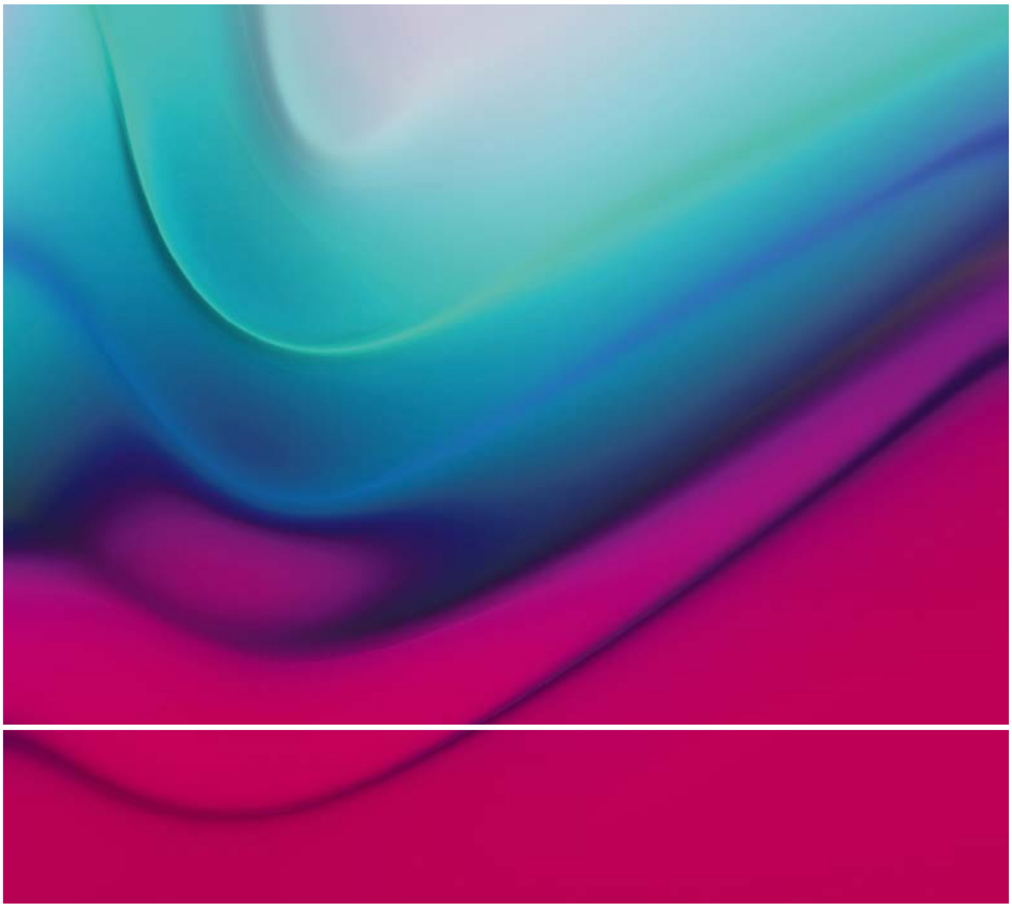
Markus Schubnell

Thermal Analysis of Food



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Preface

This handbook provides an overview of the use of thermal analysis techniques for analysis of foods. We first present an overview on the used techniques including differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA), as well as combined techniques such as TGA-humidity generator or TGA-evolved gas analysis, This is followed by chapters dealing with some general aspects of the main constituents of food (proteins, carbohydrates, lipids), a discussion of some fundamental effects important with food, and some remarks regarding the interaction of food (or materials in general) with water. The focus of this handbook, however, are 40 applications illustrating the use of thermal analysis techniques for the characterization of typical foods.

I hope that these applications will find wide interest and stimulate new ideas for both experts and newcomers to this rather complex but immensely interesting and widespread field.

I would like to thank all the application specialists in the Thermal Analysis Group at METTLER TOLEDO, Switzerland for their help, discussions and support. In particular, Dr. Domenico Regonini (for performing many measurements and evaluations, and for reviewing the manuscript), Nicolas Fedelich (for helping me with some TGA-evolved gas analysis measurements) and Dr. Thomas Oberholzer. Special thanks go to Dr. Naomi Towers and to Dorothea Gloor for the final proofreading and plot layout.

Nänikon, Switzerland, November 2025

Dr. Markus Schubnell
METTLER TOLEDO

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1 Introduction to Thermal Analysis

According to the International Confederation for Thermal Analysis and Calorimetry (ICTAC), "Thermal analysis (TA) is the study of the relationship between a sample's property and its temperature as the sample is heated or cooled in a controlled manner." This includes analysis in well-defined atmospheres, as well as isothermal measurements [1]. Different techniques are used depending on the measured property. The most commonly used techniques are described in Table 1.1.

Table 1.1: Overview on the most commonly used techniques in thermal analysis.

Technique	**What it measures**
TGA Thermogravimetric analysis	Mass of a test specimen as a function of temperature or time.
DTA Differential thermal analysis	Temperature difference between the test specimen and an inert reference, as a function of temperature or time.
DSC Differential scanning calorimetry	Heat flow into (endothermic processes) or out of (exothermic processes) a test specimen as a function of temperature or time.
TMA Thermomechanical analysis	Dimensional changes of a test specimen as a function of temperature or time.
DMA Dynamic mechanical analysis	Stiffness (= ratio of applied force amplitude and the resulting displacement amplitude) of a test specimen; based on the stiffness, the phase shift between force and displacement amplitude, and the geometry of the test specimen, the storage and loss modulus, as well as the ratio of the loss and the storage modulus (i.e., tan δ or loss factor) of the material are calculated as a function of temperature, time, frequency, imposed force, or displacement amplitude.
Hot-stage microscopy	Transmittance of a test specimen under polarized light as a function of temperature or time.
DVS Dynamic vapor sorption	Mass of a test specimen as a function of time when exposed to a specific humidity profile at a certain temperature.

