Thermal Analysis

Introductory
Handbook

Volume 2

Thermal Analysis in Practice
Tips and Hints

METTLER TOLEDO

Thermal Analysis in Practice
Tips and Hints

Disclaimer

This application handbook presents selected application examples. The experiments described were conducted with the utmost care using the instruments specified in the conditions at the beginning of each application. The results were evaluated according to the current state of our knowledge.

This does not however absolve you from personally testing the suitability of the examples for your own methods, instruments and purposes. Since the transfer and use of an application is beyond our control, we cannot of course accept any responsibility for the use of these methods.

When chemicals, solvents and gases are used, the general safety rules and the instructions given by the manufacturer or the supplier must be observed.

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Preface

Thermal analysis is one of the oldest analytical techniques. Throughout history, people have used simple heat tests to determine whether materials were genuine or fake.

The year 1887 is looked upon as the dawn of present-day thermal analysis. It was then that Henri Le Chatelier, the famous French scientist, carried out his first thermometric measurements on clays.

Just a few years later in 1899, the British scientist Roberts-Austen performed the first differential temperature measurements and so initiated the development of DTA.

Commercial instruments did not however appear until the 1960s. Since then, thermal analysis has undergone fifty years of intense development.

As a result, the use of thermal analysis has expanded into many new research and application fields in different industries. In many cases, the thermal analysis techniques employed to analyze new materials require specific accessories and measurement parameters as well as special sample preparation.

This new handbook is designed to help you navigate through the different measurement techniques, method parameters and sample preparation procedures. The aim is to provide you with useful tips and hints on how to obtain the best possible results from your measurements.

The handbook summarizes the practical knowledge and expertise of our thermal analysis applications team. It is the result of many years of experience obtained from the analysis of an extremely wide range of samples. Detailed information about the tips and hints given here can be found in articles published in past issues our biannual UserCom technical customer magazine.

We hope that the information given in this handbook will help you get the most out of your thermal analysis equipment.

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1. Introduction

1.1 How to use this handbook

The handbook is intended as a compendium of tips and information to help you get reproducible and reliable results in thermal analysis when using DSC, TGA, TMA and DMA. It is of course not possible to cover every aspect of these techniques in this small handbook. More complete and detailed background information is however available in the many references given on the various topics.

The handbook covers all the main topics involved in an analysis. It begins with a general introduction dealing with the choice of the correct measurement technique and is followed by sections on how to design an experiment and an overview of measurement precision. The topics include the sample, experimental parameters, evaluations, calibration and adjustment, and some miscellaneous points.

METTLER TOLEDO offers many different possibilities for studying thermal analysis in more detail through the availability of numerous specialist handbooks, UserCom customer magazines, application notes, webinars, e-training courses or videos. More information on all this can be found at www.mt.com/ta-news.

For an in-depth general introduction to thermal analysis, we recommend our "Thermal Analysis in Practice" handbook.

1.2 Choosing the thermal analysis technique

The thermal analysis technique that can be used to measure a particular property depends on the effect or property you want to measure. The following table gives an overview of the best (🟩) and alternative (🟦) techniques:

	DSC	TGA	TMA	DMA
Physical properties				
Specific heat capacity	🟩	🟦	–	–
Expansion coefficient	–	–	🟩	🟦
Young's modulus	–	–	🟦	🟩
Physical transitions				
Melting and crystallization	🟩	–	🟩	🟩
Evaporation, sublimation, drying	🟩	🟩	–	–
Glass transition, softening	🟩	–	🟩	🟩
Polymorphism (solid-solid transitions)	🟩	–	🟩	–
Liquid crystals	🟩	–	–	–
Purity analysis	🟩	🟦	–	–
Chemical properties				
Decomposition, degradation, pyrolysis, oxidation, stability	🟦	🟩	–	–
Composition, content (moisture, fillers, ash)	🟩	🟩	–	–
Kinetics, reaction enthalpies	🟩	🟩	🟦	🟦
Crosslinking, vulcanization (process parameters)	🟩	–	🟦	🟩

1.3 How to design an experiment

The following diagram gives an overview of how to design an experiment. The individual steps in the process are not independent of one another – for example, sample preparation might need to be reassessed after the measurement results have been evaluated [UC 21/1].

♦ The most important point before beginning an analysis is to be absolutely clear about the property you want to measure and the results you hope to get.
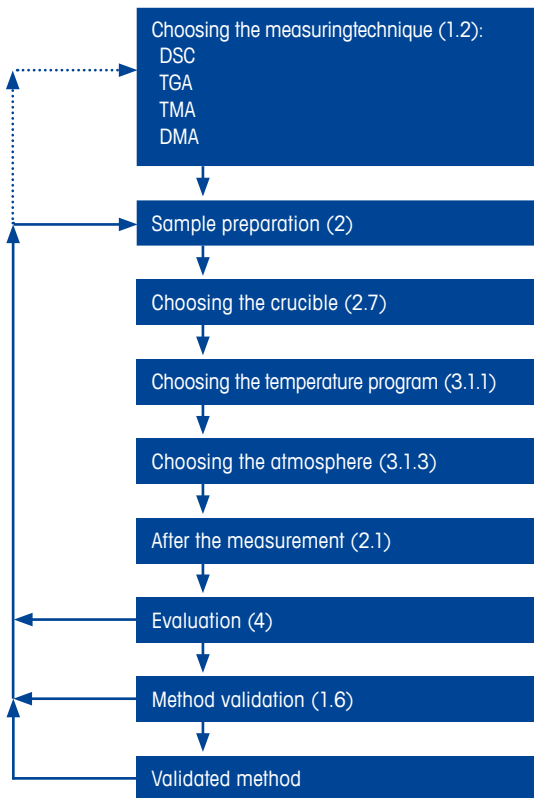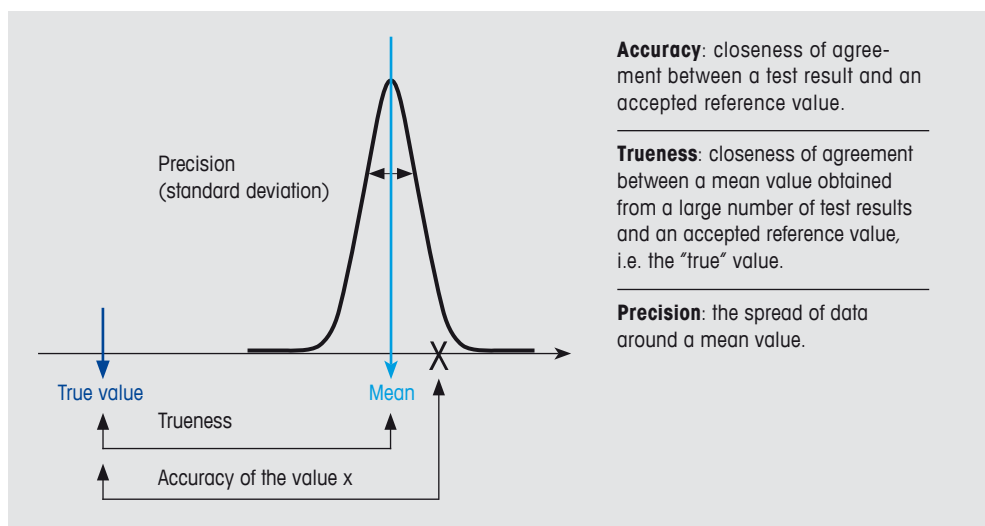
♦ A more detailed description of the steps involved in the process is given in different chapters and sections of this handbook. The relevant chapter and section numbers are enclosed in brackets after the names of the steps.
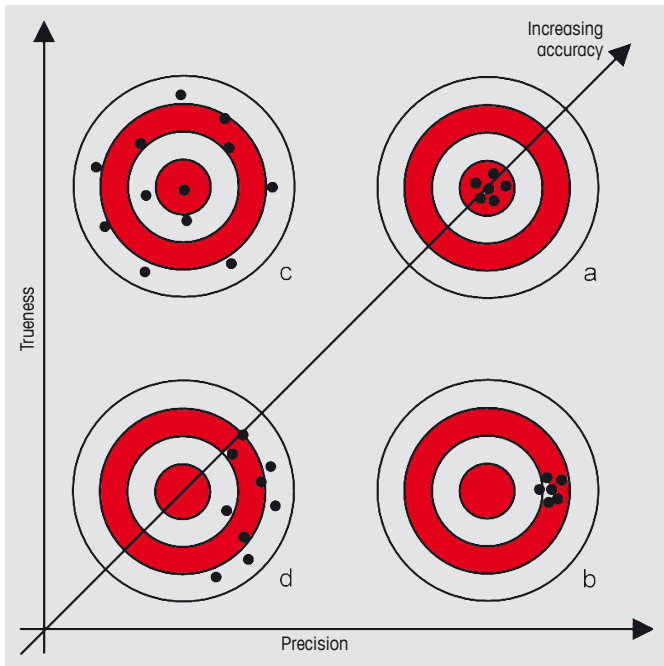
```
Choosing the measuringtechnique (1.2):
    DSC
    TGA
    TMA
    DMA
        ↓
Sample preparation (2)
        ↓
Choosing the crucible (2.7)
        ↓
Choosing the temperature program (3.1.1)
        ↓
Choosing the atmosphere (3.1.3)
        ↓
After the measurement (2.1)
        ↓
Evaluation (4)
        ↓
Method validation (1.6)
        ↓
Validated method
```

1.4 Precision, accuracy, trueness

♦ For a detailed description of method validation, accuracy, repeatability, measurement errors and other issues related to the quality of data, please consult our "Validation in Thermal Analysis" handbook [www.mt.com/ta-handbooks]. This handbook gives an in-depth description of the terminology used and discusses many examples of DSC, TGA, TMA and DMA analyses.

♦ A shorter summary entitled "Precision, accuracy, trueness" is given in [UC 29/1].

Precision
(standard deviation)

True value

Mean

Trueness

Accuracy of the value x

Accuracy: closeness of agreement between a test result and an accepted reference value.

Trueness: closeness of agreement between a mean value obtained from a large number of test results and an accepted reference value, i.e. the "true" value.

Precision: the spread of data around a mean value.

Using the above terminology, we can now classify results as follows:

a Precise, true and accurate.

b Precise, untrue and inaccurate.

c Imprecise, true and inaccurate.

d Imprecise, untrue and inacurate.

1.5 Uncertainty of measurement
The total measurement uncertainty is made up of all the possible errors involved in the individual steps of the analysis. For example, the influence factors shown in the cause-and-effect (or fishbone) diagram play a role in the measurement of the enthalpy of fusion by DSC.
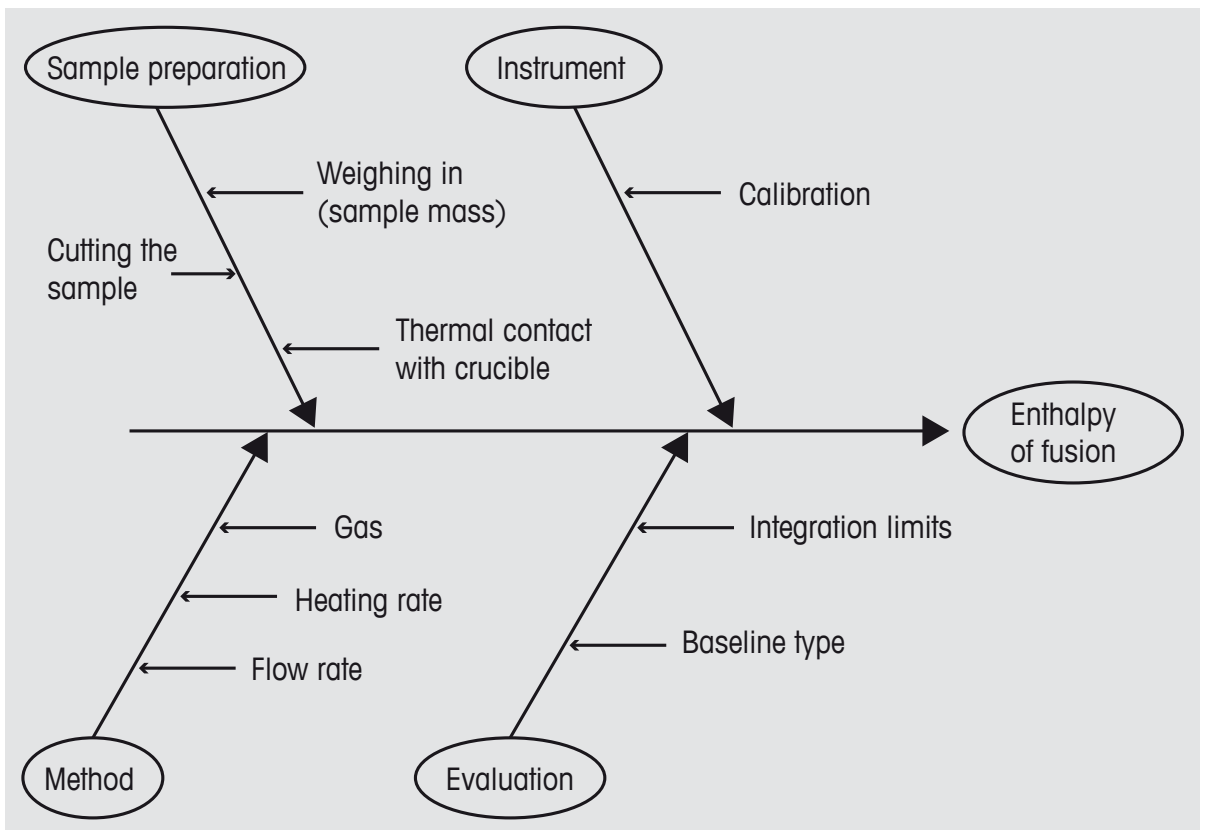
Estimates for the individual contributions of uncertainty for this example are given in the table below:

Source	Uncertainty of measurement
Mass of the test specimen	±20 µg (e.g. reproducibility of the balance; if the mass is about 10 mg, this corresponds to ±0.2%)
Putting the substance into the crucible	negligible
Thermal contact with the crucible	±0.5% (estimate)
Heating rate	negligible
Gas and gas flow	negligible if the instrument has been adjusted under the same conditions as the measurement
Adjustment	±1.5% (uncertainty of the calibration material)
Integration limits and baseline type	±3% (statistics of repeated evaluations)

The contributions can then be added together according to the rules of propagation of uncertainty to obtain a value for the combined uncertainty:

$$\pm\sqrt{(0.2\%)^2 + (0.5\%)^2 + (1.5\%)^2 + (3\%)^2} = \pm3.4\% \ (p_c = 68\%)$$

♦ A more detailed description of measurement uncertainty can be found in [UC 30/1].
♦ For TGA measurements, it is important to be aware of the minimum sample weight according to USP when measuring very small sample masses or residues. A complete description of the influence of the minimum weight of a balance specifically for TGA is given in [UC 41/14].

