (Contd.)

Feature	Definition of feature and guidance for assessment	Reasoning
2 - [illegible]		
( ) [illegible]		
(i) Innovation	The company's record for developing instruments with innovative features	Demonstrates knowledge and understanding of