1.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a technique to measure the mass of a test specimen as a function of temperature (dynamically) or time (isothermally) in a controlled atmosphere. Mass decreases during vaporization or due to gases released during decomposition. Mass increases when the sample is reacting with the atmosphere in the furnace to form a solid product (e.g. oxidation or nitrification of metals). In dynamic experiments, TGA curves are usually displayed as a function of the reference (programmed) temperature.

A test specimen may exhibit multiple mass changes when heated. The temperature at which the first mass change (unrelated to moisture) occurs, characterizes the thermal stability of the sample in the atmosphere used. If the qualitative sample composition is known, it may be possible to quantify its composition using the TGA curve. In many applications, a test specimen is heated in an inert atmosphere up to a specified temperature (pyrolysis). Once the specified temperature is reached, the furnace atmosphere is switched from inert to air or oxygen. In this second step, residual carbon remaining after pyrolysis, or filler carbon black, will be burnt off.

TGA measurements are often displayed as the first derivative of the TGA curve, the so-called DTG curve, which corresponds with the rate of change of the sample mass. Steps due to loss (or gain) of mass in the TGA curve then appear as peaks in the DTG curve. This often facilitates the identification of overlapping mass changes. Usually, the limits for the step evaluation of TGA curves are based on the DTG curve. The DTG curve corresponds with the rate of change of the sample mass. Figure 1.1 shows a typical TGA curve and its first derivative (DTG curve).

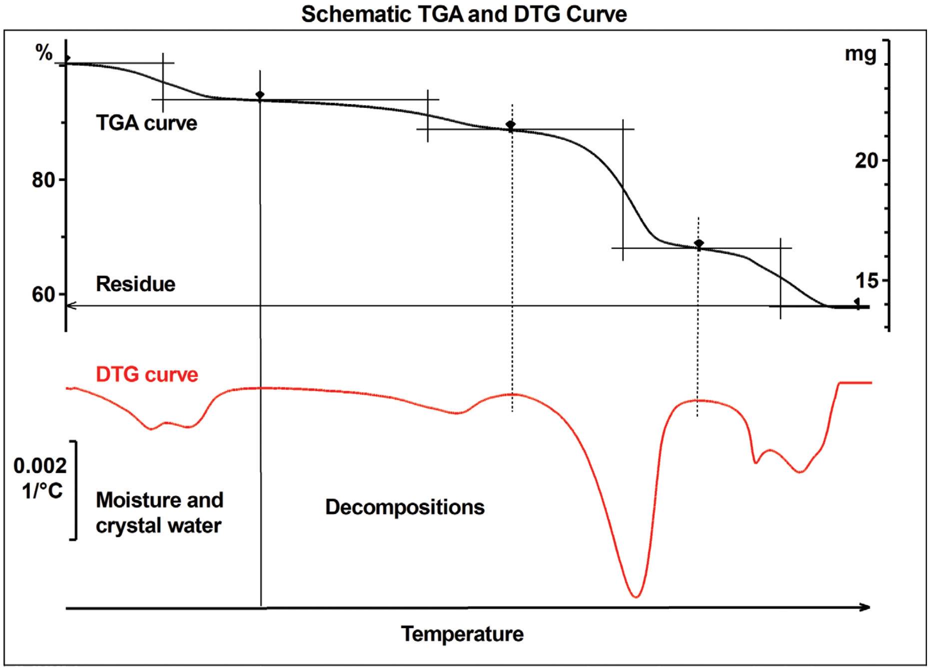

Figure 1.1: Schematic TGA curve and its first derivative (DTG curve). At low temperatures, one often observes some mass loss related to volatiles (e.g. humidity) and/or crystal water. This is followed by the thermal decomposition. In practice, test specimens are typically run in a first temperature segment (e.g. up to 600 °C) in inert atmosphere (pyrolysis), and in a second segment (e.g. up to 1000 °C) in air or oxygen.

Nowadays, TGA instruments are frequently equipped with SDTA®, DTA or DSC capabilities. This allows the user to distinguish between exothermic and endothermic mass-change processes, as well as the identification of effects that are not caused by mass changes, such as glass transitions, melting, or solid-solid transitions up to 1600 °C. This is far beyond the accessible temperature range of dedicated DSC instruments. Moreover, specific heat capacities can be determined up to 1600 °C.

1.2 Differential Thermal Analysis (DTA, SDTA)

In differential thermal analysis (DTA), a test specimen and a reference (usually an empty crucible) are subjected to a defined temperature program in a furnace. The temperature difference between the test specimen and the reference is measured. If a thermal event occurs in the test specimen, such as a phase transition or a chemical reaction, the additional uptake or release of energy changes the rate at which the test specimen changes temperature. This results in a temperature difference between the test specimen and the reference. For example, during an exothermic reaction, the temperature difference between the test specimen and the reference is larger than before or after the reaction.

