

STANDARDISATION AND QUALITY ASSURANCE

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Abstract

Modern DSC instruments generally give very reproducible results that are ideal for quality assurance work. However, various corrections are needed before quantitative data are obtained. Since the corrections differ from one type of instrument to another, it is important to ensure that they are all properly carried out. Without these corrections, it is fruitless to compare data from different sources. The types of problem, and their solutions, are discussed.

Keywords: calibrants, quality assurance, quantitative data, standard procedures

Introduction

Most types of thermal analysis are relative techniques from which quantitative data are obtained by comparison of the signal from the 'unknown' with that from some 'standard' material. The derivation of truly quantitative data may require numerous corrections and this will be illustrated for DSC, one of the more mature techniques of thermal analysis. Before considering these, it must be emphasised that simple relative measurements are often enough for some types of quality assurance work. For example, it may be sufficient to know that a sample gives a DSC peak of a particular size (however measured) at a given temperature (again, however measured). The 'standard' could be taken from a specific batch of the same material as the unknown, a batch that is known to fulfil a given set of requirements. Absolute values of both temperature and peak size may be unknown but, provided results from both unknown and standard fall within certain agreed limits, a consistent product can be assured. (It is essential to use *some* form of standard to guard vs. changes due to the instrument rather than the sample.)

The above type of relative measurement is widely used and perfectly acceptable for many applications. For example, local arrangements between supplier and user to ensure that today's material is the same as yesterday's (within mutually agreed limits – every experiment has uncertainties associated with it) and is therefore fit for a particular purpose. However, problems arise when several parties become involved. Various types of instrument may be used and these can respond in different ways to a specific 'event'. To minimise problems of this type, written national and international standards are being developed to ensure that consistent experimental

procedures are followed: ISO Standards for DSC work on polymers (in the 11357-1 to 6 series) are one example. It becomes increasingly important to ensure that there is numerical agreement between results from several instruments and the simple reproducible 'standards' described above must now be replaced by 'calibrants' with thermodynamically well defined properties.

It is when data from different instruments are being compared that it is essential to make all relevant corrections because their relative importance may vary from instrument to instrument and from sample to sample. An additional source of uncertainty could be the almost-universal reliance on manufacturers' software to process data: it is generally unclear what algorithms are used, a set of 'standard data' treated by the several manufacturers' programs would be a valuable and revealing exercise. In the following sections some problems of DSC are briefly discussed. Although solutions are suggested, the main intent is to make users aware that direct comparison of data from different sources is impossible without modifications to existing procedures.

Temperatures

It is essential to calibrate the temperature scale of a DSC because the sensors are located at some point away from, rather than within, the sample. The basic procedure is simple: the known melting temperatures (T_{fus}) of a series of pure materials are used to construct a calibration curve of 'temperature correction' (ΔT) vs. the 'apparent' (or indicated) temperature (T_a). It is almost universal to take the extrapolated onset temperature (T_c) as that point on the DSC curve that represents T_{fus} . In fact, T_c is really where the majority of melting starts whereas the true fusion temperature is at the end of melting, where the most perfect crystals vanish. This last temperature is not immediately available from a dynamic DSC curve because of heat transfer effects. The distinction between 'start' and 'end' of melting is trivial (on a DSC scale, where $\pm 0.1^\circ\text{C}$ is a desirable goal) for the pure metals that are widely used for calibration. The ΔT vs. T_a curve is therefore meaningful but subsequent derived temperatures may be incorrect because most materials that are routinely examined fall far short of the purity (99.9% as a very approximate guide) needed to ensure a $< 0.1^\circ\text{C}$ melting range. There will certainly be differences between T_{fus} determined by DSC in this way and by, say, the clearing temperature observed in the capillary tube of a conventional melting point apparatus.

The ΔT vs. T_a curve is a function of experimental conditions, especially the heating (or cooling) rate (β). A different calibration is needed whenever there are changes. The instrumental software may claim to allow for these but, even if originally true, there is no guarantee that subsequent usage has not changed performance in an unknown way. A very comprehensive investigation of all aspects of DSC calibration has been made by the German Thermal Analysis Group (GEFTA) [1]. Their recommendation for optimum accuracy is that all fusion temperatures are determined by extrapolation of $T_c(\beta)$ to $T_c(\beta=0)$. This gives a meaningful temperature provided rate effects are insignificant which, in turn, implies that the $T_c(\beta)$ vs. β

curve is linear. This is not true for many solid/solid transitions – even if the evidence of a single DSC run implies a simple first order event. Extra care is therefore needed when transition temperatures are being determined.