1.6 Method validation

There are three ways to obtain validated analytical methods; the details are summarized in the table below.
For a detailed description of method validation, please refer to our "Validation in Thermal Analysis" handbook.
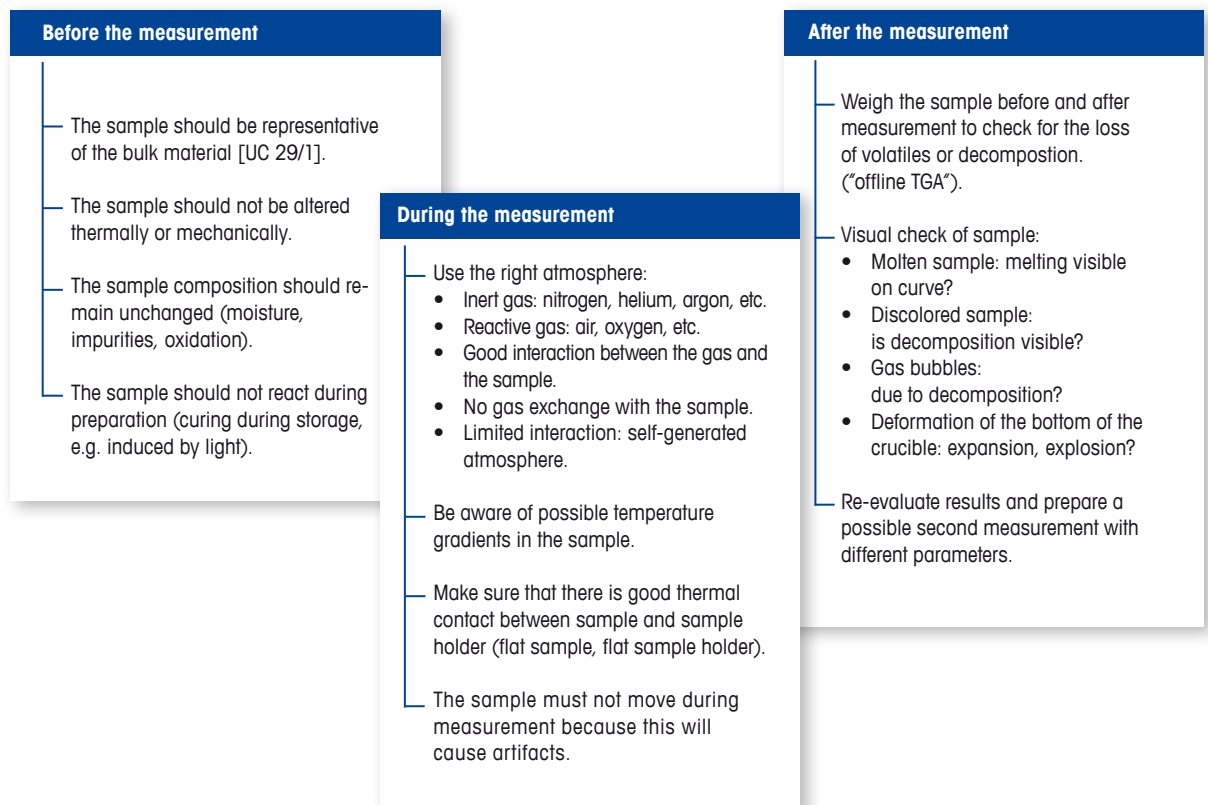
Analytical method validation	Inter–laboratory studies	International standards
• The method is designed from the very beginning by the user and tested for the relevant variables (e.g. operator, sample preparation, instrument, environment, accuracy, repeatability). Several iterations to optimize the method parameters might be needed. • The method is exactly that required by the user. • Validation of the method can take a long time.	• A specific analytical method is tested by all the participating labs using multiple specimens. The results are submitted to a central organizing body that evaluates the data and issues recommendations for the expected accuracy of the method. • A large amount of data can be obtained relatively quickly. • Reproducibility (repeatability between different labs) can also be tested.	• A published method can be used as it is described. The accuracy and precision to be expected are given in the standard documentation. • This is the easiest way to obtain a validated method. • The method might not fully meet the requirements or might not include particular tests. • Many international standards are available, for example from ISO, ASTM, and so on. See Chapter 20 in the "Thermal Analysis in Practice" handbook for a complete list of standards relevant to thermal analysis.

2 Samples

This chapter describes sample-specific issues. We will begin by discussing some general requirements for sample preparation that apply to DSC, TGA, TMA and DMA. Afterward, we will focus on the sample requirements for individual instruments. We will then finish with sample containers and sample holders, that is, with crucibles for DSC and TGA, and clamping assemblies for TMA and DMA.

2.1 General requirements for samples
Some of the requirements for the sample and sample preparation are common for DSC, TGA, TMA and DMA:

Before the measurement

— The sample should be representative of the bulk material [UC 29/1].

— The sample should not be altered thermally or mechanically.

— The sample composition should remain unchanged (moisture, impurities, oxidation).

— The sample should not react during preparation (curing during storage, e.g. induced by light).

During the measurement

— Use the right atmosphere:
  • Inert gas: nitrogen, helium, argon, etc.
  • Reactive gas: air, oxygen, etc.
  • Good interaction between the gas and the sample.
  • No gas exchange with the sample.
  • Limited interaction: self-generated atmosphere.

— Be aware of possible temperature gradients in the sample.

— Make sure that there is good thermal contact between sample and sample holder (flat sample, flat sample holder).

— The sample must not move during measurement because this will cause artifacts.

After the measurement

— Weigh the sample before and after measurement to check for the loss of volatiles or decompostion. ("offline TGA").

— Visual check of sample:
  • Molten sample: melting visible on curve?
  • Discolored sample: is decomposition visible?
  • Gas bubbles: due to decomposition?
  • Deformation of the bottom of the crucible: expansion, explosion?

— Re-evaluate results and prepare a possible second measurement with different parameters.

For further information, see the following literature: [UC 3/1] [UC 29/1].

♦ To check the temperature gradient in the measured sample, place a piece of indium above and below the sample and measure the temperature difference by means of the two onsets (DSC, TGA, TMA, DMA).

♦ To prevent moisture entering the sample during the waiting time on the robot table, use the lid piercing accessory (DSC, TGA) [UC 20/17].

2.2 Sampling

Several important points should be considered during the sampling process. These include:

- Which production lots should be examined?
- At which point or points of a production lot or from which part or parts of a production lot should samples be examined?
- Are the sampling point and the sample size representative of the production lot with regard to possible inhomogeneity? Does the selected sample allow us to draw conclusions about the bulk sample?
- How large should the sample size be with regard to volume and number of items?
- How often should a material property be determined and how many samples should be measured?
- Are the samples taken at different points and then mixed together again to form a composite sample (or aggregate sample) or are they processed separately as test samples?
- Are the samples always representative of the bulk material from which they were taken?

The diagram shows an example of a typical sampling procedure [UC 29/1]:
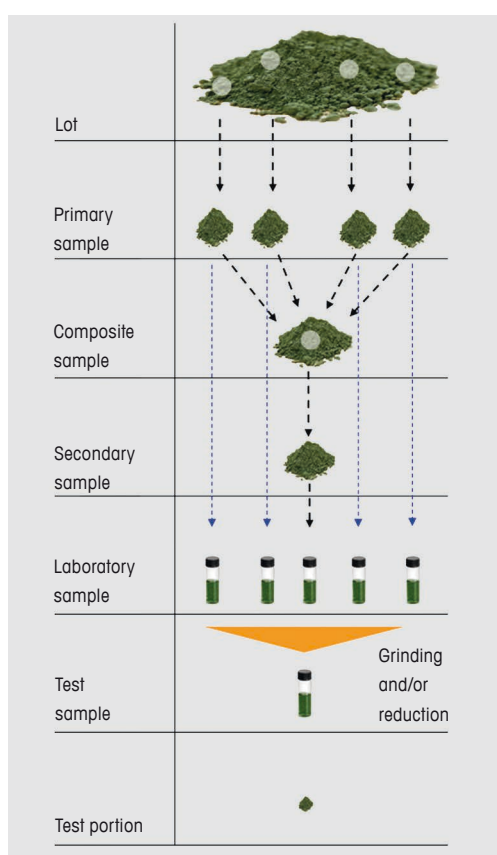
2.3 DSC samples

2.3.1 Sample size

The recommended sample amounts for DSC measurements are:

Organic samples	2 to 10 mg
Inorganic samples	5 to 50 mg
Samples with strong exothermic effects	0.5 to 1 mg
Unknown samples	0.5 to 1 mg

Use larger sample amounts:
- to detect weak effects,
- to measure filled or diluted samples,
- for measurements at low heating rates.
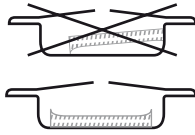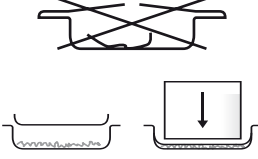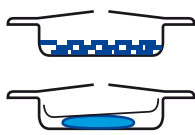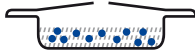
Use smaller sample sizes:
- for measurements at high heating rates.

2.3.2 How to fill a crucible

The best way to insert different types of samples into DSC crucibles is shown in the table below:

Sample type	Sample preparation	Example
Fine powders and liquids	Spread the sample as evenly as possible over the bottom of the crucible. Powders: use the funnel supplied with your DSC instrument to prevent grains of powder soiling the rim of the crucible. Liquids: transfer the sample with the aid of a spatula, syringe or needle (shake suspensions before sampling).	
Flat disks	Place a flat disk on the bottom of the crucible.	
Samples with rough edges	Insert the sample with the flat side facing downward to ensure optimum contact with the crucible.	
Films **Fibers** **Other soft or light samples**	Movement of a light sample in the crucible can be restricted by placing the lid of a 20-µL light aluminum crucible on top of the sample to secure it in place.	
Fibers **Films**	Cut the film or fiber into small pieces and place them on the bottom of the crucible. Wind the fiber around a pair of tweezers, wrap the resulting fiber coil in a piece of aluminum foil and use the lid of a 20-µL light aluminum crucible to press the sample down onto the bottom of the crucible.	
Hard and coarse samples	Grind any coarse samples to a fine powder in a mortar. Make sure that the mechanical force does not induce any changes in the sample, for example polymorphic transitions.	
Exothermic samples **(e.g. explosives)**	Dilute the sample with an inert substance such as Al_2O_3 powder to prevent auto-acceleration and to absorb the energy released during the exothermic reaction.	

♦ When performing measurements above 150 °C, make sure you punch a small hole in the crucible lid to prevent the crucible from exploding due to sample evaporation.

♦ Make sure that the bottom of the crucible remains flat when the crucible is sealed in the crucible press (do not overfill the crucible!). A flat bottom guarantees good thermal contact between the crucible and the sensor and results in an optimum signal.

The following points are important for the reference crucible:
- The reference crucible should be of the same type as the sample crucible.
- If dilute systems are measured, the reference crucible can be filled with an inert substance to compensate for the heat capacity of the sample matrix. The amount of inert substance (e.g. aluminum oxide) placed in the reference crucible should produce about the same heat flow as the sample matrix [UC 25/21]. See Section 3.2.3 for an example.
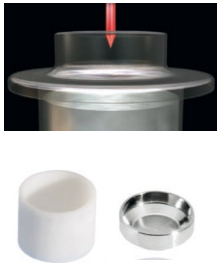
2.4 TGA samples

2.4.1 Sample size
Most TGA measurements are performed using sample amounts of 1 to 30 mg, very often about 10 mg. Smaller and larger masses can of course be used.

◆ TGA measures the mass loss of the individual constituents of a mixture. This means that the most important mass is the mass of the minor constituent, that is, the constituent you want to measure. Its mass should be greater than the minimum weight of the balance used. See for example UserCom [UC 41/14] about USP minimum weight, [UC 21/1] for a calculation example, or the "Validation in Thermal Analysis" handbook [www.mt.com/ta-handbooks].

◆ Use sample masses that are as similar as possible to measure a series of samples or to compare different samples. This eliminates the possibility of artifacts due to samples of different size. If samples of different sizes have to be compared [UC 12/17] and onset temperatures are important, use absolute scaling. (See Section 4.1 for an example).

2.4.2 How to fill a crucible
Most samples can be prepared in the same way as for DSC (see Section 2.3.2).
The table below refers specifically to TGA sample preparation.

Sample type	Sample preparation	Example
Powders	Spread powders evenly over the bottom of the crucible; do not overfill. Use just enough material to observe the effects that you want to measure.	
Liquids	Liquids will generally already start to evaporate during sample preparation. To prevent this or to take it into account: • Use aluminum crucibles that can be hermetically sealed and use the lid piercing kit to open the crucible just before measurement. • Use aluminum oxide crucibles with an aluminum lid and program the robot to remove the lid just before the measurement (the crucible is not as tight as the previous option). • Determine the mass of the sample just before the start of the measurement. To do this, you need to know the mass of the crucible and the balance should be able to equilibrate (i.e. sample evaporation should not be too fast). In this case, the starting mass will not be 100%!	
Films and fibers	Can be cut in small pieces and placed in the crucible. Films can be cut in long strips, wound around the tip of a pair of tweezers and placed in a crucible. The film will expand out to the sides of the crucible. A length of fiber can also be wound around a pair of tweezers and the resulting ball placed inside the crucible.	
Foaming materials	Measure materials that foam using the aluminum oxide lid with the pre-drilled hole to stop foam overflowing over the rim of the crucible. Additionally, if space is available on the sensor, a larger, second crucible can be used to surround the first crucible and collect the material that overflows. ◆ If a sudden increase in mass is observed on the TGA curve, the foam has come into contact with the top of the furnace! ◆ If foaming is expected, a sample can be prepared and heated externally with a small burner to monitor the process and avoid damage to the balance.	
Explosive materials	Only use small sample amounts in order to minimize the recoil of the sensor and to prevent damage to the balance. Limit auto-acceleration in the sample by surrounding the sample with inert aluminum oxide powder.	