The DTA curve is a plot of this temperature difference as a function of the reference temperature (which is equal to the program temperature) or, in the case of isothermal experiments, time. The DTA curve delivers information about characteristic temperatures of melting, chemical reactions, solid-solid transitions, and more. If chemical reactions occur, one can also conclude whether it is exo- or endothermic.

METTLER TOLEDO provides SDTA™ (single DTA). With this technique, no reference crucible is needed. Instead, the DTA signal is calculated as the difference between the measured temperature of the test specimen and the program temperature (which by definition is equivalent to the reference temperature). This concept is particularly valuable with techniques in which it is not possible to simultaneously measure a reference temperature, such as TMA and DMA.

METTLER TOLEDO TGA instruments can be equipped with three different sensor types. The SDTA-sensor is equipped with a single thermocouple to measure the sample temperature only. With the DTA- and DSC-sensors, the temperature of the reference crucible is also measured. Compared to the DTA-sensor, the DSC-sensor offers higher sensitivity. In the software, calibration curves are stored for each sensor type, and the respective curves are displayed in mW. This allows quantitative evaluation of thermal effects, such as melting or reaction enthalpies. The calibration curve can be adjusted and recalibrated by the user.

1.3 Differential Scanning Calorimetry (DSC)

A differential scanning calorimeter measures the difference between the respective heat flows of a test specimen and a reference (usually an empty crucible) as a function of program temperature or time. This difference defines the net heat flow (in mW) into or out of the test specimen subjected to the temperature program.

Thermal effects such as melting, crystallization, evaporation, or chemical reactions, manifest as peaks on the DSC curve. Integrating these peaks with respect to time, provides the melting, crystallization, evaporation, or reaction enthalpies. Characteristic temperatures (onset, peak, and endset) further describe these peaks. In addition, the DSC curve provides information on the specific heat capacity of the sample. Glass transitions manifest as step-like changes on the DSC curve and can be evaluated for the glass transition temperature, as well as intensity (step height expressed as the change in specific heat capacity during the glass transition). In dynamic experiments, where the program temperature increases or decreases over time, DSC curves are always displayed as a function of the reference temperature.

1.3.1 Conventional DSC

In conventional DSC, the test specimen is heated or cooled at a constant rate or, in some cases, held at a constant temperature. Temperature programs often consist of several segments joined together, such as isothermal, heating, and cooling segments. With unknown samples, we generally recommend to use heating-cooling-heating cycles.

A typical DSC heating curve is shown in Figure 1.2. By convention, DSC curves are displayed as a function of the reference, or program, temperature. According to ICTAC, the heat flow curve is displayed in such a way that exothermic peaks are oriented upwards, endothermic peaks downwards. The change in the curve at the beginning of the measurement is called the "initial deflection" (1). During this part of the measurement, the instrument cannot follow the imposed temperature program. The magnitude of the initial deflection depends on the heat capacity of the test specimen and on the heating rate.

In an ideal, perfectly calibrated DSC instrument, the heat flow, φ, of a test specimen in sections without any effects (i.e., without peaks or step-like changes) is given by the heating rate, β, multiplied by its mass, m, and its specific heat capacity, c_p. At the glass transition, the heat capacity of the sample increases and therefore a step-like change of the DSC curve is observed (2). After the glass transition, the test specimen is at least partially liquid. A broad, rather symmetric endothermic peak after (or occasionally before) the glass transition may indicate evaporation of some volatiles (3). Upon further heating, the liquid fraction may crystallize (4). Crystals will melt at a higher temperature (5). At a certain temperature, the test specimen will start to decompose (6).

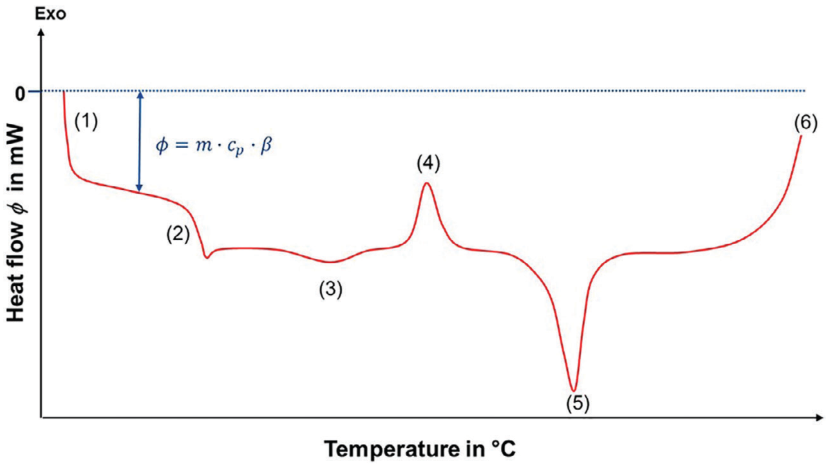

Figure 1.2: Schematic DSC curve with typical thermal events: (1) initial deflection; (2) glass transition; (3) evaporation; (4) crystallization; (5) melting; (6) decomposition.

1.3.2 Temperature-Modulated DSC (TMDSC)

From a physical point of view, the heat flow measured by a DSC consists of two components, namely the sensible and the latent heat flow. The sensible heat flow is driven by changes in the temperature of the test specimen and hence its heat capacity. In contrast, the latent heat flow is related to structural changes in the test specimen, such as phase transitions or chemical reactions. The two heat flow components cannot be separated using conventional DSC. Temperature-modulated DSC (TMDSC) methods make such a separation possible to some extent.

