

ANALYTICAL METHODS COMMITTEE REPORT

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www.rsc.org/methodsEvaluation of Analytical Instrumentation. Part XXV:
Differential Scanning Calorimetry

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The Analytical Methods Committee has received and approved the following report from the Instrumental Criteria Sub-Committee.

Introduction

This report was prepared for the Analytical Methods Committee (AMC) by the author with contributions and critical review from other members of the Instrumental Criteria Sub-Committee: S. Greenfield (Chair), C. B. Braungardt, S. J. Hill, K. E. Jarvis, G. Lord, M. Sargent (Vice Chair), P. J. Potts and M. West. The Thermal Methods Group, to whom the AMC expresses its thanks, also reviewed the report prior to publication.

All users of analytical equipment should be familiar with the basic principles of its operation, the main areas of application, key features and aspects of day-to-day use. The aim of this report is to provide a general overview of the technique followed by an objective evaluation of the instrumentation and its capabilities in tabular form. The table of selection criteria is a unique aspect of this series of reports, providing a checklist of features to be considered in purchasing and using complex analytical instrumentation. Most features relate to the instrumentation itself but more general factors such as installation in the laboratory, service requirements and manufacturer support are also considered. A brief description is provided for each feature together with an explanation of its importance and, if appropriate, guidance on how it may be assessed.

Other reports

The Analytical Methods Committee has published the following reports in the series:

Part I. Atomic absorption Spectrophotometers, Primarily for use with Flames, *Anal. Proc.*, 1984, **21**, 45. Revised in *Analyst*, 1998, **123**, 1407.

Part II. Atomic absorption Spectrophotometers, Primarily for use with Electrothermal Atomizers, *Anal. Proc.*, 1985, **22**, 128. Revised in *Analyst*, 1998, **123**, 1415.

Part III. Polychromators for use in Emission Spectrometry with ICP Sources, *Anal. Proc.*, 1986, **23**, 109.

Part IV. Monochromators for use in Emission Spectrometry with ICP Sources, *Anal. Proc.*, 1987, **24**, 3.

Part V. Inductively Coupled Plasma Sources for use in Emission Spectrometry, *Anal. Proc.*, 1987, **24**, 266.

Part VI. Wavelength Dispersive X-ray Spectrometers, *Anal. Proc.*, 1990, **27**, 324.

Part VII. Simultaneous Wavelength Dispersive X-ray Spectrometers, *Anal. Proc.*, 1991, **28**, 312.

Part VIII. Instrumentation for Gas-Liquid Chromatography, *Anal. Proc.*, 1993, **30**, 296.

Part IX. Instrumentation for High-performance Liquid Chromatography, *Analyst*, 1997, **122**, 387.

Part X. Instrumentation for Inductively Coupled Plasma Mass Spectrometry, *Analyst*, 1997, **122**, 393.

Part XI. Instrumentation for Molecular Fluorescence Spectrometry, *Analyst*, 1998, **123**, 1649.

Part XII. Instrumentation for Capillary Electrophoresis, *Analyst*, 2000, **125**, 361.

Part XIII. Instrumentation for UV-VIS-NIR Spectrometry, *Analyst*, 2000, **125**, 367.

Part XIV. Instrumentation for Fourier Transform Infrared Spectrometry, *Analyst*, 2000, **125**, 375.

Part XV. Instrumentation for Gas Chromatography-Ion-Trap Mass Spectrometry, *Analyst*, 2001, **126**, 953.

Part XVI. Evaluation of General User NMR Spectrometers, *Accred. Qual. Assur.*, 2006, **11**, 130–137.

Part XVII. Instrumentation for Inductively Coupled Plasma Atomic Emission Spectrometers, *Accred. Qual. Assur.*, 2005, **10**, 155–159.

Part XVIII. Differential Scanning Calorimetry, *Accred. Qual. Assur.*, 2005, **10**, 160–163.

Part XIX. CHNS Elemental Analysers, *Accred. Qual. Assur.*, 2006, **11**, 569–576.

Part XX. Instrumentation for Energy Dispersive X-ray Fluorescence Spectrometry, *Accred. Qual. Assur.*, 2006, **11**, 610–624.

Part XXI. NIR instrumentation for process control, *Accred. Qual. Assur.*, 2006, **11**, 236–237.

Part XXII. Instrumentation for liquid chromatography/mass spectrometry, *Accred. Qual. Assur.*, 2007, **12**, 3–11.