The aluminum oxide lid with the pre-drilled hole can also be used to prevent sample material jumping out of the crucible and thereby contaminating the TGA sensor.

2.5 TMA samples

General sample preparation for bulk samples:

- Samples should have parallel surfaces.
- Samples should not be more than 10 mm in height (20 mm with the shorter rest pictured (a) below).
- The surfaces of samples should be as smooth as possible.
- Use silica spacer disks to separate sticky samples or samples that decompose from the probe and sample support (b).

◆ CTE measurements should be performed with as little force as possible to avoid sample compression. The applied force can be spread over the whole sample surface area by using silica disks (b).

◆ A sample size of about 5 mm is needed in order to measure the CTE with a good accuracy.

(a)   (b)
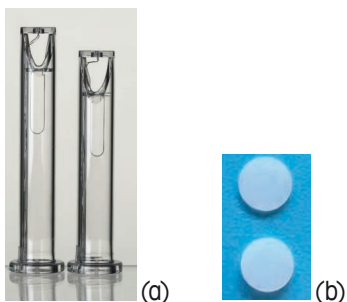
2.6 DMA samples

The following points should be taken into account for DMA samples:

- The sample geometry must be accurately known. Any inaccuracy in the sample dimensions results in a large error in the modulus. Use smooth and parallel surfaces only.
- The stiffness of the sample must be at least 3 to 5 times less than the stiffness of the clamps and the instrument. If this is not the case, the modulus that is measured will be too low. A calculator for sample stiffness can be found at: www.datacomm.ch/mschubnell.
- The sample must be clamped correctly (sufficiently tightly but not overstressed); otherwise the movement of the sample in the clamp is measured and not the actual deformation of the sample. In this case, the modulus that is measured will be too small.
- Samples that are clamped above the glass transition temperature and then cooled to below the glass transition should be re-clamped at the start temperature.
- The thermocouple must be carefully and reproducibly positioned – temperature differences of up to 5 K between measurements can occur if the position of the thermocouple is not exactly the same. See Section 5.5.2. for an example.
- The thermocouple must not touch the sample or the furnace.
- Be aware of the clamping direction for non-isotropic samples.

Instructions for sample preparation in the DMA shear mode can be found in [UC 29/14] and [UC 34/15].

2.7 Crucibles

Crucible requirements:

- The crucible material must be inert and not show any effects in the measured temperature range.
- The melting point of the crucible must be higher than the effects that you want to observe in the sample.
- Crucibles must be inert to the sample and its end products in the applied temperature range unless a catalytic effect is desired, for example:
  - oxidation measurements with copper crucibles, or
  - chemical reactions using platinum crucibles.

♦ Samples that do not contain volatile constituents are usually measured in 40-µL standard aluminum crucibles with a pierced lid (this can also be used for TGA/DSC measurements up to 640 °C!).

♦ Crucibles with pin cannot be used in the sample robot.

♦ Check the weight before and after measurement. If the difference is less than 30 µg, the crucibles have held tight.

♦ In TGA measurements, the height-to-width ratio of crucibles influences diffusion, see [UC 9/22].

♦ Information about sample atmospheres can be found in Section 3.1.3.

Background information about crucibles is given in [UC 5/3].

The table below presents an overview over the individual DSC and TGA crucibles (see also www.mt.com/ta-crucibles):
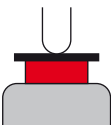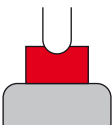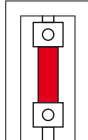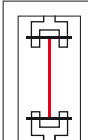
Type of crucible	Remarks	Picture
Standard aluminum crucible **max. temp: 640 °C** **40 µL (also 25, 100 and 160 µL)** **(DSC, TGA, TMA, e.g. for curing liquids)**	• This is the most frequently used crucible. • Available with or without a pin. • Can be sealed hermetically, available with a 50 µm hole or larger hole in the lid (see also Section 3.1.3).	
Light aluminum crucible **max. temp: 640 °C** **20 µL** **max. temp: 640 °C** **(DSC, TGA)**	• This crucible has the shortest time constant. • It can be used with a lid to compress flexible samples (films, fibers, powders). • A self-generated atmosphere is produced with a closed lid. The crucible is not hermetically sealed. • The lid can also be pierced to improve gas contact.	
Copper crucible max. temp: 750 °C **40 µL (DSC)**	• It can be used to provide a catalytic effect for oxidation studies. No lid is available.	
Gold crucible **max. temp: 750 °C** **Gold-plated crucible** **max. temp: 350 °C** **40 µL (DSC)**	• This is a very inert crucible. ♦ Cold welding is more difficult after long storage times – heat to 500 °C before use. ♦ Molten metal samples can form alloys and create holes in the crucible.	
Platinum reusable crucible **max. temp: 1600 °C** **30, 70, 150 µL** **(TGA, DSC)**	• This is used for good quality heat flow measurements at temperatures above 640 °C. • It can also be used as to promote catalytic effects. ♦ Use sapphire spacer discs for platinum-platinum contact above ~1000 °C (e.g. DTA sensor of TGA/DSC) in order to avoid welding or fusion. ♦ Molten metals can form alloys and create a hole in the crucible. Be aware of platinum poisons such as tin, lead, zinc, aluminum, silver, gold, phosphorus, arsenic, antimony, bismuth, silicon, boron, free carbon and salts or oxides of heavy metals (reduction of salts to metals at high temperatures).	
Medium-pressure crucible made of stainless steel **Max. temp: 250 °C**	• Needs special dies (male-female) for the crucible sealing press. • It can be closed without an O-ring for measurements in a self-generated atmosphere.	

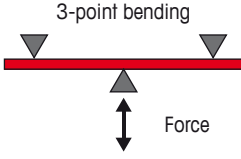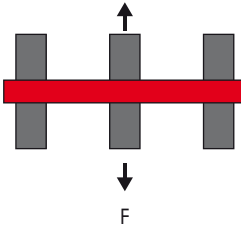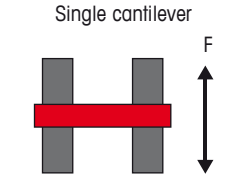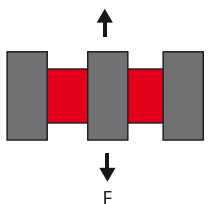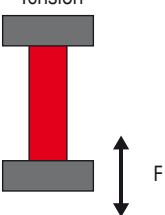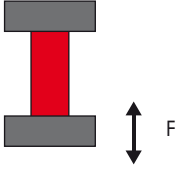| Type of crucible	Remarks	Picture
High-pressure crucible made of gold-plated steel **Max. temp: 400 °C** **25, 40 µL (DSC)** **Various other high-pressure crucibles are available.**	• Used for safety measurements and to suppress overlapping effects (e.g. vaporization). • Special toggle press is needed with die. • The lid is pressed into the crucible with a force of about 1 metric ton so that a membrane, which serves both as seal and burst disk, seals the crucible tightly (weigh the crucible before and after measurement to check that it remains tight).	
Aluminum oxide crucible **Max. temp: 2000 °C** **30, 70, 150, 300, 600, 900 µL** **(TGA, DSC)**	• Most frequently used crucible for TGA measurements and is available in different sizes. • It can be used with a pierced alumina lid. • Aluminum lids are available for unstable samples. • Reusable. • It can be used over the complete temperature range but be aware of interactions at very high temperatures.	
Sapphire/PCA crucible **Max. temp: 2000 °C** **70 µL (TGA, DSC)** **(TGA, DSC)**	• For melting metals (Fe, Ni). • Non-porous. • Reusable.	
Oxidation 3-point ceramic support **Max. temp: 2000 °C** **[UC 34/9] (TGA)**	• Only for use with solid samples. • Ideal for exposing the maximum surface area to the furnace atmosphere (e.g. in oxidation studies).	

2.8 Clamping assemblies

The TMA and DMA instruments do not use crucibles – the sample is clamped directly in the instrument by means of different clamping assemblies. The assembly used depends on the sample geometry and the property being measured.

For TMA: The table shows the deformation modes used to measure the properties of different types of materials [TMA E-Learning course, www.mt.com/ta-etraining].

|	TMA measurement modes				
	Dilatometry	Penetration	Bending	Tension	Tension
	 Bulk Films	 Bulk Coatings	 Bars	 Films	 Fibers
Effect					
Expansion, shrinkage	✓	✓	X	✓	✓
Glass transition	✓	✓	⌇⌇	✓	✓
Melting	✓	✓	✓	✓	✓
Polymorphism	✓	✓	X	X	X
Decomposition	✓	✓	X	✓	✓
Swelling	✓	X	X	X	X
Viscous flow, creep	✓	✓	✓	✓	✓
Curing, hardening	X	⌇⌇	⌇⌇	X	X
Young's modulus	⌇⌇	X	⌇⌇	⌇⌇	⌇⌇
Stress/Strain	✓	X	✓	✓	✓
	✓ is possible		X is not recommended		⌇⌇ DLTMA

For DMA: The table shows details of the deformation modes used to measure the properties of different types of materials [UC 23/1].

Modes	Advantages	Comments	Applications	Modulus measured
3-point bending Force	It yields very accurate modulus values for hard samples. A large range of sample dimensions is possible.	It requires an offset force. It puts high demands on sample preparation (parallel flat surfaces).	Samples with small modulus changes (composites, etc.). All glassy materials.	Young's modulus (E' and E'')
Dual cantilever F Single cantilever F	A large range of sample dimensions is possible.	The sample length is not well-defined. Thermal expansion of the sample leads to horizontal stresses in the sample holder. This results in artifacts in the measurement curves.	Samples that soften, for example during a glass transition. Thermoplastics. Composites.	Young's modulus (E' and E'')
Shear F	This is the only mode that yields the shear modulus. High frequencies are possible.	In general, it corresponds to the true deformation of materials in practical situations. The sample is held in place only by friction. The sample needs reclamping after cooling.	All polymers. Powders (as pressed tablets). Pastes. Viscous liquids (e.g. bitumen, waxes, oils).	Shear modulus (G' and G'')
Tension F	Yields the most accurate modulus values (Young's modulus). Easy to calculate the geometry factor.	Requires an offset force. High modulus values can be determined with suitable sample geometry.	Films and fibers. Thermoplastics. Elastomers are also possible.	Young's modulus (E' and E'')
Compression F	Is the only way to determine the Young's modulus of foams. It is easy to calculate the geometry factor.	Requires an offset force. Unsuitable for stiff samples.	Foams made from polymeric materials. Elastomers are also possible.	Young's modulus (E' and E'')

For small deformations of isotropic materials, the relationship between the shear modulus and Young's modulus is:

$$G = \frac{E}{2(1+\mu)}$$

Where μ is Poisson's ratio, with a value between 0 and 0.5. This means that E is generally 2 to 3 times greater than G (for isotropic materials). See the "Thermal Analysis in Practice" handbook, p 194 ff.
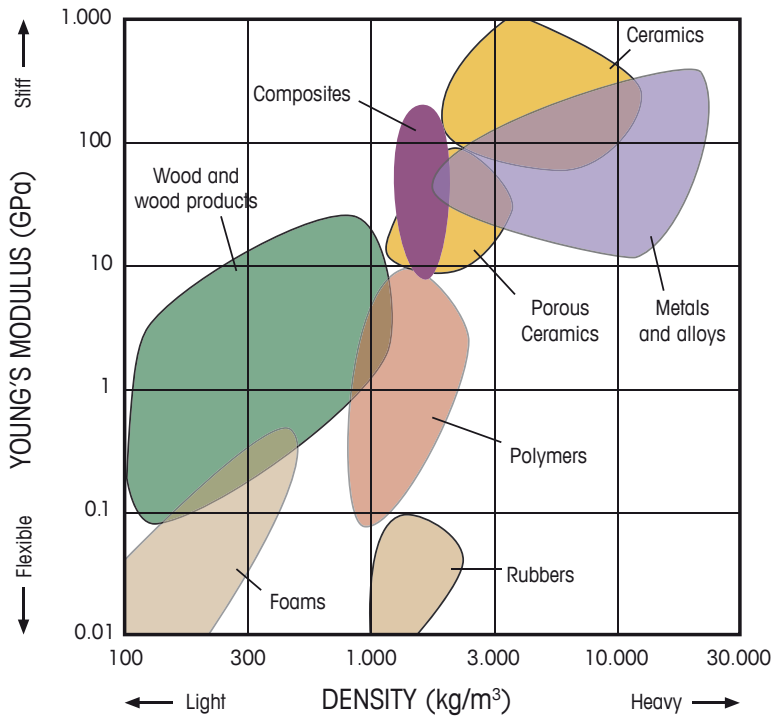
Some modulus values of well-known materials:

Diamond	1 000 000 MPa
Al$_2$O$_3$	380 000 MPa
Steel	210 000 MPa
Poly-paraphenylene terephthalamide (DuPont™ Kevlar®)	130 000 MPa
Silicon	128 000 MPa
Aluminum	70 000 MPa
Glass	70 000 MPa
PET	4 000 MPa
Polyamide (DuPont™ Nylon®)	2 000 MPa
PTFE	500 MPa
LDPE	100 MPa
SBR	10 MPa
Silicone oil	1 MPa

from www-materials.eng.cam.ac.uk/mpsite/interactive_charts/stiffness-density/NS6Chart.html

3 Experiments

3.1 Method parameters

A step-by-step description of method development can be found in the "Thermal Analysis in Practice" handbook, Chapter 19, in the "Validation in Thermal Analysis" handbook, Chapter 4, Part 2, and in various UserCom articles, for example [UC 21/1], [UC 22/1] and [UC 23/1].