In TMDSC, a temperature modulation is superimposed on the underlying heating rate of a conventional DSC measurement. METTLER TOLEDO offers two types of modulation: alternating DSC (ADSC) and TOPEM™. ADSC is a technique that uses a sinusoidal modulation of the underlying temperature program [2, 3]. TOPEM™ is a more advanced technique that applies a stochastic, i.e., non-periodic temperature modulation, to an underlying temperature program [4, 5, 6].

IsoStep™ is not a temperature-modulated technique in the sense defined above. Instead, it uses a temperature program consisting of a series of short duration (typically around 1 min) isothermal and dynamic segments with low heating (or cooling) rates (typically around 1 K/min). The three techniques are briefly described in the next sections.

ADSC, TOPEM and IsoStep can also be used as quasi-isothermal methods (i.e., with an underlying scan rate of 0 K/min (ADSC/TOPEM), or bouncing between two isothermal temperature levels with slow heating and cooling segments in between (IsoStep).

1.3.2.1 IsoStep

IsoStep™ is a simple method to differentiate between latent and sensible heat flow. A typical temperature program is displayed in Figure 1.3. The data from the dynamic segments is used to determine the heat capacity and thus the sensible heat flow. The data from the isothermal segments yields the latent heat flow.

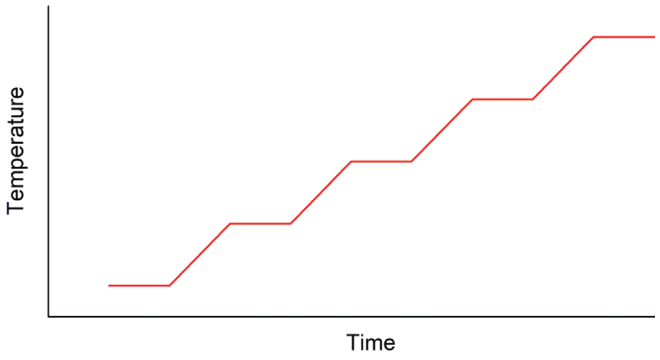

Figure 1.3: IsoStep™ temperature program consisting of different isothermal and dynamic segments. Segment durations are typically around 1 min; the heating (or cooling) rate in the dynamic segments around 1 K/min.

1.3.2.2 ADSC

The temperature program ($T(t)$) of an ADSC experiment can be described by:

$$T(t) = T_0 + \beta_u \cdot t + T_a \cdot \sin\left(\frac{2 \cdot \pi}{t_p} \cdot t\right).$$

Here, T_0 is the start temperature, β_u the underlying heating rate, T_a the temperature modulation amplitude and t_p the duration of the periodically changing temperature, as illustrated in Figure 1.4. For quasi-isothermal measurements, the underlying heating rate is set to zero.

As a result of the temperature modulation, the measured heat flow also changes periodically. The measured heat flow curve can be separated into two components, the underlying signal and the periodic signal. This is shown in Figure 1.5. The moving average of the modulated heat flow over one period yields the underlying signal (this is the "total heat flow"), which corresponds to the conventional DSC curve measured at the same underlying heating rate (see Figure 1.5, lower left).

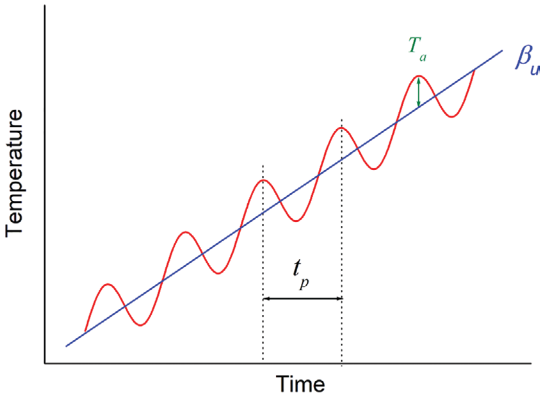

Figure 1.4: Typical ADSC temperature program.

In addition, one obtains the periodic signal component (recorded modulated heat flow curve minus the calculated total heat flow curve, see lower right diagram in Figure 1.5). From this signal, the so-called reversing heat flow is calculated as the heat flow component that follows the heating rate. The difference between the total heat flow and the reversing heat flow is, by definition, the non-reversing heat flow.

The complex heat capacity, $\left|c_p^*\right|$, is calculated according to

$$\left|c_p^*\right| = \frac{A_\phi}{A_\beta} \cdot \frac{1}{m},$$

where A_ϕ and A_β denote the amplitudes of the modulated heat flow and heating rate, and m is the sample mass. The phase angle φ between the modulated heat flow and the modulated heating rate is used to calculate the in-phase heat capacity, c_p^{in}, according to

$$c_p^{in} = \left|c_p^*\right| \cdot \sin(\varphi).$$

The reversing heat flow, ϕ_{rev}, is calculated according to

$$\phi_{rev} = m \cdot \beta_u \cdot c_p^{in}.$$

To obtain the correct reversing heat flow, the phase angle φ must be properly calibrated. It should be noted that different implementations of sinusoidally modulated DSC apply different procedures to calculate the reversing heat flow, and the results for the reversing and non-reversing heat flow depend on the implementation. Only the curves for the total heat flow and $\left|c_p^*\right|$ are independent of the actual implementation. Furthermore, the reversing and non-reversing heat flows do not correspond exactly with the latent and sensible heat flows.