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Part XXIII. Portable XRF instrumentation, *Accred. Qual. Assur*, 2008, 13, 453–464.

Part XXIV. Instrumentation for quadrupole ICP-MS, *Anal. Methods*, 2010, 2, 1206–1221.

An overview of differential scanning calorimetry

Introduction

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 $0.5 \times 0.5 \text{ m}^2$.

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.

Key areas of application

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.

Key features

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

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

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.* $200 \text{ }^\circ\text{C min}^{-1}$). Power-compensation instruments, having smaller thermal mass furnaces, can achieve faster heating rates (typically up to *ca.* $750 \text{ }^\circ\text{C min}^{-1}$). Solid-state (*i.e.* etched silicon chip) calorimeters, possessing very little thermal mass, can achieve heating rates of the order of $10^6 \text{ }^\circ\text{C s}^{-1}$. 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 $-60 \text{ }^\circ\text{C}$ at $-100 \text{ }^\circ\text{C min}^{-1}$.

Basic principles

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 $600 \text{ }^\circ\text{C}$) 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.

Heat-flux DSC. 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).

Power compensation DSC. 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.

DSC measurements

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 $f(T,t)$).

$$\frac{dq}{dt} = C_p \frac{dT}{dt} + f(T, t) \quad (1)$$

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

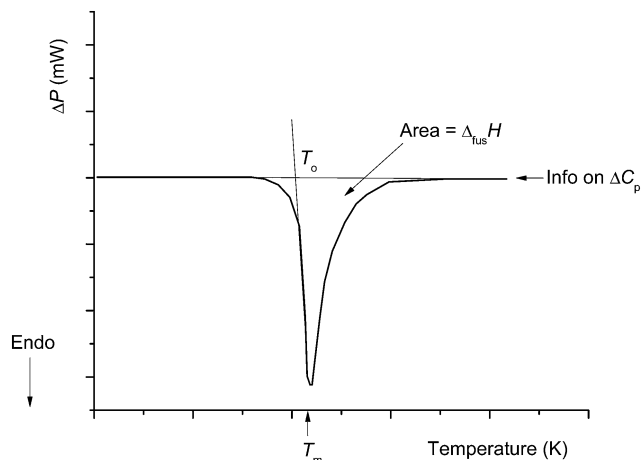


Fig. 1 Typical DSC data (in this case a melt endotherm) and the parameters that can be obtained.

manufacturers and so the direction should be indicated on the y-axis. Several parameters may be determined, including the heat of fusion (ΔH_{fus}), obtained by integrating the area under the curve (note: with respect to time not temperature), the extrapolated onset temperature (T_o), the peak maximum temperature (T_m), and the change in heat capacity (ΔC_p).

DSC data show a dependency upon heating rate, faster rates resulting in larger but broader peaks, Fig. 2. Thus, as the heating rate increases, sensitivity increases but at the expense of resolution (separation of events). Selection of the most appropriate heating rate will depend on the nature of the sample and will often involve a compromise between sensitivity and resolution. Typically, heating rates of 10–20 °C min⁻¹ are used.

Modulated temperature DSC (MTDSC)

In this case the linear (underlying or average) heating rate is modulated by a periodic function. The modulation can have any

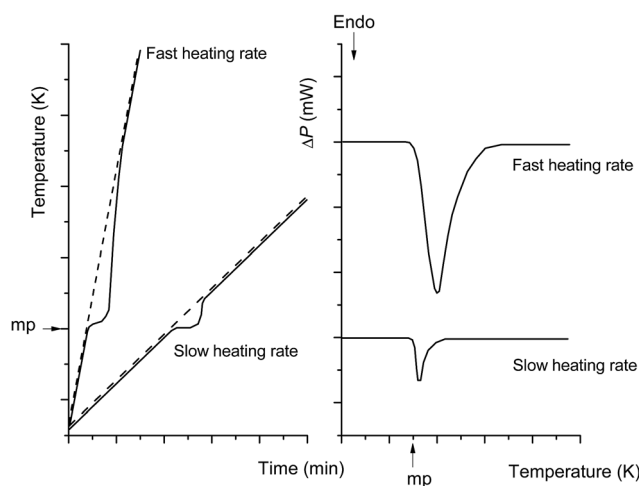


Fig. 2 Effect of heating rate on DSC data, showing (left figure) the change in temperature with time of S (solid line) and R (dotted line) and (right figure) the corresponding plots of power with temperature.