3.1.1 Temperature range

Start temperature (DSC example)	End temperature (DSC example)
The measurement should begin about 3 minutes before the first thermal effect of interest occurs in order to allow for instrument settling time. If the applied heating rate (β) is 10 K/min, this gives a start temperature of 3 (min) x 10 (K/min), or 30 K below the first thermal effect. This allows a flat baseline to be recorded before the effect occurs.	The measurement should be terminated about 2 minutes after the last thermal effect of interest has occurred. If the applied heating rate is 10 K/min, this gives an end temperature that is 2 (min) x 10 (K/min), or 20 K higher than the last thermal effect. This allows a good baseline to be recorded for the evaluation.

◆ The start and end temperatures depend on the instrument settling times and the applied heating rates.
◆ The temperature range (K) before and after the first and last effects is given by the instrument-dependent equilibration time (min) x the heating rate (K/min), as shown in the above example.
◆ The temperature range can be reduced by decreasing the heating rate (for example if no actively cooled instruments are available). If the heating rate is increased, the temperature range will also have to be increased.

The settling times of the individual instruments are approximately:

DSC	TGA	TMA	DMA
1 min	3 min	6 min	7 min
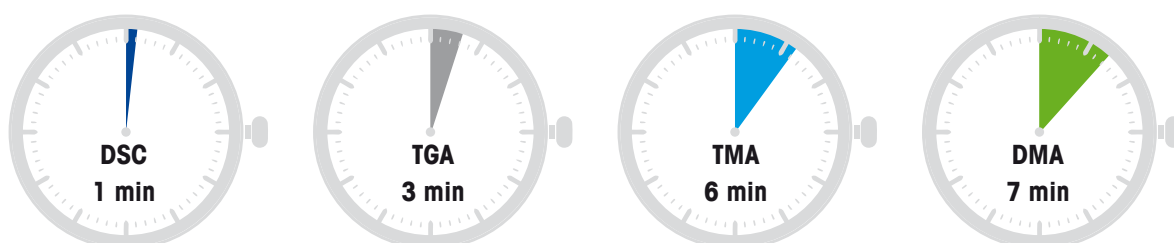
◆ When unknown samples are investigated, it is best to cover a wide temperature range (using the lowest start temperature and a high end temperature) in order to obtain a complete overview of the sample effects. Decomposition of the sample should be avoided whenever possible in DSC, TMA and DMA measurements.

3.1.2 Heating and cooling rates

DSC	TGA	TMA	DMA
• Normal heating rates: 10–20 K/min • For highly exothermic materials: 1 K/min • For temperature-modulated techniques: 1–2 K/min.	• Normal heating rates: 10–30 K/min • Higher or lower heating rates for special applications.	• Normal heating rates: 2–10 K/min, typically 5 K/min.	• Normal heating rates: 2–5 K/min, typically 3 K/min.

◆ The cooling rates that can be achieved depend on the specific instrument configuration, for example whether air cooling, cryostat cooling, an IntraCooler, or liquid nitrogen cooling is available.

Influence of higher or lower heating rates:

Higher heating rates	Lower heating rates
• Resolution is poorer. • Signal-to-noise ratio is better. • Temperature gradients in samples are larger. • Smaller samples can be measured. • Measurement time is shorter.	• Resolution is better. • Signal-to-noise ratio is poorer. • Temperature gradients are smaller. • Larger samples can be measured. • Measurement time is longer.

Influence of heating rate on measured effects: The influence of the heating rate depends on the type of effect that is being measured. An overview of how the different effects change with heating rate is given below (all the curves were measured by DSC; only some of the changes are observed with TGA, TMA or DMA).

Further background information can be found in [UC 23/20] (variation of the heating rate in TGA and DSC, measurements of melting and decomposition). The effect of the variation of heating and cooling rates on DSC, FDSC and TGA measurements is discussed in [UC 39/1]. The influence of the heating rate on melting is also discussed in [UC 2/1].

Effect	Example
Chemical reactions Chemical reactions shift to higher temperatures with increasing heating rates. The example shows DSC curves of the curing reaction of an epoxy resin measured at three different heating rates. The peak width and signal-to-noise ratio increase with increasing heating rate.	
Glass transition The glass transition temperature shifts to higher temperatures with increasing heating rates. The example shows DSC curves of the glass transition of polystyrene measured at four different heating rates. The signal-to-noise ratio increases with increasing heating rate.	
Reorganization Reorganization processes can be suppressed by using higher heating rates. This depends on the rate of reorganization of the particular material and the heating rates used. The "Flash DSC" webinar presents further information on metastable materials. See www.mt.com/ta-ondemand.	

◆ Variation of the heating rate can also be used to separate overlapping effects.
See Section 3.2.4 for more detailed information.

3.1.3 Atmospheres

The following method gases are used in the various instruments:

DSC	TGA	TMA	DMA
• In general: inert N_2 gas. • For oxidation studies (OOT or OIT): O_2 or air. • For special applications or high-pressure DSC: CO_2, He, Ar.	• In general: inert N_2 at lower temperatures, above 600 °C air or O_2 • For special applications: He, Ar, CO_2, or a gas with a defined H_2O content.	• In general: inert N_2 gas • For decomposition studies (not usual): O_2 or air.	• In general: N_2 or air. • For humidity studies: a gas with a defined H_2O content.

**In addition, protective gases are used:**
- with the DSC to prevent condensation when cooling;
- with the TGA as purge gas for the balance;
- and with the TMA to prevent condensation when cooling.

◆ The purge gas is normally N_2 but other gases might also be used.

Gas exchange between sample and furnace atmospheres (see Sections 2.1 and 2.7):

In DSC measurements, gas exchange with the environment is not always required or desirable. The table below presents an overview of the different possibilities for DSC measurements:

No lid – open crucible	50-µm hole in lid	Hermetically sealed crucible
• The pressure in sample is constant. • There is free gas exchange with the surroundings. • Used to measure reactive systems, for example the oxidation induction time (OIT).	• This creates a 'self-generated' atmosphere. • It reduces gas exchange. • Vaporization shifts to the boiling point • Decomposition reactions shift to higher temperature.	• The measurement is performed at constant volume. • There is no gas exchange. • It suppresses vaporization and shifts decomposition reactions to higher temperature.
Black curve in the figure: The water in the crucible has already evaporated at a temperature well below the boiling point.	Red curve in the figure: The water evaporates at the boiling point of water (NB. this measurement was performed at an altitude of about 440 meters above sea level).	Blue curve in the figure: The temperature has no relevance; the crucible bursts when the pressure becomes too high.
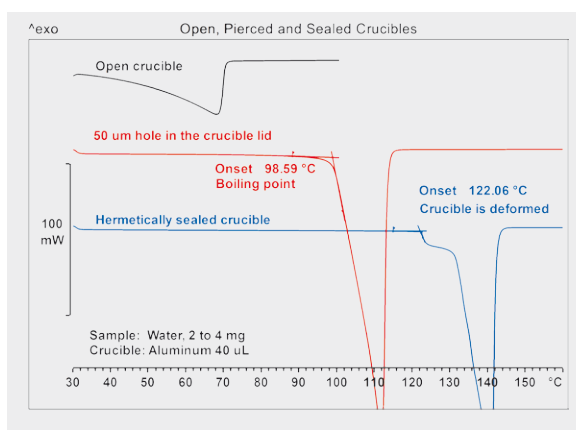
[UC 22/1]

◆ In TGA, TMA and DMA measurements, there is always an exchange of gas between the sample and the atmosphere.

3.1.4 Other parameters
In TMA measurements, force is an additional method parameter. The different combinations of temperature and force and the results that can be obtained are presented in the table below (the most common measurements are highlighted in in boldface type):

Force / Temperature	Constant force	Alternating force	Changing force	Ramped force
Temperature ramp	**Glass transition** **Melting** **CTE** Crystallization Polymorphism Decomposition Foaming	**Modulus** **Curing** **Glass transition** Melting Crystallization		
Isothermal temperature	**Swelling**	**Modulus** **Curing** **Crystallization**	**Creep** **Viscous flow**	**Stress-strain**

DMA methods involve the use of many different parameters. These include the temperature range, heating rate, measurement frequency, force, and displacement. It is not possible to describe these parameters in any detail this in handbook. We therefore refer you to other literature for further information, for example for general information to [UC 23/1], for 3-point bending to [UC 28/9], for shear to [UC 29/14], or to our handbooks and general literature on DMA.

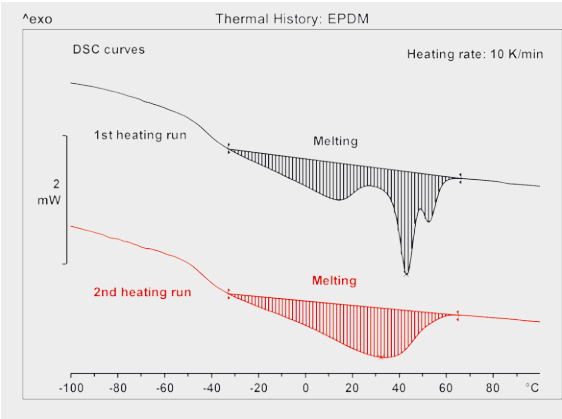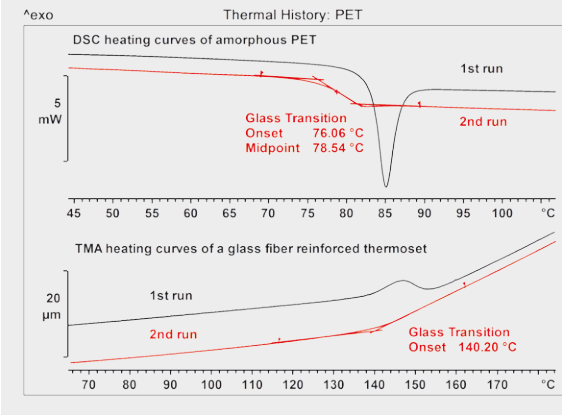### 3.2 Measurement

3.2.1 Blank/reference curves
Blank curves are used to compensate for instrumental or environmental influences on the analysis.
In the simplest case, a blank curve is a curve measured under the same conditions as the sample but without the sample. The blank curve is then subtracted from the curve measured with the sample. Blank curves must always be run under exactly the same conditions as used for the sample.

♦ If the sample is a protein in a buffer solution, the blank measurement can be the pure buffer solution.

DSC	TGA	TMA	DMA
Blank curves are normally not used except for special applications. The DSC curve is in fact a difference curve: the "sample" crucible contains the sample and the "reference" crucible is either empty or contains an inert material.	Blank curves are required if automatic buoyancy correction is switched off or not available. Special DSC sensors are available with a reference position to measure the heat flow signal (TGA/DSC only).	Blank curves are required to accurately measure length changes or small values of CTE.	Blank curves are normally not used.

3.2.2 Heating–cooling–heating

Additional information can be obtained from thermal analyses by performing multiple measurement runs. Temperature programs consisting of heating–cooling–heating cycles are used, especially in DSC measurements. Multiple measurements are much less relevant for TGA. In DMA and TMA measurements, the method is often used to eliminate the thermal history and remove internal stresses in the sample. The advantages of heating–cooling–heating cycles are given below with examples.

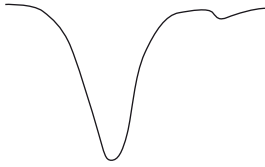| Effect	Example
To differentiate between effects due to manufacturing or storage and the true properties of materials: The melting profile of the material in the first heating run is different to that in the second heating run. The material had been stored at room temperature and had undergone reorganization. The true properties of the material are only observed in the second heating run. [UC 38/1]	
To eliminate thermomechanical history: The first heating run eliminates any internal stresses or thermal history. This allows the effect of interest to be observed in the second heating run. In this example, the first DSC and TMA heating runs each show a relaxation process at the glass transition. The glass transition can only be correctly evaluated when the second heating runs are used. [UC 38/1]	
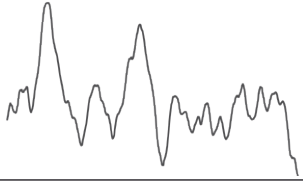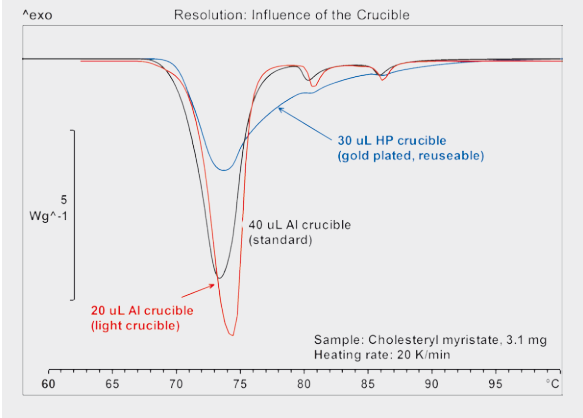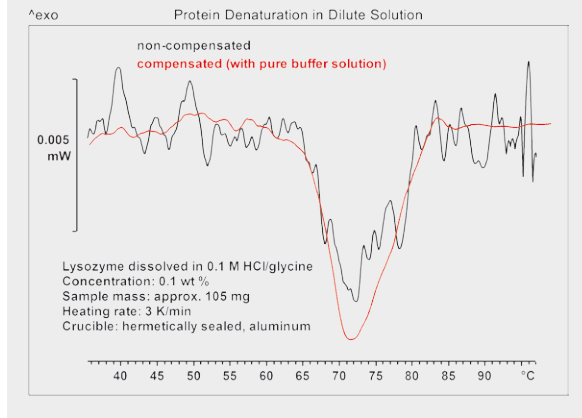
Cooling curves:

♦ Take the cooling capacity of the instrument into account when measuring cooling curves. This mainly concerns DSC and only occasionally TGA, TMA and DMA. If the cooling capacity does not match the settings used for the method, the curve may show artifacts that look like glass transitions.