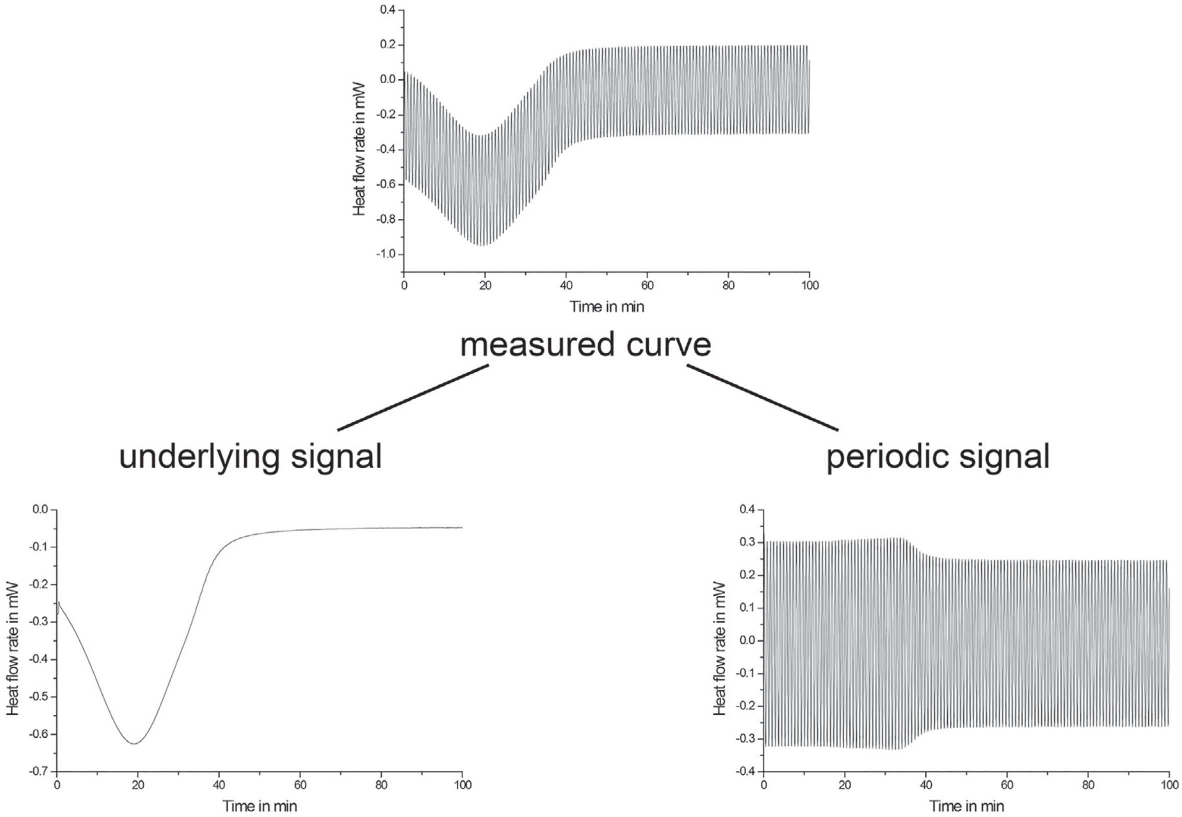

Figure 1.5: Separation of the measured ADSC heat flow curve (top) into the underlying signal (lower left) and the periodic signal (lower right) components.

1.3.2.3 TOPEM

TOPEM™ is a TMDSC technique based on a mathematical analysis of the response of a DSC (including both the apparatus and the sample) to a stochastically modulated temperature program (see Figure 1.6 left and right). As a result, the reversing and non-reversing heat flows are calculated independently, and they refer to the sensible and latent heat flows, respectively. The total heat flow is again calculated by averaging the modulated heat flow. Since the total, reversing, and non-reversing heat flows are calculated independently, TOPEM also allows for a consistency check: the total heat flow must be the sum of the reversing and the non-reversing heat flow. If this is not the case, some assumptions of modulated DSC in general are not met.