form but is typically sinusoidal, square or sawtooth. In the case of sinusoidal modulation (Fig. 3), the dependence of temperature with time is described by:²

$$T = T_0 + \beta t + A_T \sin \omega t \quad (2)$$

where T_0 is the initial temperature, β is the heating rate, ω is the frequency of the modulation and A_T is the amplitude of the modulation. eqn (1) can be rewritten to account for the modulation:

$$dq/dt = C_p(\beta + A_T \omega \cos(\omega t)) + f'(t, T) + C \sin(\omega t) \quad (3)$$

where $f(t, T)$ is the contribution to the heat-flow of any phase transitions or chemical processes (the kinetic response) once the effect of modulation has been removed and C is the amplitude of any kinetic response to the modulation. C is assumed for the purpose of this discussion to be negligible, although in practice a correction factor is often applied.

One component, $C_p(\beta + A_T \omega \cos(\omega t))$, is dependent upon heat capacity effects which, as discussed earlier, should be reversible, and so is termed the *reversing* heat flow. Heat capacity effects can be considered to occur instantaneously (except for glass transitions); since this term follows a cosine function it should therefore be 0° out of phase with the modulation in heating rate (assuming endothermic events are plotted in the positive direction – if plotted in the negative direction there will be a 180° phase lag).³

The second term, $f'(t, T) + C \sin(\omega t)$, is dependent upon a kinetic response (*i.e.* any process that the sample undergoes, which may be a physical transformation or a chemical reaction, which takes a small, but finite, time). Many processes might contribute to the kinetic response (for instance, melting, crystallisation, polymorph transformation *etc.*). Some of these processes are reversible (melting) and some are essentially irreversible (transformation to a more stable polymorph for instance), but over the time and temperature scales of a typical MTDSC experiment all of these events can be considered to

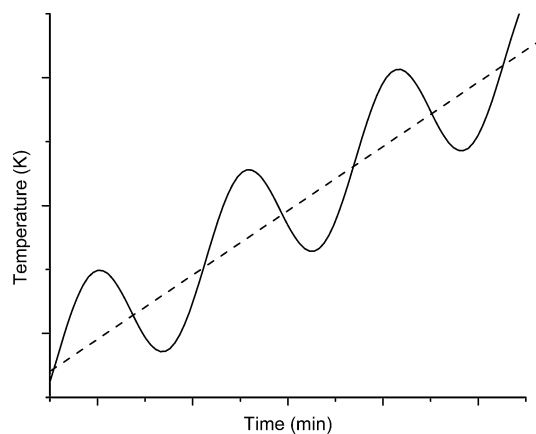


Fig. 3 Sample temperature as a function of time in MTDSC (solid line, calculated using eqn (2)) and the corresponding underlying linear heating rate (dotted line).

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:

$$\text{Underlying heat flow} = C_p\beta + f(t,T) \quad (4)$$

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}):

$$C_p = \frac{A_{\text{mhf}}}{A_{\text{mhr}}} \quad (5)$$

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:

$$\text{Reversing heat flow} = \beta \frac{A_{\text{mhf}}}{A_{\text{mhr}}} \quad (6)$$

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

$$\text{Non-reversing heat-flow} = \text{Underlying heat flow} - \beta \frac{A_{\text{mhf}}}{A_{\text{mhr}}} \quad (7)$$

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.

Experimental considerations

Pan type. 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.

Experimental parameters. 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 $2\text{ }^{\circ}\text{C min}^{-1}$, frequency 30–60 s and amplitude $0.5\text{--}1\text{ }^{\circ}\text{C}$.

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

- 1 *Principles of thermal analysis and calorimetry*, ed. P. J. Haines, Royal Society of Chemistry, Cambridge, 2002, ISBN 0854046100.
- 2 M. Reading, A. Luget and R. Wilson, Modulated differential scanning calorimetry, *Thermochim. Acta*, 1994, **238**, 295–307.
- 3 S. R. Aubuchon and P. S. Gill, The utility of phase correction in modulated DSC, *J. Therm. Anal. Calorim.*, 1997, **49**, 1039–1044.

