Thermal Analysis Application

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Method development in thermal analysis. Part 1

Introduction

The development and validation of methods is of major importance in today's quality assurance systems. The starting point is usually a trial method that is then optimized and validated in several iterative steps. The final result is a validated method that is used for SOPs (SOP: Standard Operating Procedure). The development and validation of a measurement procedure is time-consuming and costly. This means it is important to start off with a good trial method right from the beginning. The following article attempts to systematize the development of thermoanalytical methods and discusses the most important aspects involved. Figure 1 presents an overview of this process.

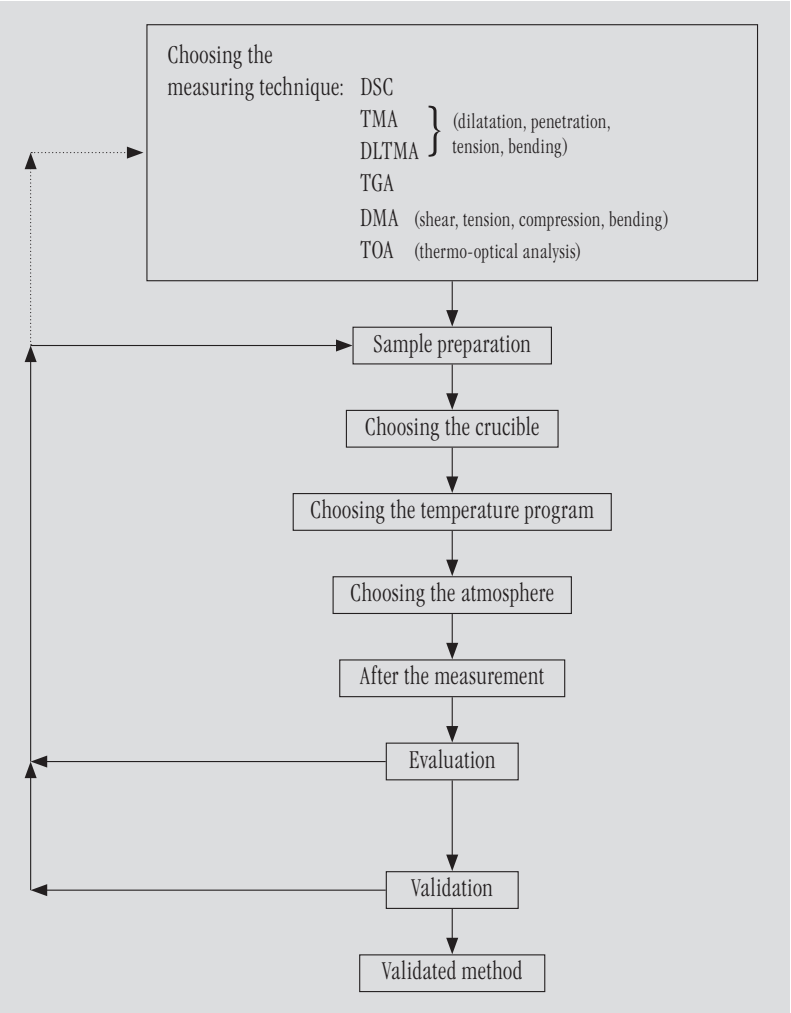

Figure 1. Procedure for developing a thermoanalytical method.

Step 1: Choosing the right measurement technique

The analytical task

Method development begins with precisely defining the information you hope to get from an analysis of the sample. Typical questions could for example be

- At what temperature does the glass transition occur?
- Does the sample exhibit polymorphism?

- How pure is my product?
- What is the moisture content of my sample? and so on.

Depending on the analytical task and the information required, you first have to decide which measurement technique to use. Table 1 presents an overview of the application possibilities of various thermoanalytical measurement techniques.

"Sensitivity"

The most important considerations at this point are basic questions that have to do with later validation of the method:

- Is the sensitivity of the method good enough to obtain the desired information?
- What possible consequences arise from the sensitivity of the method, e.g. with regard to sample size or heating rate?
- What accuracy can I expect to achieve?
- Is the accuracy sufficient for my purposes?
- Do any interfering effects have to be taken into account? Are the effects more serious with one measurement technique than with another (robustness of method)?

To answer these questions, one needs to understand the operating principles of the instruments and to have had practical experience. Particularly important is information on the signal-to-noise ratio, the long-term stability or drift, and measurement reproducibility.

Example:

What is the smallest mass loss step that can be resolved by TGA?

Answer:

The decisive point in this case is the signal-to-noise ratio of the measurement signal (balance and surroundings). As a rule of thumb, a measurable mass change should be at least four times greater than the background noise signal. Assuming that the noise is 1 µg, the minimum step height is 4 µg. If the sample mass is 10 mg, this means that mass changes of the order of 0.4 per thousand can be measured.