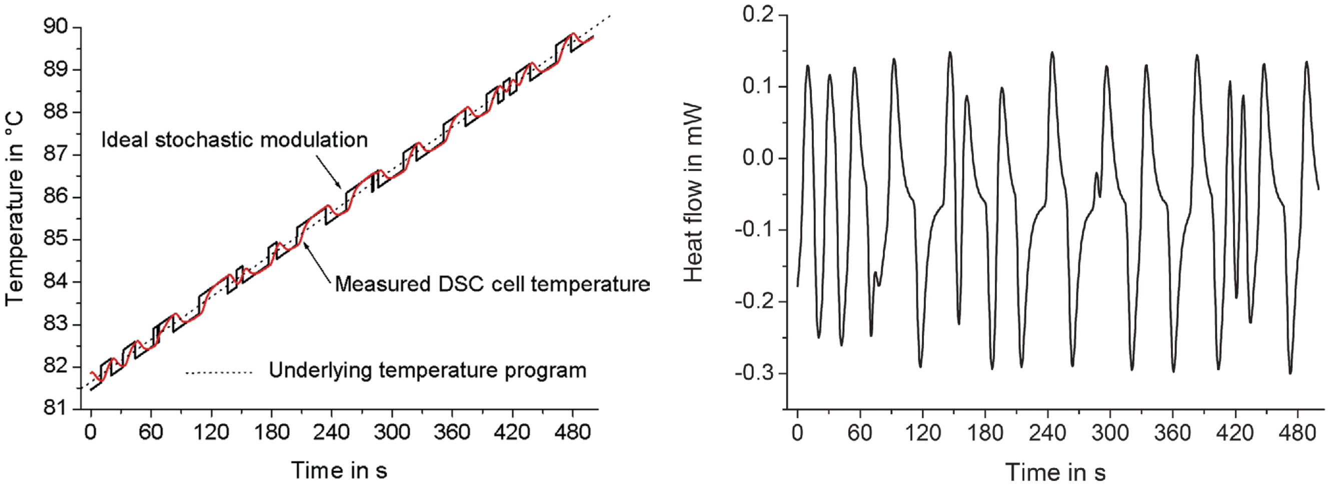

Figure 1.6: Left: The stochastically modulated temperature program against time (black) and the measured temperature response of the DSC cell (red). Right: The measured heat flow against time.

An example of a TOPEM measurement is shown in Figure 1.7. The sample was a pharmaceutical formulation. The upper diagram shows the non-reversing heat flow (blue curve) and two total heat flow curves, which are calculated by averaging the modulated heat flow curve (black) and by adding the evaluated reversing and non-reversing heat flow curves (red). The two total heat flow curves align well, proving that the TOPEM evaluation algorithm properly separates the measured DSC curve into the sensible (reversing) and latent (non-reversing) heat flows.

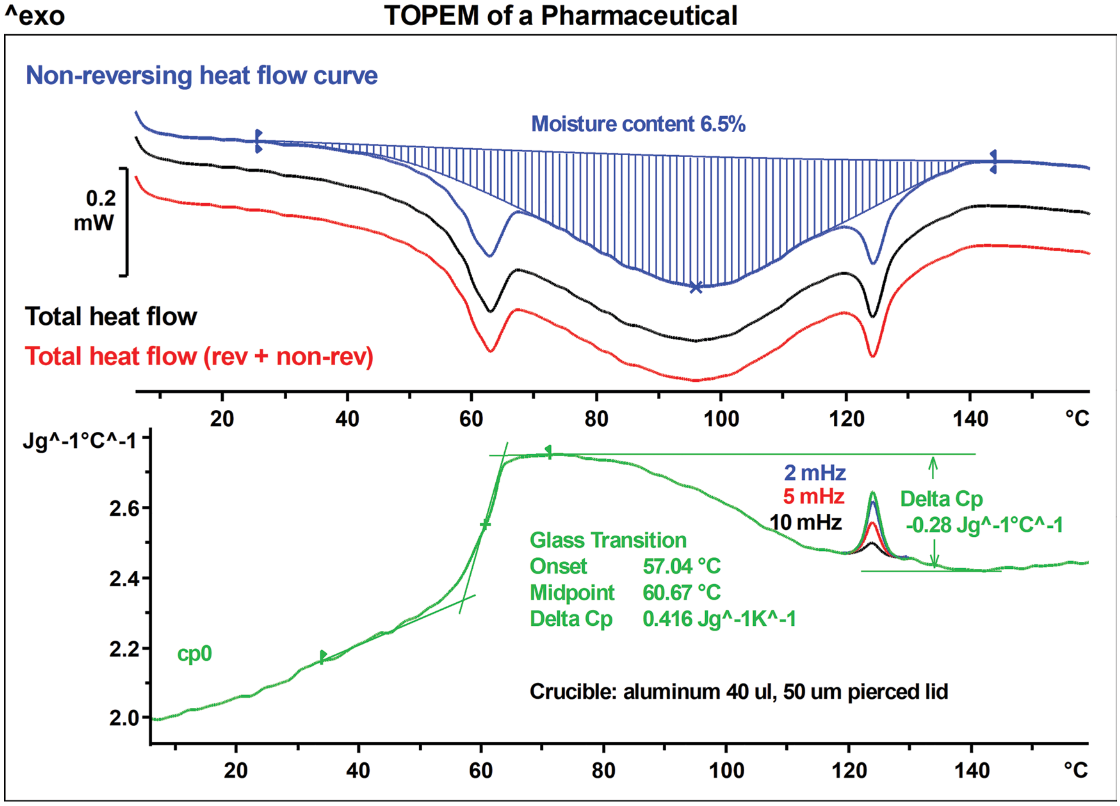

Figure 1.7: Resulting curves of a TOPEM measurement showing a glass transition overlapped by evaporation of water. See S.1.3.2.3 for details.

We observe that both the total and the non-reversing heat flows exhibit a broad vaporization peak that overlaps two sharp peaks at 60 °C and 125 °C. The lower diagram displays the quasi-static heat capacity, c_{p0}, which is equivalent to the quasi-static reversible heat flow, i.e., to the sensible heat flow. It clearly shows a glass transition at around 60 °C. The decrease of c_{p0} up to about 140 °C is due to evaporation of water. The ratio of the measured decrease of the heat capacity (0.28 J/(g K)) and the specific heat capacity of water (4.18 J/(g K)) is an estimate of the mass loss due to release of water (6.7%). This is consistent with the water content calculated from the DSC evaporation peak on the non-reversing (or the total) heat flow curve, corrected for the two overlapping endothermic peaks (green hatched area, 6.5% water content (assumption: evaporation enthalpy of water equals 2248 J/g)).