Table 2 Selection criteria for DSC instruments

Feature	Definition of feature and guidance for assessment	Reasoning
1 Instrumental criteria		
(a) Instrument design		
	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
(b) General design features		
(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 whether the software can switch between them automatically	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.
(iv) Purge gas flow rate	The rate at which the purge gas flows over the sample and reference materials Determine the minimum rate at which the purge gas flows through the DSC	High flow rates will require cylinders to be changed more frequently and may reduce the number of experiments that can be performed overnight with an autosampler
(iii) Control of flow rate	The method by which purge gas flow rate is modulated Is the flow rate controlled by a regulator on a cylinder or by mass-flow controllers?	Mass-flow controllers will give a more consistent flow-rate. The flow rate will affect thermal contact of the sample and reference pans with the instrument
(c) Cooling system		
	The cold-stage against which the furnace(s) operates. Determine the type of cold stage(s) available. Consider the types of sample to be investigated and the lowest temperatures/cooling rates needed	The cold-stage determines the lowest operating temperature of the instrument and the maximum cooling rates attainable
(i) Circulating water/oil bath	An external bath that circulates cooling water or oil around the DSC Determine if an external circulating water/oil bath is required and whether it can be controlled with the software	Minimum temperature limited to freezing point of cooling fluid. Heat removal proportional to flow rate
(ii) Refrigerated cooling system (RCS)	An electronic cooling system utilising a refrigerant gas Determine if an RCS unit is available and whether it can be controlled with the software	Minimum temperature is likely to be around $-130\text{ }^{\circ}\text{C}$. Useful for sub-ambient experiments down to <i>ca.</i> $-90\text{ }^{\circ}\text{C}$ and will achieve faster cooling rates than a circulating bath
(iii) Liquid nitrogen	Liquid nitrogen is circulated around the cold stage with an external pump Determine if a liquid nitrogen circulator is available and whether it can be controlled with the software	Will achieve lowest cold-stage temperature (<i>ca.</i> $-196\text{ }^{\circ}\text{C}$) and so fastest cooling rates. Needs training in handling and use of liquid nitrogen. May require oxygen monitor and special signage in laboratory
(e) Heating/cooling rates		
(i) Maximum heating rate	Maximum rate at which temperature can be changed The fastest heating rate that can be used to heat the sample Determine the fastest heating rate. Make sure that the rate of data capture gives sufficient data resolution	Faster heating rates reduce run-times, increase sensitivity (but reduce resolution) and allow identification of kinetic transitions. Power-compensation designs typically have faster maximum heating rates. Solid-state chip calorimeters have fastest heating rates ($>10^6\text{ }^{\circ}\text{C min}^{-1}$)

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 will change depending upon the type of cooling system used. If liquid nitrogen to be used, consider gas handling and training	Faster cooling rates allow quicker sample turnover as well as ability to match processing conditions Liquid nitrogen cooled instruments will have the fastest cooling rates, but users must be trained in gas handling
(iii) Temperature modulation	The ability to use a mathematical function to modulate the heating rate with Determine if a modulation function is available in the software	Temperature modulation allows deconvolution of the data into 'reversing' and 'non-reversing' signals. Particularly useful for identifying glass transitions
(iv) Maximum operating temperature	The highest temperature S and R can reach. Determine the maximum operating temperature	Using a LN2 cold stage might limit the upper temperature. Inorganic materials might require higher temperatures than organic materials. Limit will affect selection of pan material
(f) Pans	The container in which the sample and reference materials are enclosed	
(i) Pan material	The material from which the pans are constructed Determine the range of pans available. Typically pans are aluminium, but gold, aluminium oxide, stainless steel, glass or platinum may also be used. Some instruments use fixed crucibles (generally made of Hastelloy).	Aluminium pans have good thermal conductivity and low reactivity so are a good general choice. Gold forms an alloy with indium. Aluminium reacts with gallium and can potentially alloy with many CRMs if overheated. Single-use pans are machine-pressed, so may have traces of lubricating oil, so should be washed prior to use
(ii) Pan seal	The type of seal between the pan lid and base Determine the range of pan seals. Usually pans are open (non-hermetic), air-tight (hermetic) or pressure-sealed. Hermetic seal usually formed by cold-welding lid to base in a press, so determine whether press is supplied with instrument	Samples that lose volatile components will behave differently in hermetic and non-hermetic pans. A pinhole is often created in the lid of a hermetic pan to allow controlled release of volatile components. Hermetically sealed pans can withstand pressure up to 300 kPa (~3 atm). Pressure-seals formed with O-rings or washers. Can withstand pressures greater than 300 kPa.
(iii) Pan designs	The range of pan designs available from the manufacturer Determine the range of pans available from the manufacturer. Consider also that pans may be available from other suppliers	Different pans may be needed depending upon the application. These may need different presses. Some pans have locating pins so they are centred in the cell. Pans are generally not transferable between instruments from different manufacturers. Open pans allow simultaneous spectroscopic investigation
(iv) Pan cost	The cost of the pans Determine the cost of the pans from the manufacturer	Pans are usually single-use, so are the largest consumable cost. Pans usually sold in packs. Some instruments, usually design for studying liquids, have either fixed crucibles or reusable stainless steel pans
(v) Press	The type of press used to seal the pan and lid Determine the number of different presses required to seal the range of pans. Determine whether the press can be used with different pan types and whether it can form both hermetic and non-hermetic seals	Easier to have a single press that can be used with all pan types and seals. Make sure the sealing force is consistent each time the press is operated
(g) Sample loading	Factors affecting loading of the S and R pans in the instrument	
(i) Loading temperature	The temperature range over which pans can be loaded into the instrument Determine the loading temperature range. Pay particular attention to whether samples can be loaded at sub-ambient temperature	Some samples are temperature-sensitive and may need to be loaded at sub-ambient temperature. Consider also the temperature of the autosampler (part iii)
(ii) Sensitivity to loading position	The effect on the data from placing the pans on different positions of the DSC sensors Determine if there is a mechanism to ensure pans are loaded repeatedly	Off-centre pans can affect heat flow measurement. Use of an autosampler ensures consistent pan positioning, as does use of pans with a locating pin. This effect is minimised with a greater number of thermocouples