	DSC	TGA/SDTA	TMA/SDTA	DMA/SDTA
Physical properties				
• Specific heat capacity	•••			
• Coefficient of expansion			•••	
• Young's modulus			•	•••
Physical transitions				
• Melting and crystallization	•••	•	•	•••
• Vaporization, sublimation, drying	•••	•••		
• Glass transition, softening	•••		•••	•••
• Polymorphism (solid-solid transitions)	•••		•••	
• Liquid crystals	•••			
• Purity determination	•••			
Chemical properties				
• Decomposition, pyrolysis, oxidative stability	•••	•••		
• Composition, content (moisture, fillers), ash	•	•••		
• Kinetics, reaction enthalpy				
• Cross-linking, vulcanization (process parameters)	•••	•••	•••	•••

Table 1. Overview of the application possibilities of different thermoanalytical techniques. ••• means "very suitable", • means "less suitable".

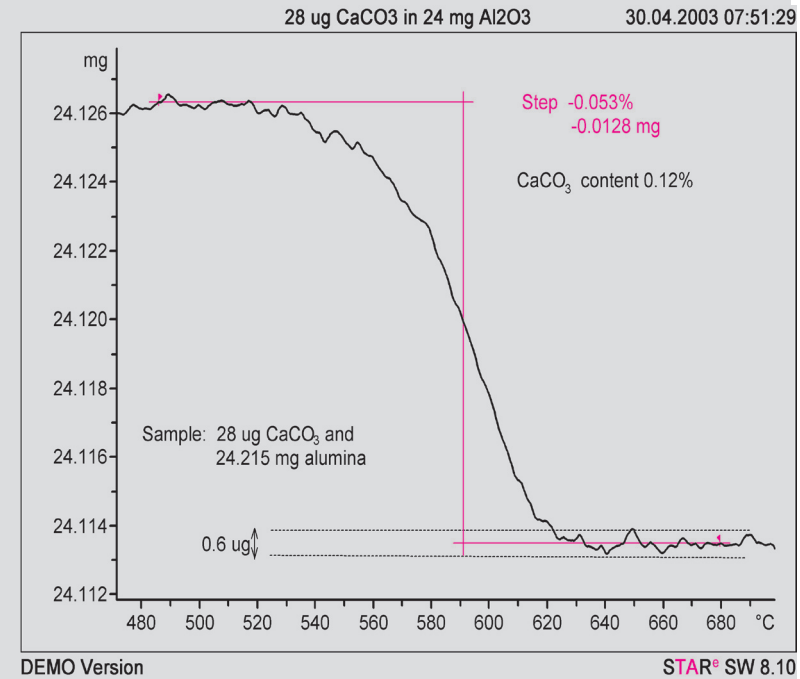

Figure 2. Calcination of 28 µg calcium carbonate in 24.215 mg aluminum oxide: The $CaCO_3$ loses CO_2 up to about 600 °C (calcination). From stoichiometric considerations, a step of 12.3 µg is expected from the decomposition reaction of calcium carbonate.

However, the accuracy with which such a small mass step can be measured also depends on the width of the step. An example of a very low mass loss step is shown in Figure 2.

Comment: Here, under the accuracy of a measurement (related terms also used are trueness or bias), we mean the closeness of agreement between the mean value of a set of results and the

accepted true value of the quantity. Accurate results of course require good precision. Precision is the closeness of agreement between independent measurement results on identical samples. It is a measure of the scatter or spread of the measurement results and is usually expressed as the standard deviation (often calculated as the relative standard deviation or the coefficient of variation). In the case of a purity determination, for example, it was known that the true value for the degree of purity of the sample was 98.4%. The result of a purity determination by DSC was 98.6 ± 0.1%. The deviation from the true value (i.e. the accuracy) is therefore 0.2%, and the precision 0.1%. Whether this is acceptable or not depends on your own requirements and is a matter to be considered in the validation.

Measurement mode

Once you have decided to use a particular measurement technique (here DSC, TGA, TMA or DMA), the next question concerns the measurement mode in which the in-strument is to be operated. Table 2 summa-rizes various instrument-specific measurement modes and their use.

Step 2: Sampling and sample preparation

The most important points concerning sampling and sample preparation can be summarized as follows:

- Is the sample representative of the total amount? To obtain reliable results, you may have to measure several samples and compare the results.
- Sample processing: To obtain optimum thermoanalytical results, samples often have to be mechanically processed (e.g. cut, ground, polished, etc.). This affects samples both mechanically and thermally: It may in some cases lead to undesirable changes in a sample (e.g. with polymorphous substances).
- Thermal pretreatment: Annealing at a suitable temperature eliminates the thermal history of the sample. The information obtained then relates

Measurement technique	Special measurement modes	Use
DSC	TM DSC (ADSC, IsoStep®)	Separation of changes in c_p from non-reversing events (vaporization, crystallization, chemical reactions)
TGA	MaxRes	For automated optimized temperature resolution of neighboring mass changes
TMA/DLTMA	• Dilatation (low load on sample)	Mode to measure the coefficient of thermal expansion
	• Penetration (large load on sample)	Particularly suitable for the analysis of thin films (glass transition, melting temperature, film thickness)
	• Tension	For fibers and films, shrinkage
	• Bending	Glass transition of filled materials and other stiff samples
DMA	• Tension	Above all for fibers and thin films
	• Compression	Foams, elastomers
	• Shear	Elastomers, most thermoplastics, powder, pastes
	• Bending	Fiber-reinforced plastics, thermoplastics, thermosets

Table 2. Special measurement modes for different TA techniques and their applications.