The first peak on the non-reversing (and the total heat flow curves) is due to an enthalpy relaxation during the glass transition. The second peak is more difficult to explain. With TOPEM, it is also possible to analyze the frequency dependency of thermal effects [7]. This was done for the second peak at 2, 5 and 10 mHz. The results show that the peak temperature is independent of frequency. This indicates that this peak is due to melting of some crystalline compound in the formulation.

In this example, TOPEM and its ability to obtain information on the frequency dependency of a thermal effect in a single measurement is necessary to fully understand the behavior of the sample. Obtaining similar results by ADSC measurements would require measuring the sample at several different frequencies.

1.3.3 High-Pressure DSC (HPDSC)

A high-pressure DSC is an instrument, in which DSC measurements can be conducted at pressures between 10 mbar and 100 bar. This can be used to study the impact of pressure on various chemical reactions such as hydrogenation reactions or to determine the vapor pressure of liquids or melts (ASTM E1782). The METTLER TOLEDO high pressure DSC is technically identical to a standard DSC, embedded within a pressure vessel.

1.3.4 Fast Scanning Calorimetry ("Chip Calorimetry")

DSC instruments can currently operate with maximum heating and cooling rates of around 100–500 K/min (depending on the temperature and specific instruments). However, these rates are not sufficient to mimic technical cooling processes such as casting, where cooling rates between typically 10 K/s and 100 K/s are applied. In failure analysis, it is important to measure the response of the original material, which requires heating rates high enough to prevent reorganization processes. For many materials, potential reorganization can only be suppressed when heating rates of several thousand K/s are applied, leading to the development of so-called chip calorimeters, also known as fast-scanning calorimeters.

The Flash DSC from METTLER TOLEDO is a commercial chip calorimeter [8]. Depending on the mass of the test specimen and the sensor type, maximum heating and cooling rates around 50,000 K/s and 30,000 K/s can be applied. Such high rates are only possible if the signal time constant of the calorimeter (including the test specimen) is in the order of milliseconds. This can be achieved with tiny test specimens and furnaces.

Figure 1.8 shows the most commonly used Flash DSC sensor. The calorimeter is printed on a 2 µm thin membrane embedded in a ceramic support (Figure 1.8, left). Sample and reference are heated individually, and their respective temperatures measured (Figure 1.8, middle). The test specimen is placed directly on the sensor (Figure 1.8, right). The test specimen (and reference) area on the sensor have a characteristic size of 0.5 mm and are coated with aluminum. The reference side is usually left empty. The heated area is the inner square, limiting the maximum size of a test specimen to about 50 µm. The required mass of the test specimen depends on the purpose of the measurement and the scanning rates used. The typical mass for experiments with scan rates of 100 K/s is around 0.5–1 µg. Smaller masses are needed for higher heating rates.

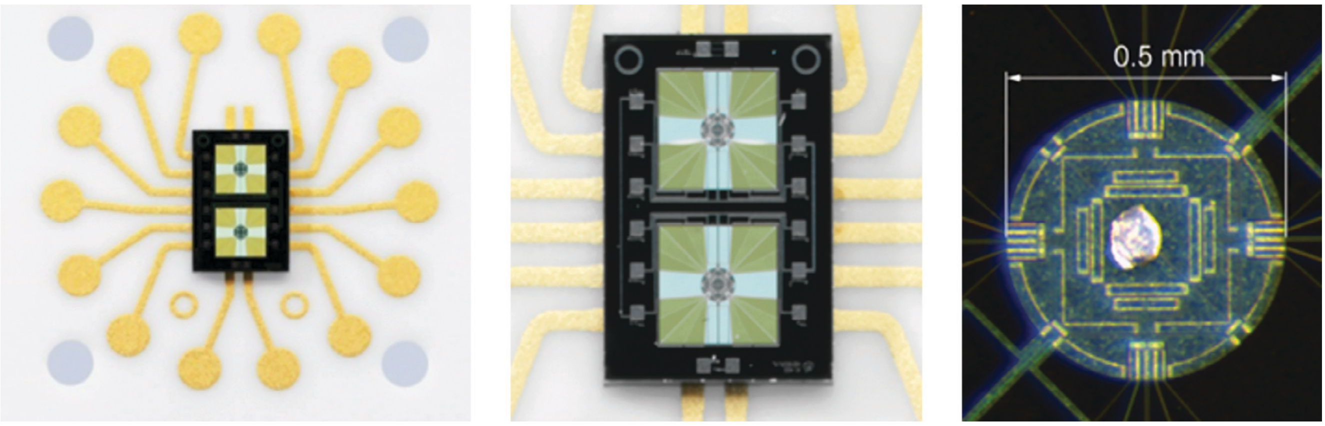

Figure 1.8: Left: Flash DSC sensor; Middle: close up of sample and reference side of a Flash DSC sensor. Right: close up of the sample side with a test specimen on the sensor.

Figure 1.9 presents two DSC curves of amorphous polyethylene terephthalate (PET). The blue curve was measured in a conventional DSC at 10 K/min. As the temperature increases, the sample undergoes several thermal events, including the glass transition, followed by an exothermic cold crystallization peak where the liquid amorphous sample crystallizes, and finally an endothermic melting peak. However, the cold crystallization process involves a structural reorganization of the initial sample, meaning that the DSC curve does not accurately represent the original material after the onset of this peak. To obtain an accurate characterization of the original material, high heating rates are needed to suppress such reorganization processes.

