

MICRO THERMAL ANALYSIS CALIBRATION, REPEATABILITY AND REPRODUCIBILITY

Roger L. Blaine¹, C. Gray Slough¹ and Duncan M. Price²

¹TA Instruments, Inc., New Castle, DE, USA

Rblaine@tainst.com

²Loughborough University, Loughborough, UK

ABSTRACT

Micro Differential Thermal Analysis (μ DTATM) and Micro Thermomechanical Analysis (μ TMATM) are representatives of the emerging technology known as Micro Thermal Analysis (μ TATM) in which thermal analysis is performed on test specimens as small as $2 \times 2 \mu\text{m}$. Like any thermal analysis technique, interpretation of results benefits from accurate temperature information and knowledge of precision of the resultant measurement. However, μ TA temperature calibration is more challenging than with its macro relatives since the calibrant comes into direct contact with the platinum sensor. This paper describes suitable calibration strategies based upon organic chemicals and polymers. Precision information for several test specimens is reported.

INTRODUCTION

Micro Thermal Analysis (μ TATM) is an emerging technology in which thermal analysis is performed on small specimens as small as $2 \times 2 \mu\text{m}$. The sensor is a microscopically fine $5\mu\text{m}$ diameter, "V" shaped platinum wire. Current is passed through the wire to raise its temperature and the temperature of the specimen according to a linear program. The resistance of the wire is simultaneously measured to yield sample temperature information. Most of the energy in the probe is transferred to the heat capacity of the test specimen. During a transition, however, additional power is needed. When this signal is compared to that of a reference, a micro differential thermal analysis (μ DTATM) signal results. Moreover, the probe is loaded with a small force, so that it penetrates into melted specimen resulting in a second analytical signal, that of micro thermomechanical analysis (μ TMATM). Additionally, the use of a sinusoidal temperature program, like that of Modulated DSC (MDSC®) and modulated TGA (MTGATM), permits the μ TA to "see" into the test specimen to a depth dependent upon the frequency of modulation. Due to the small thermal mass of the sensor, heating rates up to $25 \text{ }^\circ\text{C/s}$ are used.

The μ TA sensor is mounted on the tip of an Atomic Force Microscope (AFM) probe. This permits imaging capabilities of the AFM to be used to map the surface area of interest and to select the appropriate regions for subsequent thermal analysis.

Micro thermal analysis is currently a qualitative tool; that is, it is primarily used to identifying the material being examined. Application examples include characterization of multi-layer film (1), investigation of pharmaceutical matrices (2) and identification of different phases in polymer blends (3). The temperature at which a transition takes place is the primary output signal. Like all thermal analysis techniques, interpretation of results requires detailed temperature calibration procedures and an understanding of the precision of the temperature measurement.

CALIBRATION MATERIALS

A good reference material has a number of desirable properties including a well-documented value, availability in a suitable form for analysis, homogeneity, stability, low toxicity, and traceability to a national reference laboratory (NRL). In traditional DTA and TMA, metals like indium, tin, and zinc meet these criteria. These metals are not suitable for temperature calibration in μ TA, however, as they may alloy with the platinum sensor with which they come in to contact.

Organic calibration materials are more suitable for calibration in μ TA as they do not react with the platinum sensor and the sensor is easily cleaned at the end of an experiment by “burning off” at 500 °C in air. The British Laboratory of the Government Chemist (LGC), a national reference laboratory, conveniently offers eleven organic reference materials with melting temperatures ranging from 41 to 285 °C. Six of these standard reference materials, which are used as calibrants in this study, are presented in Table 1 along with their nominal melting temperatures.