♦ Effects that overlapped in a heating run are sometimes separated in a cooling experiment (see Section 3.2.4).

♦ Crystallization during cooling is often the best method to distinguish between polymers that have aged differently. An example of this is shown in [UC 20/1].

3.2.3 Resolution and sensitivity

The table presents an overview of the terms resolution and sensitivity and shows how you can influence these two important quantities. In thermal analysis, this mainly concerns DSC and TGA/DSC and to a lesser extent TMA and DMA.

Unfortunately, most measures lead to the optimization of one or the other, that is, either the resolution improves, or the sensitivity, but never both at the same time.

	Resolution	Sensitivity
Definition	Resolution is the ability to separate close-lying effects.	Sensitivity is the ability to reliably detect weak effects.
Technical expression	Signal time constant (peak height-to-width ratio).	Signal-to-noise ratio (SNR).
How to improve the resolution or the sensitivity	• Use lower heating rates. • Use lighter crucibles. • Use a smaller sample mass. • Improve the contact between the sample and crucible. • Select gases with high thermal conductivity (e.g. helium) as the atmosphere. • Use a higher sampling rate.	• Use higher heating rates. • Use a larger sample mass. • Compensate the heat capacity of the sample using an inert material such as Al_2O_3 powder on the reference side. • Use a higher sampling rate.

| Resolution	Sensitivity
This example shows the influence of thermal mass on resolution. The melting and liquid-liquid transitions of a liquid crystal were measured using three different types of crucible of widely different masses. The red curve was measured with the lightest crucible, the black curve with the standard aluminum 40-µL crucible, and the blue curve with a heavy, high-pressure crucible:	If dilute systems are measured, the reference crucible can be filled with an inert substance to compensate for the sample matrix. The amount of the inert substance (e.g. aluminum oxide) placed into the reference crucible should produce about the same heat flow as the sample matrix [UC 25/21].

3.2.4 Overlapping effects

This topic mainly concerns DSC using different heating rates and atmospheres and to a lesser extent TGA, TMA and DMA. Overlapping effects can be separated by:

- Changing the heating rate: some events shift depending on the heating rate (e.g. chemical reactions) whereas others do not (e.g. melting). Two different types of overlapping effects can therefore be separated by increasing the heating rate, for example see [UC 41/24].
- Changing the atmosphere: overlapping effects can be separated by suppressing evaporation or shifting the reaction equilibrium using suitable atmospheric conditions (e.g. pressure), for example see [UC 41/22].
- Using modulation techniques: different effects exhibit different behavior and can be separated when the temperature is modulated. Various modulated techniques are available, see Section 3.3.1 for further information.
- Performing a second heating run: some effects are only observed in the first heating run (stress release, chemical reactions) and are not present in the second heating run. An example is shown below from [UC 38/19]. See also [UC 38/1].
- Performing cooling runs: some effects might overlap in the heating run but are separated on cooling (e.g. glass transition and the melting due to supercooling), for example see [UC 20/3].
- Lower heating rates, lighter crucibles, or smaller sample sizes improve resolution.
- For TGA: Use the vacuum accessory to measure at lower pressures (down to 10 mbar) and thereby separate overlapping volatiles and pyrolysis [UC 26/14].
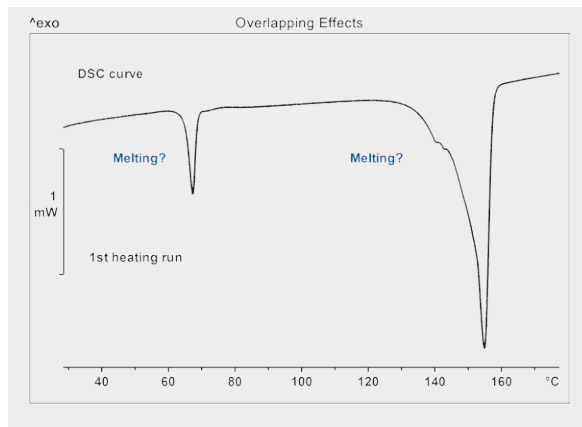
The first heating run of a sample from a PLA biodegradable beaker seems to indicate two melting peaks.
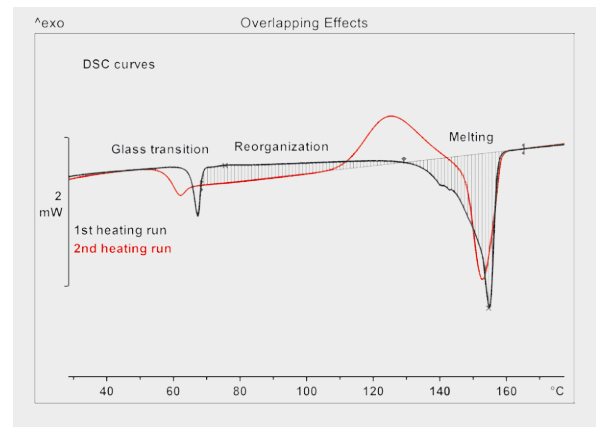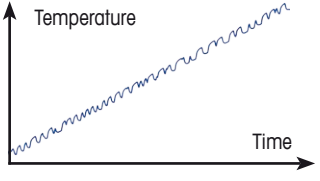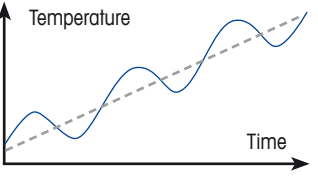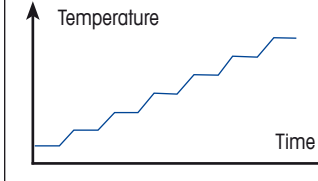

The second heating run (red line) shows that the peak in the first heating run is not due to melting but is caused by the overlap of a glass transition and a reorganization process. The baseline from the second heating can now be used to correctly evaluate the curves (hatched areas).

3.3 Special analyses

3.3.1 Temperature-modulated DSC

Temperature-modulated DSC techniques can be used to separate overlapping effects (see Section 3.2.4) and to accurately measure specific heat capacity. This topic is described in detail in the "Thermal Analysis in Practice" handbook", Chapter 15 and in several UserCom articles. The most important are: [UC 22/6] (general temperature modulation), [UC 22/16] (**TOP**EM®), [UC 25/13] (description of latent and sensible heat flow). A dedicated webinar entitled "Temperature-Modulated DSC Techniques (TMDSC)" is also available.

|	TOPEM®	ADSC	IsoStep®
What is it?	Multi-frequency temperature modulation.	Single frequency temperature oscillation.	Sequence of isothermal and dynamic segments.
Temperature program			
What is measured?	Total, sensible and latent heat flow, quasi-static c_{p0}	Total, sensible and latent heat flow.	Sensible and latent heat flow, quasi-static c_{p0}
Comments	This is the most versatile technique. No reference is required.	The technique is widely used. A reference material is required (for c_p).	This is the simplest technique. A reference material is required (for c_p).

3.3.2 Fast scanning calorimetry (Flash DSC)

Flash DSC expands the possible heating and cooling rates to thousands of Kelvin per second. A UserCom article with many tips about how to perform measurements correctly with the Flash DSC is given in [UC 36/17]. The article describes how silicone oil can be used to measure the first heating run, to correct drift for samples that stick to the sensor and deform it, how to estimate the size of the sample on the sensor, and other points.

The two curves below show PBT specimens measured with (right) and without (left) silicone oil. The curves recorded without silicone oil on the left clearly show artifacts due to stress on the thin sensor membrane caused by the PTB. The artifacts can be eliminated by using silicone oil as a contact medium between sample and sensor as shown in the curves on the right.
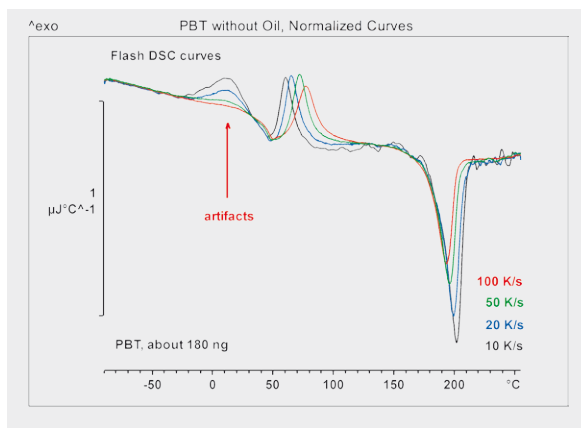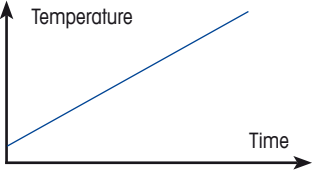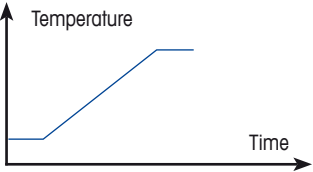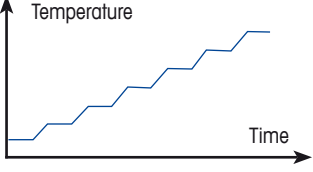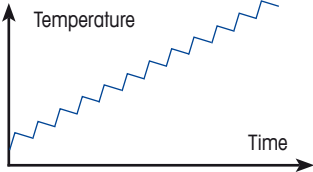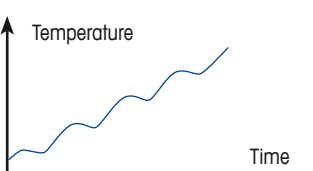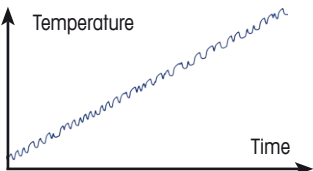

Curves recorded without the use of silicone oil.
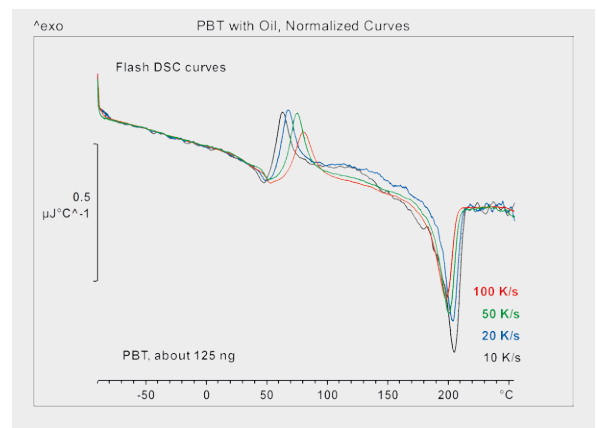
Curves recorded with a thin film of silicone oil between the specimen and sensor.

3.3.3 Specific heat capacity

There are many different ways to measure the specific heat capacity of materials by DSC. The table presents an overview of the available methods. A more detailed description can be found in [UC 7/1] and in the webinar on "Specific Heat Capacity Determination".

	Method	Advantages	Disadvantages
Direct	Temperature / Time	Is very easy to use. Shortest measurement time.	Not very accurate (>5%). Perfect heat flow calibration is needed.
Sapphire	Temperature / Time	High accuracy (>2%). No heat flow calibration is needed. Is compliant with DIN 51007 and ASTM E 1269.	Three measurements are required.
IsoStep®	Temperature / Time	High accuracy (>2%). Large temperature ranges. Can separate overlapping effects.	Three measurements are required (when using sapphire reference); requires more time.
Steady State ADSC	Temperature / Time	Also yields the isothermal c_p (for underlying rate = 0).	Not very accurate (>4%). Long measurement times. Heat flow adjustment is needed.
ADSC	Temperature / Time	Very low heating rates can be used. The quasi-isothermal c_p can be determined. Is less affected by drift and relatively accurate (>3%). Can separate overlapping effects.	Three measurements are required. Long measurement times. Frequency dependent.
TOPEM®	Temperature / Time	Very low heating rates can be used. Only one measurement is needed. The quasi-isothermal c_p can be determined. Less affected by drift and very accurate (>2%). Can separate overlapping effects.	Long measurement times.

Some general tips for the accurate determination of c_p by DSC:

Crucibles:	Measurement:	Sample:

• Position the crucibles reproducibly on the sensor (for very accurate measurements, do not use a robot).
• Whenever possible, use the same crucibles for all three measurements.
  If this is not possible, use crucibles with small mass differences (<0.01 mg).
  ♦ This is also important for the reference crucible!
• For crucibles with different masses, apply crucible mass correction.
• Recommendation: use 40-µL aluminum crucibles with a sample mass of 10 to 20 mg (for organic materials).
• Sometimes the enthalpy measurement (and thus the c_p) is more reproducible when 30-µL aluminum oxide crucibles are used (provided the instrument is adjusted for these crucibles). This is due to the very flat and non-deformable base of this crucible.
	• Allow the instrument to stabilize before performing the measurement.
	• Check the reproducibility using repeated measurements.
	• Average different measurements to improve the accuracy.
	• Use blank-curve subtraction (except for **TOP**EM®).
		• Ensure good thermal contact between sample and crucible.
		• Try to make the heat flow of sample (s) and reference (r) similar:
		  $c_{p,s} \times m_s \approx c_{p,r} \times m_r$ or
		• C_p (sample) $\approx C_p$ (reference).
		• Use larger sample masses.