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
(h) Calibration	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
(i) Data acquisition and control software	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 (<i>e.g.</i> 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
(j) Connectivity	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 be mounted above the sample pan Determine whether there is an accessory that allows the probe to be mounted	Spectrophotometric data can identify chemical species (and physical form) as a function of temperature. Requires open pans, which may affect quality of thermal data

Table 2 (Contd.)

Feature	Definition of feature and guidance for assessment	Reasoning
2 Non-instrumental criteria		
(a) Previous instruments		
(i) Innovation	The company's record for developing instruments with innovative features Determine the track record of the company in terms of instrument development and innovation	Demonstrates knowledge and understanding of the technique and user requirements
(ii) Reliability record	The company's record for instrument reliability Determine the reliability record of the instrument. Consider asking to speak with existing customers	Reflects good design and manufacturing quality and indicates likely servicing and maintenance schedule
(iii) Similarity of operation, layout and design (including software) to existing instruments in the laboratory	The degree of similarity of the instrument to those already in use Determine any differences between the current instrument and any previous types. Check to see if any instruments are already in use in the workplace	Similarity of design and operation means that operators can draw on in-house expertise, resulting in reduced costs and time for training. It may also minimise the cost of spares and fittings
(iv) Confidence in the supplier	The confidence gained from past experience or experience of other users Talk with existing customers and users	A good working relationship ensures the instrument will be used to its maximum potential and should minimize service and maintenance time
(b) Servicing		
(i) Service support	The availability of service support from supplier or third-party Determine whether a service plan is available or enquire about service call out response times and cost. Consider whether independent service engineers are available	Essential to ensure continued operation of instrument over planned lifetime with minimum down-time for service and maintenance
(ii) Calibration and validation service	Availability of calibration and validation service from supplier or third-party Determine whether there is an installation, validation and calibration service available.	Often a requirement as part of a Quality Management System or if data to be used in regulatory submissions
(iii) Availability, cost and delivery of spares and consumables	The range of stock carried by, or quickly available to, the supplier or third-party Determine spares availability and ask to speak to existing customers or users	Will reduce instrument down-time and define day-to-day operating costs
(iv) Effectiveness of service support	The ability of a service agent to identify and fix faults based on previous user experience Ask to speak to existing customers or users	Will reduce instrument down-time
(c) Technical support		
(i) Applications department	Access to advice from the application specialists Determine whether the supplier has a applications laboratory and whether it has application specialists	Application specialists will be able to advise on experiment design and data interpretation with respect to specific sample types
(ii) Technical information	The range and quality of technical information, including the instruction manual, application notes and lists of papers Ask to see technical information	Helps operators to design experiments and optimise measurements for new applications
(iii) Telephone and internet assistance	Support available <i>via</i> telephone or internet, including software updates Determine the level of technical support	Rapid availability of assistance reduces need for service call-out. Can be judged by reference to other users experience
(iv) Training	The training available during or following installation of instrument Determine whether training is provided upon installation and whether training can be offered to new users	Helps to ensure operators use instrument effectively
(v) User meetings	Meetings, conferences and technical briefings organised for users of the instrument by the manufacturer or third-party Determine if user meetings are offered	Other users are often the best source of advice for solving problems and developing new applications