DSC/TGA	TMA	DMA
• Optimum contact of the sample with the crucible (thermal conductivity) • Sample must not move within the crucible • Sample must not react with the crucible	• Surfaces of the sample should ideally be flat and parallel • For dilatometry, use a quartz glass disk between the sample and the probe to distribute the force exerted by the probe uniformly over the sample	• Geometry of the sample must be known exactly • Sample must be properly mounted in the clamp • Possibly adjust force on the sample at the start temperature • The thermocouple must not touch the sample or the furnace and should always be placed in the same position

Table 3: Important aspects of sample preparation for different TA techniques.

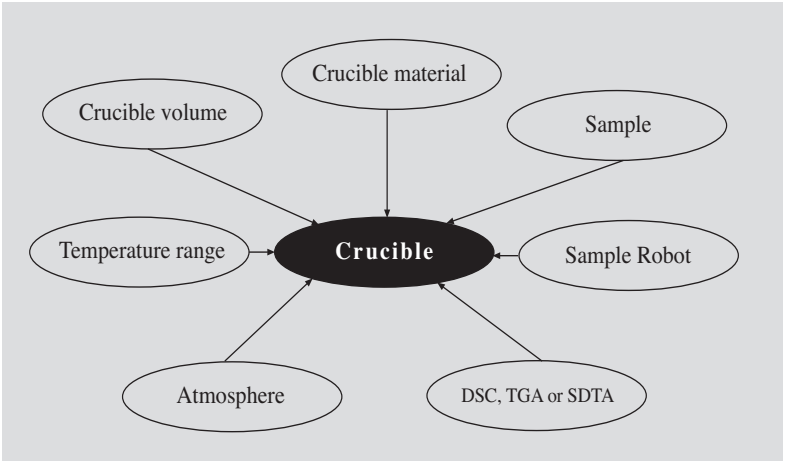

Figure 3. Factors influencing the choice of crucible.

solely to the material under investigation. If the sample is not annealed, information about the conditions under which it was produced, i.e. its thermal history, can also be obtained.
- Sample geometry and sample size. The sample should be no larger than is necessary to determine the result with the desired accuracy (i.e. as large as necessary but as small as possible).
- Insertion of the sample in the crucible (DSC, TGA) or in the instrument (TMA, DMA). See Table 3 for specific details.

Typical questions about sample size

How much sample do I need to determine a residue of 1% with an accuracy of ±1%?

Answer

In this case, the accuracy of the thermogravimetric measurement depends mainly on the reproducibility of the blank curve. For example, if the reproducibility is 10 µg in the temperature range considered, then these 10 µg represent 1% of the measured residue. The residue must therefore be at least 1 mg. Since the residue is about 1% of the original sample, a sample mass of at least 100 mg must be used.

What is the sample thickness needed to determine a coefficient of thermal expansion (CTE) of 20 ppm/K over a temperature interval of 10 K with an accuracy of ±2%?

Answer

On heating the sample through 10 K (ΔT = 10 K), the thickness of the sample with a CTE of 20 ppm/K increases by 200 ppm ($CTE = \Delta L/\Delta T \cdot 1/L_0$). Assuming that the change in thickness of the sample in this temperature interval can be determined with an accuracy of about 20 nm, the change in sample thickness over this 10-K interval must be about 1 µm (ΔL = 1 µm). This change corresponds to 200 ppm of the original sample thickness (L_0). This must therefore be at least 5 mm.

Step 3: Choosing the crucible (DSC and TGA only)

The most important considerations regarding the choice of crucible are the
- Volume of the crucible (sample mass; with the TGA, also gas exchange).
- Heat capacity and thermal conductivity of crucible: this influences the resolution (separation of thermal events) and sensitivity of the DSC or SDTA signal).
- Crucible material: the sample must not react with the crucible material.

Further aspects are presented in Figure 3. For a detailed discussion, see UserCom 5.

Recommendations: For DSC, we recommend the use of the small 20-µL aluminum crucibles: these crucibles have the lowest heat capacity and give the best sensitivity and time resolution. For the TGA, we recommend the 30-µL alumina crucible as standard crucible. If the temperature range of the measurement is below 600 °C, and if a reaction with the sample is not expected, the 40-µL aluminum crucible can also be used for TGA. The advantages are the excellent thermal conductivity and a much better SDTA signal due to its low heat capacity. In addition, the crucible can be disposed of after use and does not have to be cleaned.

Besides the standard crucibles, we also offer a variety of special crucibles manufactured from different materials (gold, platinum, copper, sapphire and Pyrex glass) for different conditions (normal, medium and high pressure). They are available in a number of different sizes.

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