For information and tips on specific heat capacity determination at elevated temperatures with the TGA/DSC instrument (up to 1600 °C), please refer to [UC 27/1], [UC 28/1], and [UC 39/24].
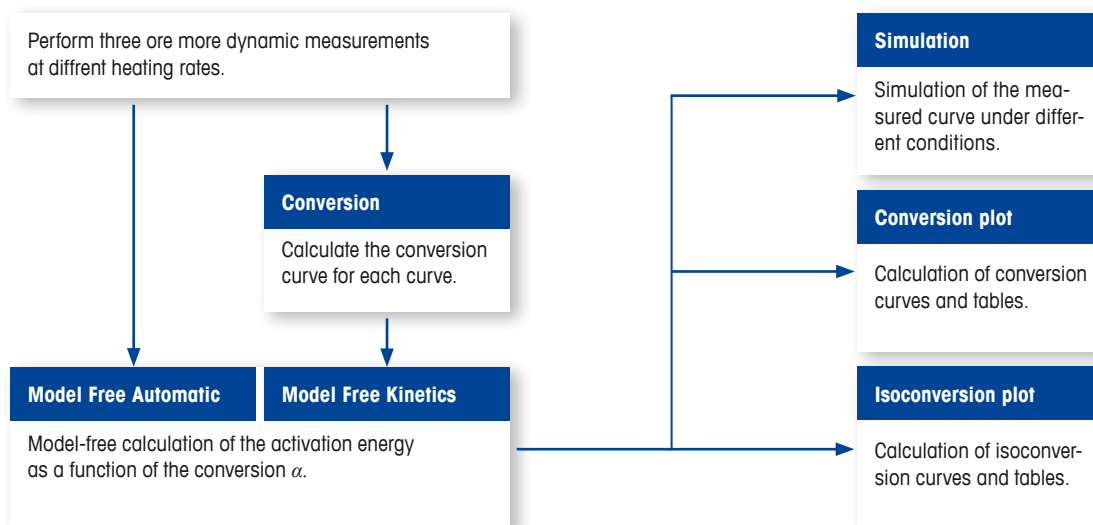
3.3.4 Kinetics

Background information on kinetics can be found in several UserCom articles (e.g. in [UC 8/1], [UC 21/6] and [UC 10/9]), or in the "Thermal Analysis in Practice" handbook, p 111 ff. A webinar dealing with kinetics can be downloaded at: www.mt.com/ta-ondemand.

Three different options are available for kinetic evaluations. The following table indicates which to use:

nth Order Kinetics	Model Free Kinetics (MFK)	Advanced Model Free Kinetics
• Uses a simple model. • Is only valid only for very simple reactions. • Assumes that the activation energy (E_a) is constant. • Specified by ASTM standards (e.g. ASTM E698, ASTM E1641). • The temperature program can be dynamic or isothermal.	• No prior selection of a kinetic model is required. • It can be used for simple and complex reactions. • It provides reliable predictions for various conditions. • The activation energy (E_a) varies with the degree of conversion (α) and reflects the complexity of the reaction. • It requires dynamic heating curves.	• No prior selection of the kinetic model is required; it uses an advanced mathematical procedure. • It can be used for simple and complex reactions. • It provides reliable predictions for various conditions. • The activation energy (E_a) varies with the degree of conversion (α) and reflects the complexity of the reaction. • Any temperature program can be used: isothermal, dynamic or combinations of the two. • Cooling curves cannot be used.
$\rightarrow$ **Simple method**	$\rightarrow$ **Advanced method**	$\rightarrow$ **Sophisticated method**

The basic procedure for DSC and TGA evaluations using model free kinetics (MFK) and advanced model free kinetics (AMFK) are:

Perform three ore more dynamic measurements at diffrent heating rates.

Conversion
Calculate the conversion curve for each curve.

Model Free Automatic | **Model Free Kinetics**
Model-free calculation of the activation energy as a function of the conversion α.

Simulation
Simulation of the measured curve under different conditions.

Conversion plot
Calculation of conversion curves and tables.

Isoconversion plot
Calculation of isoconversion curves and tables.

Step 1

- Measure at least three curves at different heating rates.
- Usually heating rates between 0.5 K/min and 50 K/min are used.
- If possible, use an exponential increase of heating rates, for example 1, 2, 5 and 10 K/min or 2, 5, 10 and 20 K/min.
- For the higher heating rates, it might be necessary to use smaller sample sizes.

Step 2

- Evaluate the reaction enthalpy (for DSC) or the mass loss (for TGA) and make sure that the normalized quantities are approximately the same (±10% for enthalpy, ±5% for mass loss).
- Use the same limits (and the same baselines) to calculate the degree of conversion for the different curves.
- Make sure that the conversion curves do not cross each other! If they do, change the limits for the conversion calculation.
- Make sure that both the minimum and maximum limits for the lower heating rates are lower than the limits for the higher heating rates.

Step 3

- Select all the conversion curves and calculate the apparent activation energy curve by clicking "MFK" (Model Free Kinetics)' or "Advanced MFK".

Step 4

- Define the conversion or iso-conversion parameter settings.
- Choose "Applied MFK > conversion/iso-conversion plot and table" or "Applied Advanced MFK > conversion/iso-conversion plot and table".

Step 5

- The simulated curves with the value table will now be plotted for the temperatures or times defined in Step 4.

- Whether or not the conversion curves cross is more important for AMFK than for MFK.
  If you do not get any values in the AMFK calculation tables, this is probably the reason.
- Isothermal measurements can only be used with AMFK but not with MFK.
- Make sure that the limits of the evaluations shift to higher temperatures with increasing heating rates.
- Use relevant temperatures, the simulated curves will normally reach 20% to 90% conversion.
- For curves that are difficult to evaluate, use a second measurement run of the reacted sample for baseline subtraction (see also [UC 38/1]).

Isothermal measurements are better for some applications and dynamic measurements for others. The table below lists the advantages and disadvantages of both options:

	Advantages	Disadvantages
Isothermal	• Easier to interpret. • Flat, horizontal baselines. • Less decomposition due to the lower temperatures used. • Differentiation between simple and complex reactions (via peak shape).	• Long measurement times. • The starting point of the reaction (t = 0) is not well defined for fast reactions.
Dynamic	• Short measurement times. • 100% conversion is usually reached.	• Decomposition toward the end. • Baselines questionable. • Conversion function, $f(\alpha)$, may change with temperature.

For which processes can
we use kinetic algorithms?

Reaction	DSC	TGA
Polymerization	■	–
Polyaddition	■	–
Polycondensation	■	▪
Pyrolysis	▪	■
Thermal decomposition	▪	■
Oxidative degradation	■	▪
Loss of water of crystallization	■	■

■ often used   ▪ seldom used

3.3.5 Evolved gas analysis
The decomposition products produced in a TGA instrument can be analyzed in more detail using several different evolved gas analysis techniques. The table below indicates when each technique is best:

Technique	Advantages	Limitations	Applications
MS **(Mass spectrometry)**	• Is an online technique. • High sensitivity.	• Maximum mass of 300 amu. • Interpretation requires information about the expected gasses.	• Detection of small molecules. (CO_x, NO_x, SO_x, H_2O, HCl, etc.) • Residual solvents in pharmaceuticals.
FTIR **(Infrared spectrometry)**	• Is an online technique. • Provides information about the molecular structure of the evolved gases.	• Less sensitive than MS and GC/MS.	• Detection of complex organic and simple molecules. • Pharmaceuticals. • Polymers.
GC/MS **(Gas chromatography combined with MS)**	• Mixtures of evolved gases can be separated and the gasses analyzed individually.	• Storage mode: up to 16 gas samples from one TGA scan. • Very time consuming. • Maximum mass 1050 amu.	• No restrictions.

3.3.6 Other analyses
For other special topics, we recommend the following references:
• Oxidation induction time by DSC: the "Oxidation Induction Time (OIT)" webinar and [UC 26/18].
• Purity by DSC: [UC 10/1] and the "Purity Determination by Thermal Analysis" webinar.
• Thermal conductivity by DSC: [UC 22/19]
• Optical techniques: Photocalorimetry [UC 23/10] [UC 31/13], Microscopy [UC 30/7] [UC 33/10] [UC 34/13] and Chemiluminescence [UC 20/12] [UC 26/18]) are also described in the "Thermal Optical Methods" webinar www.mt.com/ta-ondemand.
• Sorption experiments can be performed using TGA and DMA instruments: A humidity generator is connected to the TGA or DMA furnace and generates a specific relative humidity around the measured sample. The following UserCom articles are available for TGA: [UC 17/7] [UC 21/9] [UC 33/14] [UC 37/1], and for DMA: [UC 24/1]. The "TGA-Sorption" webinar is also recommended for TGA.
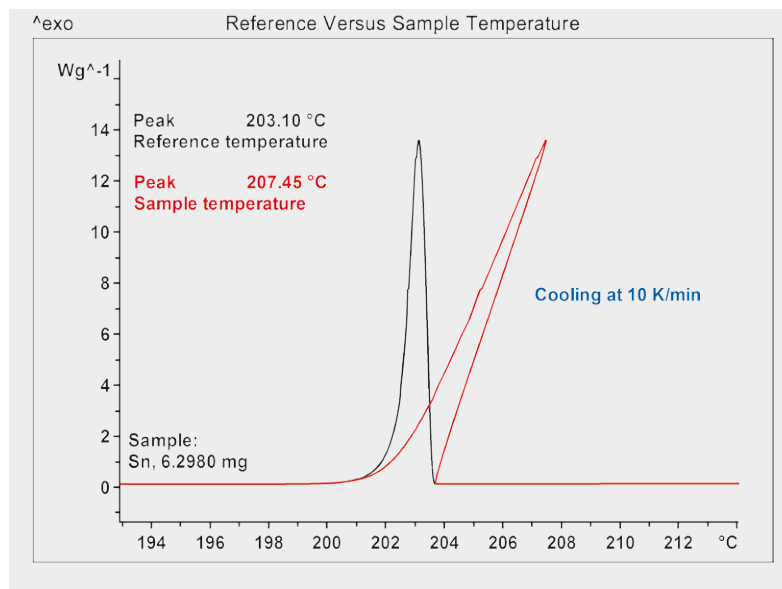
4 Evaluations

4.1 Curve presentation

Curves should be presented in such a way that the desired information can be directly obtained. The best way to plot the curve depends on the technique used (DSC, TGA, TMA or DMA), the sample measured, and the information required. References to many useful tips on how to present curves are given in the UserCom articles in Section 4.4. This paragraph describes only the most important rules for each technique.

DSC measurement curves are usually plotted against the reference temperature. This avoids the possibility of recording peaks such as the one shown in the figure below. In this cooling experiment, the sample releases heat during crystallization: The heat causes the temperature of the sample to increase while it is at the same time being cooled.

♦ The sample temperature is the temperature that should be evaluated. This is in fact the default evaluation temperature in the software.


Information about DSC reference and sample temperatures can be found in [UC 23/6] and [UC 24/11].

The main problems for TGA [UC 12/17] and TMA are similar. In particular, care should be taken when evaluating the onset values of samples of different sizes. With relative plotting, the onset temperature of the larger sample (with a larger absolute mass or length loss) appears to come at a higher temperature than that of the smaller sample. The diagram shows examples for TGA (left) and TMA (right):
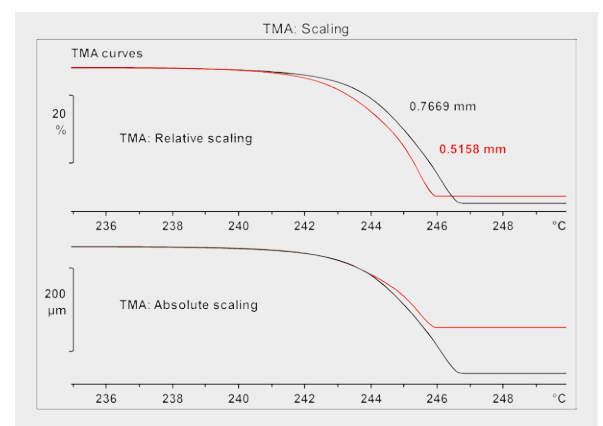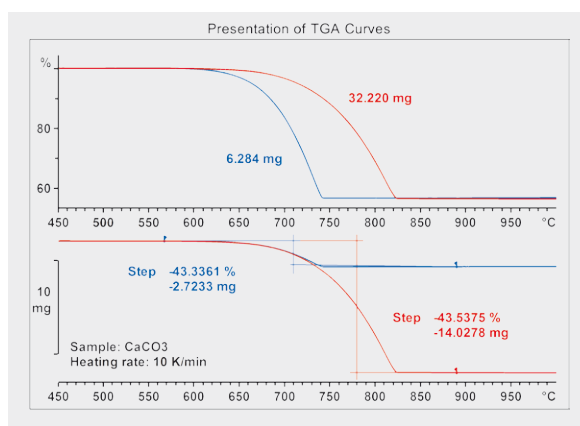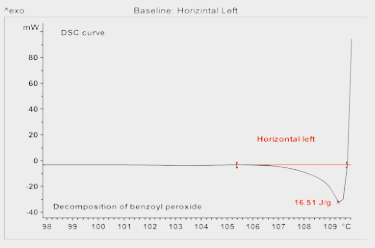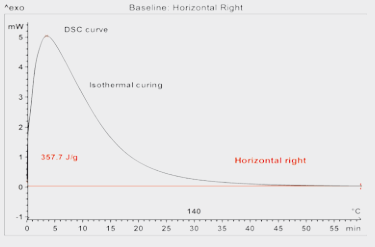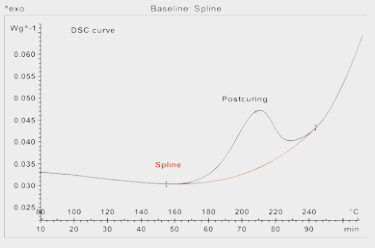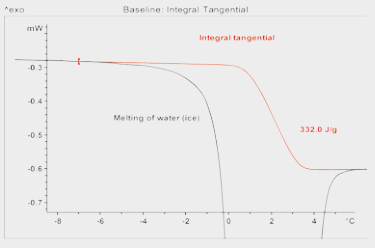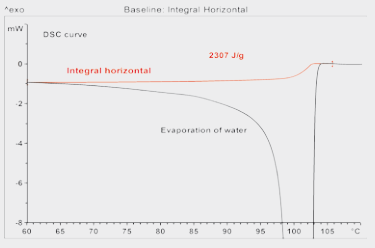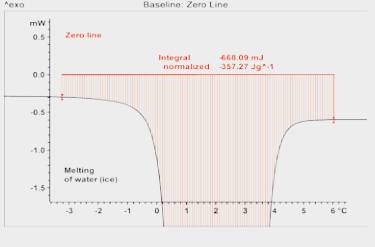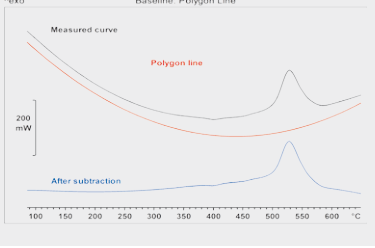
The main point for DMA curves is the logarithmic behavior of the modulus, which is the parameter determined. The modulus value changes by several decades when a sample softens; it is therefore best to plot the curve logarithmically. Otherwise, small effects (e.g. of 1 decade) would go unnoticed compared with larger effects (e.g. spanning 6 decades). This is illustrated in the two figures below, where curves were plotted on a linear y-axis and a logarithmic y-axis. In the figure on the left, the post-curing of the sample can hardly be seen whereas in the figure on the right, the change in modulus is effectively scale expanded. See [UC 15/1].
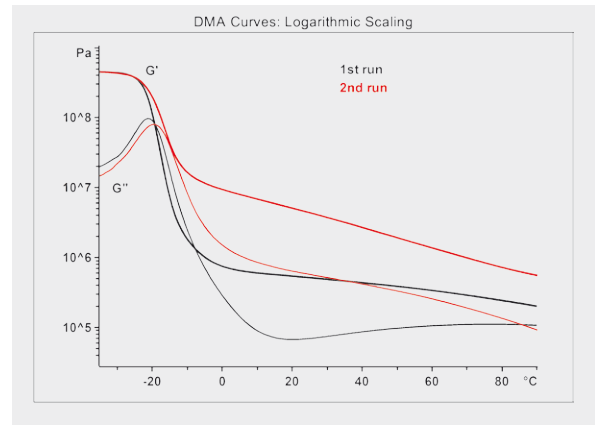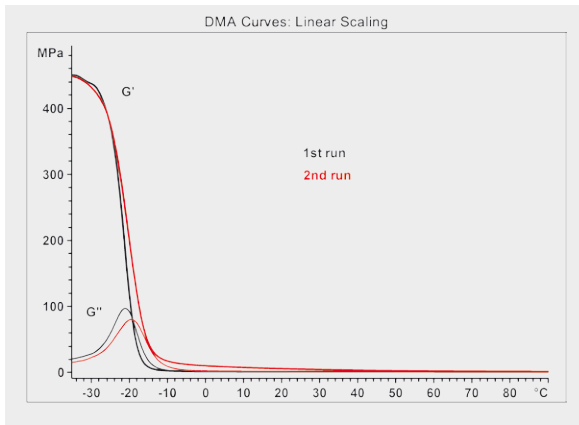