SPECIMEN PREPARATION

Organic chemicals are not ordinarily suitable for use as μ TA calibration materials in the fine powdered form in which they are received. The individual crystals are usually too small and rough to be used directly. For ease of handling, powdered organic materials need to be formed into larger crystals by recrystallizing from the melt. Suitable crystals are prepared by melting a few milligrams of the organic compound in a standard 6.3 mm aluminum DSC sample pan with an aluminum lid placed lightly (not crimped) on top. The sample is heated in a DSC at 10 °C/min to a temperature 10 °C about the nominal melting temperature, then quickly cooled. (Alternatively, the DSC sample pan may be placed for a few seconds on a hot plate set to a temperature about 10 °C above the nominal melting

Table 1
mTA Calibration Materials

Calibrate	Temperature ¹ (°C)
-----	-----
Biphenyl	69.3
Benzil	94.5
Benzoic Acid	122.4
Diphenylacetic Acid	147.3
Anisic Acid	183.3
2-Chloroanthraquinone	209.6

The certified melting temperature for each lot of material supplied is provided in the LGC certificate for each material.

temperature.) This procedure melts the material without exposing it for long periods (and potential degradation) at temperatures above the melt. The resulting organic crystals are prepared for mounting by cutting down the edges of the DSC sample pan with an Exacto® knife. These crystals may then be fixed to the μ TA sample mounts using double-sided tape to prevent the individual crystals from moving around during storage and analysis. The mounted samples are stored in small, labeled petrie dishes for future use.

The use of the aluminum sample lid during large crystal formation results in a smooth flat surface required for μ TA work. The aluminum pan and lid provide smooth, inert surfaces upon which the molten organic may crystallize. Crystals created without the use of the lids have an unsuitably ragged surface.

CALIBRATION

Most thermal analysts prefer a two-point calibration procedure. This is performed using a low temperature calibrant, such as biphenyl at 69 °C, and a high temperature one, such as anisic acid at 183 °C. A typical thermal curve for μ TA of a sample of anisic acid is shown in Figure 1. The melting endotherm is seen near 170 °C. In μ TA, the sensor is located at the surface (i.e., outside) of the test specimen, as it is in DSC, and so the extrapolated onset is used to identify the melting temperature.

Triplicate measurements of the melting temperature are made and the mean temperature is used to temperature calibrate the apparatus. The pooled standard deviation of the two triplicate measurements gives an estimation of measurement precision.

A comparison of melting temperatures observed by μ DTA versus the certified melting temperatures provided by LGC are shown in Figure 2. A straight calibration line (correlation coefficient of 99.9%) is observed for covering a 150 °C temperature range. This calibration profile is stored in the μ TA for future work. If desired, first, second or third order fits to calibration data may be used.

POLYMERS

Measuring the melting temperatures of polymeric samples is the most common use of μ TA. The μ DTA response signal for polymers has a somewhat different shape than that for pure organic chemicals. The difference in response is thought to be due to the organic melt shrinking away from the hot thermal probe and losing contact, creating the melting “peak” response. The less mobile polymer materials remain in contact and simply continue to absorb energy.

The extrapolated onset for the change in power consumption at the melt may be used to identify the polymer melting transition temperature. This value may be correlated with the melting onset temperature observed by DSC. As is observed with the organic materials, the μ DTA response with polymers is a straight line with a correlation coefficient of 99.9%. The line has the same slope as that observed with the organic chemicals but is offset to higher temperatures by about 11°C. The “turn-on” transition, which results when the temperature program passes through ambient temperature (see Figure 1), provides a second, low-temperature calibration point in each thermal curve.

A second and somewhat simpler temperature calibration procedure may be used in μ TA with polymer samples. A single, high melting polymer (the authors prefer Nylon 6, Nylon 6,6 or polyethylene terephthalate) is used to mark the high temperature end of the calibration curve and the ambient temperature “turn on” signal at the low end.

Temperature calibration with polymeric films offers a number of ease-of-use advantages, chief among these is the reduction (by half) in the time and number of experiments needed to calibrate the apparatus. The sample mounting procedure for smooth, clean and flat polymeric films is much easier. Samples are conveniently cut out with a 6.3 mm paper punch and mounted using double sided tape. Additionally, polymers have very high melting temperatures that provide a calibration range of nearly 300 °C, a range difficult to achieve with organic chemicals.

Calibration curves for organic and polymer materials may be stored separately within the instrument. The appropriate calibration curve may then be selected to match the type of test specimen being examined.