There are further problems with poorly packed and/or large samples, or at high β , when there may be a significant temperature gradient (a few degrees) across a sample. Here some average temperature is needed, particularly for specific heat work.

Ill-defined supercooling effects prevent the use of conventional materials as calibrants for cooling experiments. It is generally assumed that the $T_c(\beta)$ vs. β curve is symmetrical and can be extrapolated to negative values of β . This assumption can, and should, be tested because some liquid crystal transitions show negligible supercooling. However, the relationships between the optical phenomena that are currently used to characterise most liquid crystal transition temperatures and equivalent points (onset, peak or end?) on the DSC curve are not clear and must be established.

Solutions to most of the above problems can be devised on the basis of the GEFTA procedures and by stepping through T_{fus} (or the transition temperature) in small increments to define an isothermal value of T_{fus} [2]. Ideally, this should be the same as $T_c(\beta=0)$ and, for small samples with negligible thermal gradients, this is so. In addition, an average temperature can be derived by using the 'enthalpy lag' at the end of each run to estimate the corresponding thermal lag [2].

Enthalpy changes and specific heat capacities

Enthalpy changes

Although most applications of DSC use the instrument as a sophisticated thermometer, the above discussion shows that some care is needed to obtain true sample temperatures. Calorimetric measurements are more straightforward except for the little-discussed but important problem of the correct baseline.

Enthalpies of fusion $\Delta_{fus}h$ or transition are obtained by comparison of the area of the 'event' for the unknown with that for a calibrant or, preferably, a set of calibrants covering the relevant temperature range. The popular metal calibrants, indium, tin, etc. show little displacement of the pre- and post-melting curves (i.e. the specific heat capacities of solid and liquid, c_{ps} and c_{pl} , respectively, are similar). A simple baseline, joining low and high temperature regions, gives an area that is unambiguously related to $\Delta_{fus}h$. For many real materials, however, there is a large change in c_p ($\Delta c_p = c_{pl} - c_{ps}$) at the 'event'. The construction of a baseline to join solid and liquid regions depends on instrumental and material considerations as well as subjective decisions by the operator. Instrumental/material considerations are best illustrated by comparing a slowly heated small sample with a rapidly heated larger sample. When both cases are normalised to c_p vs. T curves, the former appears much sharper. The area defined by this curve is less (for $c_p > 0$) than for the more diffuse case because the baseline for the latter has to cover a wider temperature range before the peak returns to the liquid-only state. As a result, and because of the arbitrary way in

which the baseline is drawn, $\Delta_{\text{fus}}h$ appears to depend on heating rate and/or sample mass.

In fact, simple thermodynamic considerations show that the correct baseline is discontinuous and formed by extrapolations of pre- and post-melting parts of the curve to T_{fus} [2].

Specific heat capacity

Although one of the earliest applications of DSC was to the determination of c_p , great care is needed to define the correct baseline. (This could change with the development of modulated DSC although, even here, it can be argued that baseline problems are merely replaced by those of frequency and amplitude.)

Procedures for $\Delta_{\text{fus}}h$ and c_p work are discussed in the GEFTA recommendations. The two methods may not be equivalent: for example, $\Delta_{\text{fus}}h$ determined from a conventional area calibration may differ from that obtained from a c_p vs. T curve covering the same temperature range. The difference may range from tenths to a few percent [3] and a full discussion is given in this reference. Here it is enough to emphasise another potential source of disagreement.

Concluding remarks

The relative importance of the experimental and computational procedures needed to derive quantitative data from DSC work varies from one instrument to another. If some stage is omitted, in a quality control method, for example, numerical agreement of data from different sources cannot be expected. As befits one of the more mature techniques of thermal analysis, quantitative data *can* be produced irrespective of the origin, and individual users should ensure that their procedures and algorithms are equal to this task.

References

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