4.2 Baselines for the integration of DSC effects

Different types of baselines have to be used for integration depending on the shapes of the curves and the effects that are to be evaluated. A complete overview of when to use the different baselines is given in [UC 25/1]. Some examples of the most common baselines are shown in the table below.

Baseline type	Description	Applications	Example
Line	This is a straight line that joins two evaluation limits on the measured curve.	Used for reactions without abrupt changes in c_p that exhibit a constant increase in c_p or a constant c_p. This baseline is the default setting.	
Tangential left	This is the extension of the tangent to the measured curve at the left evaluation limit.	Used to integrate a melting peak on a measured curve which is followed by subsequent decomposition of the substance.	
Tangential right	This is the extension of the tangent to the measured curve at the right evaluation limit.	Melting of semi-crystalline plastics with a significant c_p temperature function below the melting range.	

Baseline type	Description	Applications	Example
Horizontal left	This is the horizontal line through the point of intersection of the measured curve with the left limit.	Used for peak integration when substances decompose.	
Horizontal right	This is the horizontal line through the point of intersection of the measured curve with the right limit.	Used for isothermal reactions and DSC purity determination.	
Spline	The Spline baseline is the curve obtained using a flexible ruler to manually interpolate between two given points (known as a Bezier curve). It is determined as a 2nd order polynomial through the tangents at the evaluation limits. This bow-shaped or S-shaped baseline is based on the tangents left and right.	Used with overlapping effects.	
Integral tangential	Starting with a trial baseline, the integral baseline is calculated using an iterative process. The conversion calculated from the integration between the evaluation limits on the measured curve is normalized. Like the Spline curve, this bow-shaped or S-shaped baseline is based on the tangents left and right.	Used for samples with different c_p temperature functions before and after the effect. The Line baseline would possibly cross the DSC curve and lead to large integration errors depending on the limits chosen.	
Integral horizontal	This baseline is calculated using an iterative process like the Integral tangential baseline. The S-shaped baseline always begins and ends horizontally.	Used for samples whose heat capacity changes markedly, e.g. through vaporization and decomposition. The Line baseline would possibly cross the DSC curve and lead to large integration errors depending on the limits chosen.	
Zero line	This is the horizontal line that intersects the ordinate at the zero point. It requires blank curve subtraction.	Used for the determination of transition enthalpies including sensible heat.	
Polygon line	The baseline can be determined through a curved line or a straight line from individually chosen points. The polygon line is then first subtracted from the measured curve and the resulting peak integrated using a straight baseline.	Used in special cases. This is not a standard baseline in the software; it requires the mathematics option.	

♦ Make sure that baselines are realistic and make sense. This is not the case if they cross the measurement curves, are discontinuous, or do not describe the underlying physical behavior of the sample:
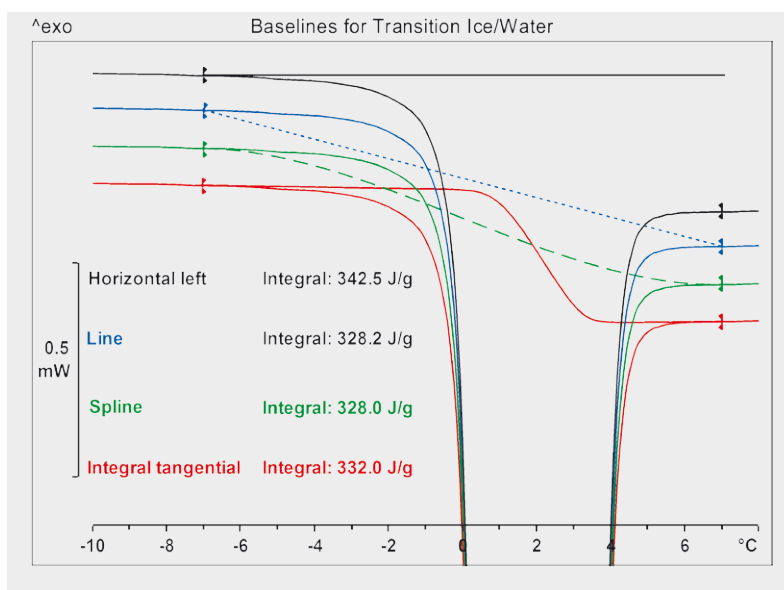
4.3 Evaluation of temperatures for different effects

Some effects can be measured and evaluated by DSC, TGA, TMA and DMA. The following table gives an overview of how the temperatures of the effects are usually evaluated for the individual techniques. Effects specific for particular techniques (e.g. beta relaxation for DMA) are not mentioned in the table.

Temperatures	DSC	TGA	TMA	DMA
Melting	Onset for pure substances. Peak maximum for polymers.	–	Onset of the decrease in length.	Onset of the decrease in the storage modulus decrease. Local maximum of the loss modulus curve. Local maximum of the tan delta curve.
Glass transition	DIN, ASTM, Richardson, METTLER TOLEDO (see the "Elastomers" handbook, Vol. 1, p 39 ff.)	–	Onset of the decrease in length. Onset of the increase of the CTE.	Onset of the decrease of the storage modulus. Local maximum of the loss modulus curve. Local maximum of the tan delta curve. DIN 65583
(Cold) Crystallization	Onset. Peak temperature.	–	Onset of the decrease in length.	Onset of the increase of the modulus. Local maximum of the tan delta curve

Temperatures	DSC	TGA	TMA	DMA
Decomposition (also oxidation)	Onset of the endothermic or exothermic effect. Onset of the OIT and OOT measurements.	Onset of the mass loss step.	Appearance of a noisy length curve.	Appearance of a noisy modulus curve.
Chemical reactions	Peak temperature.	Onset of the mass loss step.	Onset of the increase in CTE. Beginning of noise on the curve.	Onset of the increase of the storage modulus.

4.3.1 Determination of the glass transition temperature

Many articles with theory and background information are available for the glass transition.
The articles can be found in:

- Glass transition theoretical background: [UC 10/13] Part 1 (basic principles),
  [UC 11/8] Part 2 (influence of fillers, crystallinity, molecular size, crosslinking, plasticizers, etc.),
  webinar on the "Determination of the Glass Transition Temperature", www.mt.com/ta-ondemand.
- Glass transition with DSC, TMA and DMA: [UC 17/1] Part 1 (overview),
  [UC 18/1] Part 2 (determination of the glass transition temperature).

The table below presents an overview of the different techniques used to evaluate the glass transition:

Technique	Advantages	Disadvantages	Remarks
DSC	• Easy to use. • Is a widely used technique. Many standard methods are available. • Also suitable for low viscosity materials. • No special sample preparation is needed.	• Filled samples (especially when measured at low heating or cooling rates) produce only a small step in the heat flow curve.	• Good heat transfer is required between sensor and sample. • Possible overlap with other effects e.g. relaxation, evaporation.
Modulated DSC	• Separation of overlapping reversing (glass transition) and non-reversing effects. • The influence of frequency can be investigated. • No special sample preparation is required.	• Measurements usually take longer due to the low heating rates used.	• Very good heat transfer from sensor to sample is required.
TMA	• Sample handling is easy. • Even low heating rates give good results. • Very thin films (softening / penetration) can be measured. • Standard methods are available.	• Filled materials produce only small changes. This can be improved by using the bending mode. • Overlapping due to relaxation effects: use the second heating run.	• The glass transition can be measured as an increase in expansion, or as softening via penetration of the probe into the sample.
DMA	• High sensitivity for glass transitions. • Standard methods are available. • Wide frequency range.	• Relatively long measurement time due to the low heating rate.	• Requires the proper choice of sample geometry and holder. • Sample preparation can take a long time.

The sensitivity to the glass transition depends on the change in the measured signal. The different techniques measure different parameters and have different sensitivities with regard to the glass transition:

Technique	Measured property	Factor of change during glass transition
DSC	Specific heat capacity	5 to 30%
TMA	Coefficient of thermal expansion	50 to 300%
	Softening	–
DMA	Modulus	1 to 3 decades

Sensitivity

4.4 Curve interpretation

The topic of curve interpretation is too complex to be included in this handbook.

For further information, we recommend the "Thermal Analysis in Practice" handbook and our other handbooks on specific materials. There is also a large number of UserCom articles dealing with curve interpretation.

For the specific instruments, these are:

DSC curves: [UC 11/1], [UC 12/1], [UC 38/1], [UC 39/1], [UC 40/1].

TGA curves: [UC 13/1], [UC 38/1], [UC 39/1], [UC 41/1].

TMA curves: [UC 14/1], [UC 38/1], [UC 39/1], [UC 42/1].

DMA curves: [UC 15/1], [UC 16/1], [UC 38/1], [UC 39/1], [UC 43/1].

Additionally, e-training courses are available for all techniques: www.mt.com/ta-etraining.

5 Calibration and Adjustment

5.1 General

♦ Calibration is the determination of the deviation of the measurement result from a reference/literature value (it is equivalent to a check).

♦ Adjustment is the adaptation of instrumental parameters after calibration.

♦ Be aware of the certification of your reference materials: depending on the vendor's certification status and testing procedure, substances might be certified for purity, melting point, enthalpy of fusion, modulus, and so on.

The following procedure can be followed to check and improve the performance capability of DSC, TGA, TMA and DMA instruments:
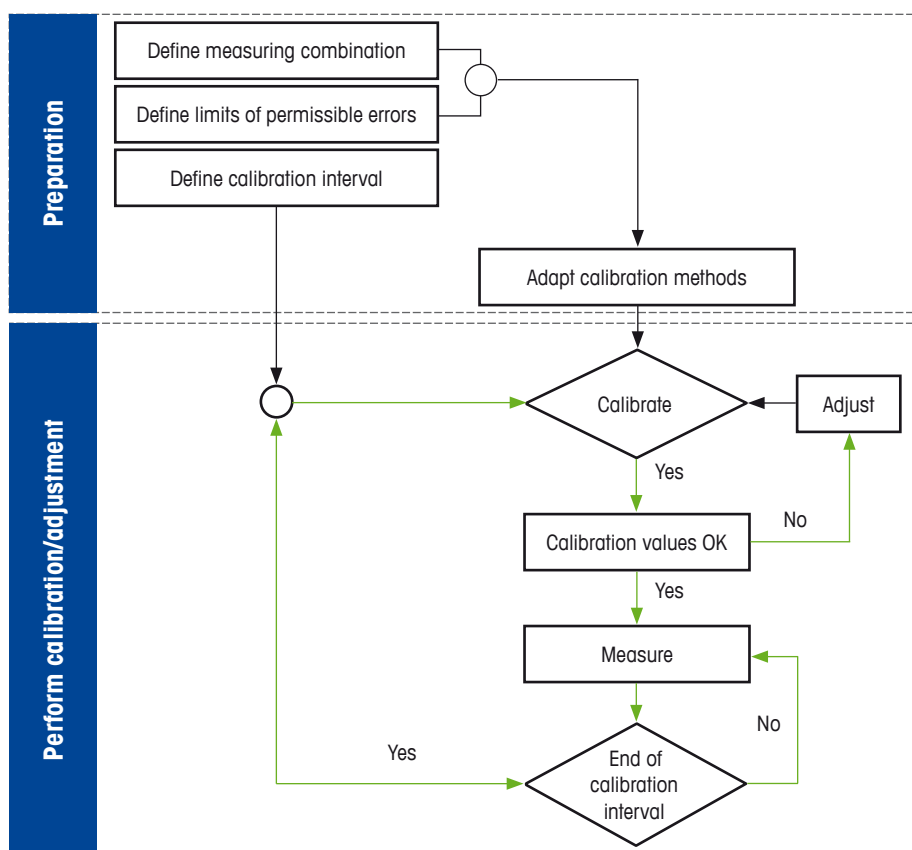
The definition of the measurement combination (blue area in diagram above) can be summarized as follows:

- **Define measuring combination**
- **Define the temperature range:**
  The adjusted temperature range should begin and end 50 K below and above the actual measurement range.
- **Define the heating rates:**
  Same heating rate as used in the methods (10, 20 K/min…).
  ♦ When the tau lag time has been adjusted, any heating rate can be used for a measurement, irrespective of whether that particular heating rate has been adjusted or not. See example below.
- **Define the atmosphere:**
  Perform the adjustment using the same atmosphere as used in the analysis/method (N_2, air…).
  ♦ The gas used influences the tau lag time and the enthalpy.
- **Define the type of crucible:**
  Perform the adjustment for the same crucible as used in your analysis/method
  (e.g. Al 40 µL, Al_2O_3 70 µL…).
  ♦ The crucible defined influences temperature, tau lag and enthalpy.