REPEATABILITY

The within-laboratory precision of measurement is known as repeatability. Replicate measurements made on both organic crystals and polymeric films indicates that the standard deviation for melting temperature determined by the μ TMA signal is about 0.2 °C while that for the μ DTA is about 2.1 °C. In addition, the μ TMA transition is about 3.5 °C higher than the extrapolated onset temperature determined by μ DTA.

The precision of temperature measurement appears to be somewhat dependent upon heating rate at the very fast rates typically employed with μ TA. Heating rates between 10 and 25 °C/s (i.e., 600 to 1500 °C/min) give consistent results, while those at lower rates between 2 and 8 °C/s (120 and 480 °C/min) have substantially poorer precision.

SUMMARY

Two point μ TA temperature calibration procedures are presented for use with organic chemicals and with polymer samples. For each class of material, the μ TA response is linear with temperature. Selection of the point on the thermal curve for identification of the transition temperature leads to bias in the reported values. The bias between μ DTA and μ TMA values is about 3.5°C. The bias between the values for organic chemicals and polymers is about 11 °C. These differences are thought to be associated with the difference in mechanical “movement” of the test specimen as it is melted.

REFERENCES

- (1) Price, D.M.; Reading, M.; Caswell, A.; Hammiche, A.; Pollock, H.M.; Microscopy Anal., **1998**, 65, 17-19.
- (2) Craig, D.Q.M.; Royall, R.G.; Reading, M.; Price, D.M.; Lever, T.J.; Furry, J.; Proc. 26th N. Amer. Therm. Anal. Soc., **1998**, 610-615.
- (3) Reading, M.R.; Hourston, D.L.; Song, Mo; Pollock, H.M.; Hammiche, A.; Amer. Lab., **Jan. 1998**, 13-17.

Figure 1
 μ TA Thermal Curve for Anisic Acid

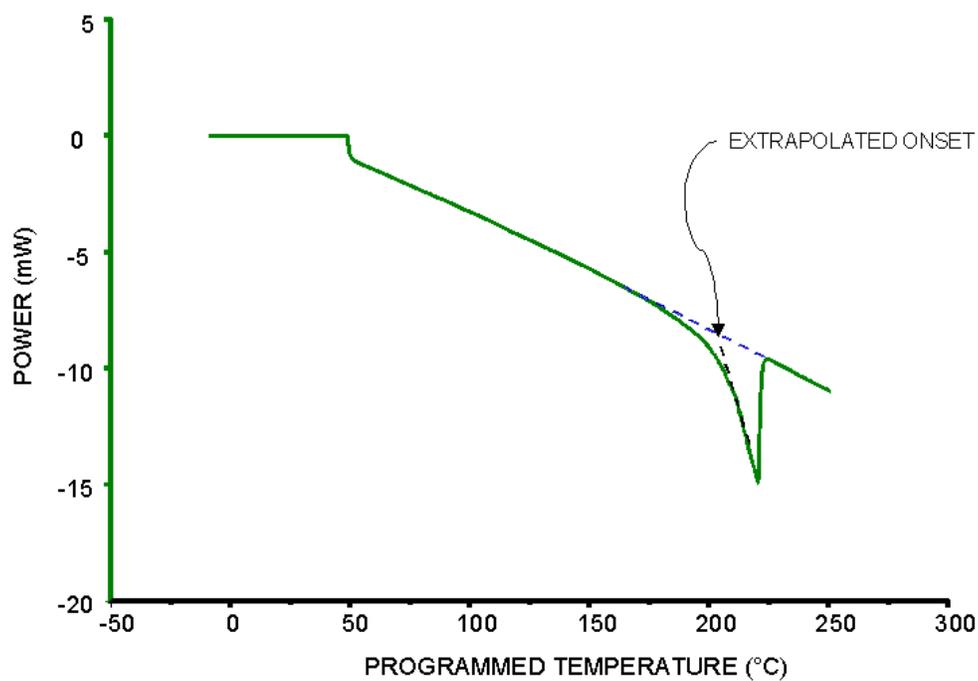


Figure 2
 μ TA Temperature Calibration