In contrast, the red curve in Figure 1.9 was obtained from a PET test specimen of the same sample using Flash DSC and a heating rate of 60,000 K/min (1000 K/s). At this high heating rate, only the glass transition is observed, indicating that the original material was fully amorphous. The difference in the glass transition temperature between the two curves is due to the large difference between the applied heating rates. Note that the DSC curves have been normalized to the respective heating rate and sample mass.

Some typical applications making use of fast scanning calorimetry are:

- Investigation of reorganization and formation of stable or metastable structures upon heating, cooling or during isothermals.
- Determination of the behavior of the original sample by suppressing reorganization processes.
- Influence of additives such as nucleation additives or fillers on the crystallization behavior.
- Study of relaxation processes in the glassy state.
- Mimicking heating and cooling processes at relevant rates.

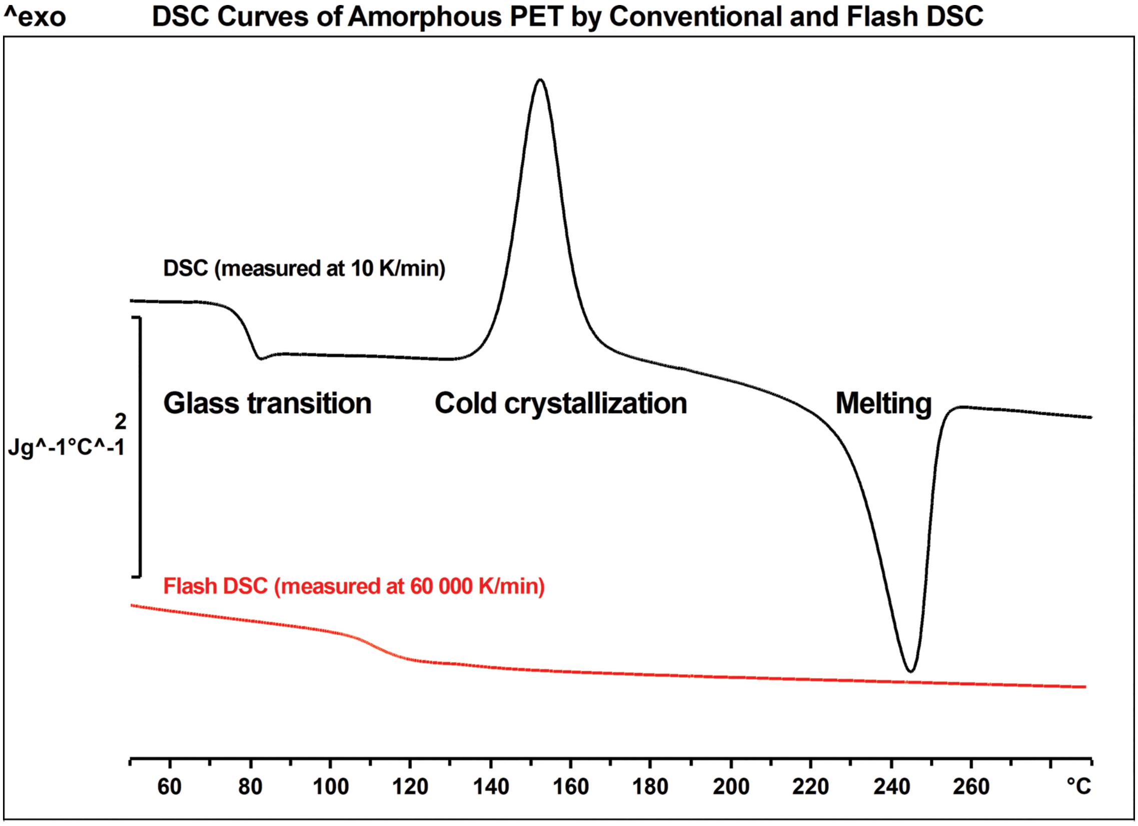

Figure 1.9: Amorphous PET measured by conventional DSC (blue curve) at 10 K/min and by Flash DSC (red curve) at 60,000 K/min. Heat flow is normalized for sample mass and heating rate.

1.4 Thermomechanical Analysis (TMA)

1.4.1 Conventional TMA

Thermomechanical analysis measures the dimensional changes of a sample as it is heated or cooled. In this technique, the position or displacement of a probe resting on the surface of the sample with a certain constant force is continuously measured as a function of temperature (dynamic experiments) or time (isothermal experiments). Figure 1.10 shows typical TMA curves. The pressure exerted by the probe and the stiffness of the sample determine whether the TMA experiment is an expansion or a penetration measurement.

In a thermal expansion measurement, a low force is applied by the probe on the surface of the test specimen. To spread the force uniformly on the test specimen, a disc (made of quartz, sapphire, or aluminum) is usually placed between the test specimen and the probe. The sample is then heated with a constant heating rate over the temperature range of interest. The linear coefficient of thermal expansion (CTE) is calculated as the slope of the measured TMA curve normalized to the initial height of the test specimen. The glass transition of a sample occurs at the temperature at which the TMA curve changes its slope significantly.

In a penetration experiment, the probe exerts a much larger stress (usually no disc is used between test specimen and probe). The softening temperature can be directly measured when the sample is heated. Materials soften at the glass transition temperature or during melting.