- **Define limits of permissible error:**
  The limits that are defined here depend on the application. The standard limits for indium
 are for example set to ±0.3 °C.
    ◆ Make sure you use realistic limits: if the reproducibility of the melting point of your substance
      is only ±2 °C (e.g. with polymers), an indium check requirement of ±0.3 °C will just waste
      the additional time needed to adjust the instrument to better than ±2 °C.

- **Define the calibration interval:**
  With a new and unknown instrument, a check should be performed once a week.
  When it becomes clear that the instrument does not drift over time, the check can
  be lengthened to once every 2 or even 3 weeks.
    ◆ Only adjust the instrument if the check is wrong! (In addition, make sure you reproduce
      the faulty check with a newly prepared indium/zinc sample).
    ◆ The long term drift of the instrument can be followed by collecting the accumulated
      check data in a spreadsheet or the statistics functionality of the S**TA**R^e software.
    ◆ An indium check only takes only 6 minutes; the indium pill can be used
      up to 25 times for normal checks.

◆ If the tau lag time is correctly adjusted, the same melting point will be obtained at all heating rates:
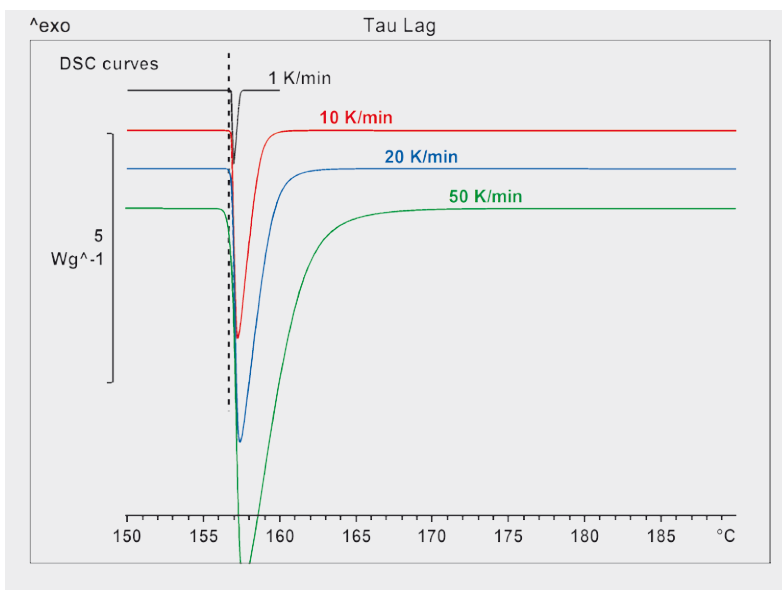
Some general adjustment tips:
- Switch on the instrument and all its cooling options and allow it to stabilize for at least two hours before performing checks.
- Do not use the data from the pre-melting of a fresh indium pill (1st heating run), use the data from subsequent heating runs (up to 25).
- The adjustment will be more accurate if the reference samples are positioned manually and not using the robot.

◆ It is up to the user to specify the tolerance limits!

Further information about calibration and adjustment can be found in the "Calibration and Adjustment in Thermal Analysis" webinar and in [UC 6/1]. Detailed information about the underlying algorithms used in the software can be found in Chapter 8 of the S**TA**R^e Software "User Handbook".

5.1.1 Calibration substances

The following table shows reference substances frequently used for DSC, TGA, TGA/DSC, TMA and DMA:

Substance	Temperature [°C]	Enthalpy [J/g]	Effect	Remarks
n-Octane (C_8H_{18})	−56.8	180.0	melting	Hermetically sealed crucible: pay attention to possible evaporation.
Water (H_2O)	0.0	335.0	melting	Hermetically sealed crucible: pay attention to possible evaporation.
Gallium (Ga)	29.8	79.9	melting	Forms alloys, very low melting temperature.
Phenyl Salicylate	41.7	90	melting	Can only be used once.
Indium (In)	156.6	28.6	melting	Has almost ideal properties.
Tin (Sn)	231.9	60.4	melting	Oxidizes, exhibits pronounced supercooling.
Lead (Pb)	327.5	24.7	melting	Oxidizes.
Zinc (Zn)	419.5	107.5	melting	Oxidizes.
Aluminum (Al)	660.3	398.1	melting	Minor oxidation.
Silver (Ag)	961.9	104.8	melting	Oxidizes.
Gold (Au)	1064.4	64.5	melting	Strong surface tension: forms spheres, difficult to measure enthalpy a second time. Very close to the maximum temperature of the 1100 °C instrument.
Palladium (Pd)	1554.0	162	melting	Very close to the maximum temperature of 1600 °C instrument.
Isatherm	144.5	N/A	Curie	Very dependent on the composition; the temperatures are slightly different for each batch: see certificate.
Nickel (Ni)	354.4	N/A	Curie	Very dependent on the composition; the temperatures are slightly different for each batch: see certificate.
Trafoperm	754.3	N/A	Curie	Very dependent on the composition; the temperatures are slightly different for each batch: see certificate.

◆ Certified reference substances can be obtained from the Laboratory of the Government Chemist (LGC), UK; National Institute of Standards and Technology (NIST), USA; Physikalische Technische Bundesanstalt (PTB), Germany. Reference standards are also described in [UC 24/9] and in [UC 9/1] (low temperatures).

## 5.2 Special adjustments for specific instruments

5.2.1 TGA Adjustment using the Curie point

The Curie effect is used to adjust the temperature of TGA instruments that do not have a temperature signal. Materials that exhibit a Curie transition are ferromagnetic at temperatures below the Curie point: they are attracted by a magnet (blue in picture) and therefore appear to be lighter. With increasing temperature, ferromagnetic materials undergo a phase transition and are no longer attracted by the magnet: their true mass is then measured.
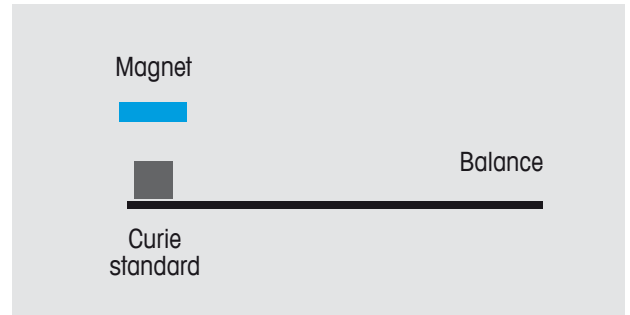
The Curie point is evaluated using the inflection point. This method has the advantage that the temperature determined is independent of the operator.
Furthermore, the inflection point corresponds to the Curie point measured by DSC.

◆ The Curie temperatures of materials may be slightly different from batch to batch.
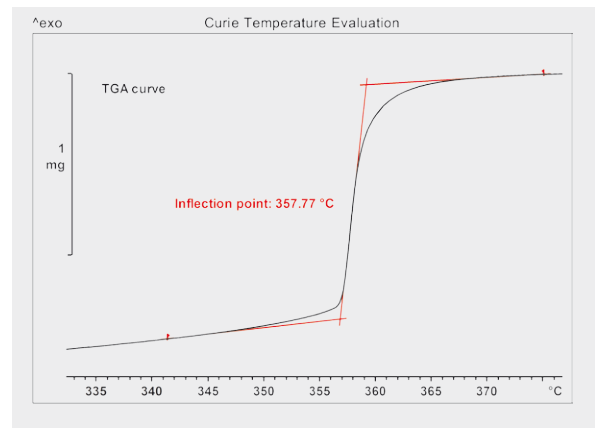
5.2.2 TMA and DMA specific calibrations and adjustments

TMA temperature adjustments can be performed using the temperature (SDTA) signal or using the sample length. In the example below, an indium pill is measured as it softens during melting:
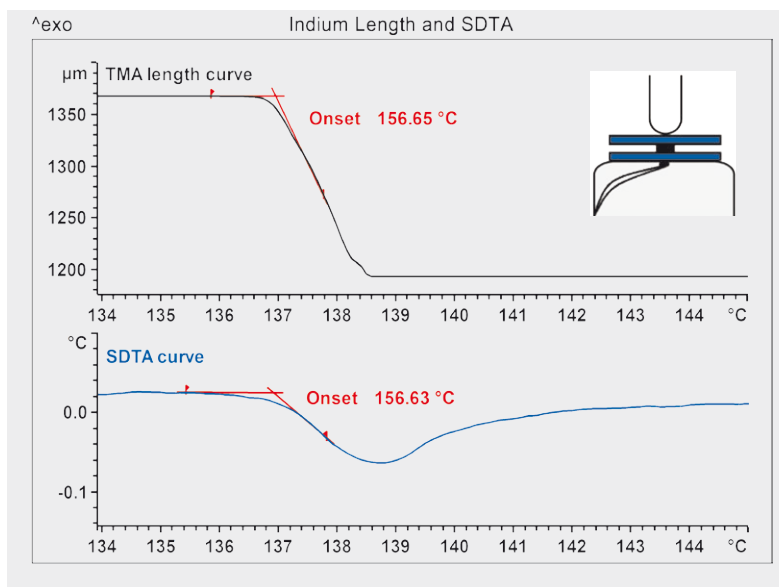
TMA force calibration according to ASTM E 2206-02 [UC 27/20]:

Ramp the force generator stepwise to find the zero point when the probe just touches the sample support and the point at which it just lifts off the sample support:
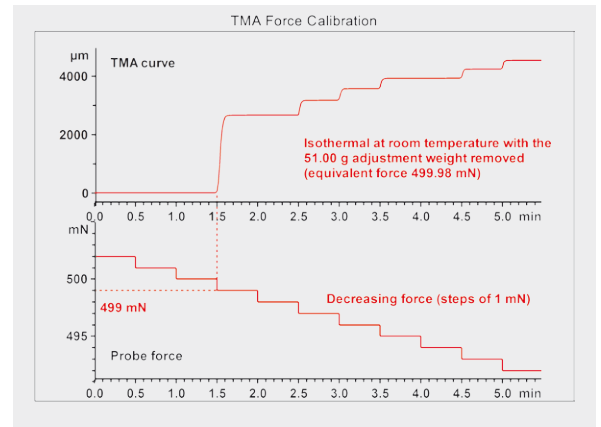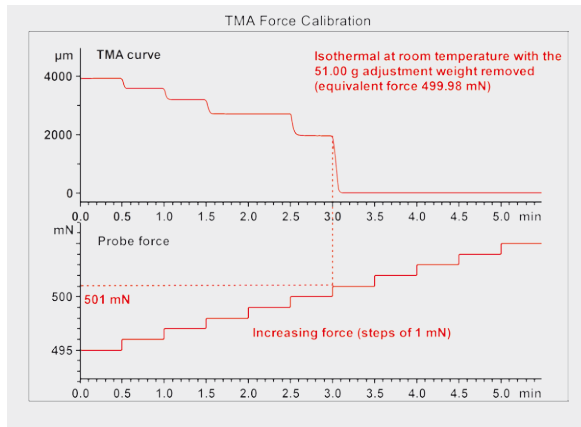
Thermocouple position for TMA and DMA adjustments:

The diagram below illustrates the effect of moving the thermocouple after adjusting the temperature of a TMA or DMA instrument. The red curve shows the calibration curve of water, the black curve is the same measurement, but with the thermocouple moved by about 1 mm. The temperature difference is more than 3.5 °C.
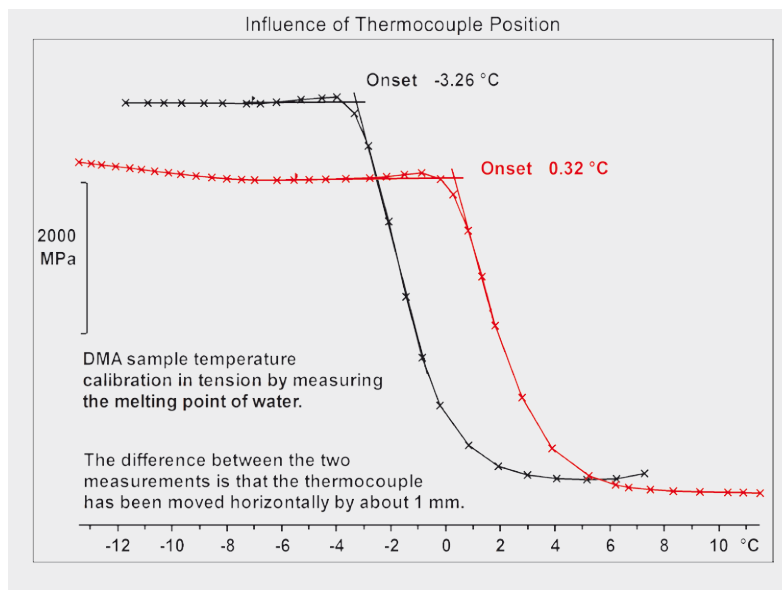
PTFE temperature calibration:

A quick and easy check for the DMA temperature involves the measurement of PTFE. PTFE can be used for all deformation modes because it can be purchased as bars or films. PTFE has several distinct transition temperatures at −97 °C, 19 °C and 30 °C (these cannot always be resolved by DMA measurements), 127 °C and 327 °C (melting, do not use for tension, bending, etc.). You can therefore quickly check the whole DMA temperature range for correct adjustment in one measurement.
See also the "Thermoplastics" handbook, p 114 ff. www.mt.com/ta-handbooks.

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