

Thermal Analysis**Author:**

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Coefficient of Thermal Expansion Measurement using the TMA 4000

Introduction

With few exceptions, all materials expand when heated. However, the extent of expansion per degree change in temperature is different

for different materials. Because structures—electronics, machinery, satellites, buildings or bridges—are constructed of multiple materials, these structures undergo stress between materials when heated or cooled. If they have not been designed to accommodate differences in expansion this stress may lead to failure.

The TMA 4000 thermomechanical analyzer (TMA) is designed to accurately measure small changes in the dimensions of a sample as it is heated over a programmed temperature range (Figure 1). It is a laboratory analyzer with a small benchtop footprint, but a large capability for simply and accurately measuring the coefficient of thermal expansion (CTE). It incorporates numerous features to optimize its ease of operation while maximizing accuracy and sensitivity.

The sample is placed in a furnace enclosure which can be maintained within a few tenths of a degree using closed-loop temperature control (Figure 2). The sample is supported by a fused quartz platform, and the sample's height is monitored by a position sensor coupled to a fused quartz probe whose weight is counterbalanced by a buoyancy float and trimmed with a force transducer. As the furnace is heated, the quartz probe, quartz platform and sample expand. The expansion of the probe and platform cancel each other out, so the output of the position sensor is a direct measure of the expansion of the sample alone. The buoyancy float damps environmental vibration and protects the quartz from breakage during sample loading.

In practice, the TMA technician simply zeros the position of the sensor with the probe on the platform, raises the probe, places the sample on the platform, lowers the probe onto the sample, raises the furnace around the sample and starts the temperature program. The resulting record shows the expansion of the sample with changing temperature.

Theory

The TMA measures the expansion of the sample as a function of its temperature. So the primary output is a plot of sample height versus temperature. Over a sufficiently narrow temperature range the expansion of the sample is a linear function of temperature. Therefore, one can also report the slope of the expansion curve over the temperature range of interest. If the expansion rate is approximately linear, one can equilibrate the sample at T1, measure its height in the TMA, then heat using the TMA temperature program to another temperature T2, equilibrate, record the height, and then calculate the expansion rate and the expansivity as: (represented by convention as alpha):

$$\alpha = \frac{1}{L_0} \left\{ \frac{\Delta L}{\Delta T} \right\},$$

where L_0 is the initial sample height at 20 °C, ΔL is the change in length (height) and ΔT is the change in temperature between the two equilibration temperatures. This alpha will be the average coefficient of expansion (CTE) for this particular temperature interval.

This CTE can also be calculated from the scanning data at a suitably slow scanning rate (after allowing time for scanning equilibration) by selecting the menu item in the software for the coefficient of thermal expansion and then inputting the two temperatures which define the temperature region over which the CTE is to be calculated. A temperature interval of 10 to 40 degrees is typical (Figure 3). This is the procedure followed by most laboratories using a TMA.



Figure 1. TMA 4000

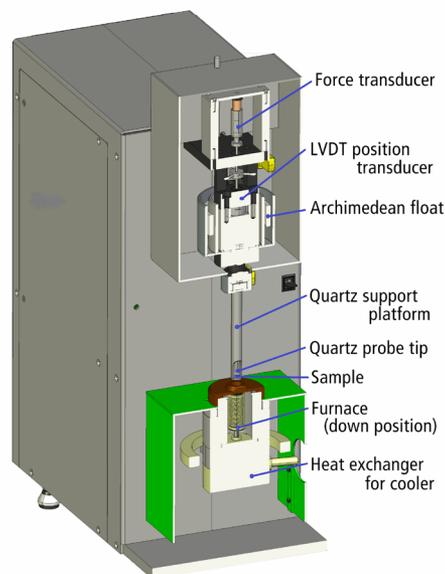


Figure 2. TMA 4000 cross section diagram showing functional components

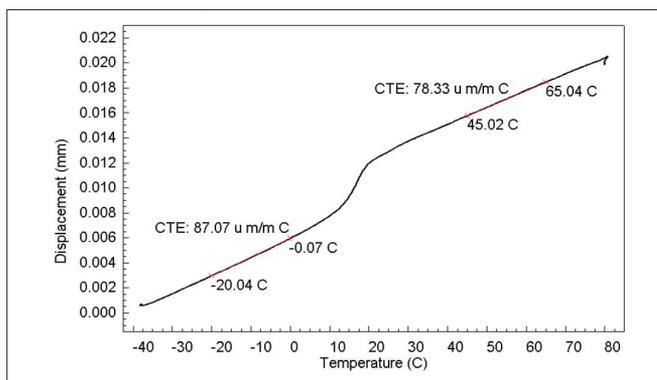


Figure 3. Determination of CTE of PTFE

For the more general case of reporting CTE as a function of temperature over a wide temperature range:

$$\alpha(T) = \frac{1}{L_0} \left\{ \frac{\partial L}{\partial T} \right\},$$

where $\left\{ \frac{\partial L}{\partial T} \right\}$ is the slope of the expansion curve at the temperature T, and L_0 is the initial sample height. When this is reported over a substantial temperature range, the slope is unlikely to be constant, and so alpha is reported as a polynomial in powers of temperature. The TMA 4000 generates the CTE data to calculate the polynomial terms.

Experimental Variables

Accurate CTE data requires a precision TMA, but it also requires good experimental technique. What are the considerations for sample handling and method development?

Sample Height. In general, the larger the expanding length, the greater the length change signal and the greater the CTE accuracy. A sample height of 10 mm is recommended for use as the standard. Because of the wide range of the LVDT and the height of the furnace (40 mm), the TMA 4000 can accommodate a sample of up to 12 or 22 mm in height depending on the probe type in use.

Sample Shape. The ideal sample would have a perfectly flat top and bottom so that any force of the probe on the sample is spread out over a wide enough surface area so as to avoid sample deformation. Accurate CTE measurements will only be obtained if the sample does not deform due to softening during the experiment. Of course, one can get reliable CTE readings from any shaped sample provided the sample geometry stays the same. The high sensitivity of the LVDT and the viscous damping of the float suspension allow very light force to be applied without noise due to environmental vibration.

Sample Orientation. Samples may not expand isotropically. For example, fibers will expand completely differently along, versus across, the fiber; and a circuit component may use a fiber filler to constrain the expansion within one axis or within one plane, and force volumetric expansion in the third direction. Characterizing such a sample requires measurement of the expansion along each of the three axes.

Probe Force. The force which the probe exerts on the sample is under the TMA operator's control. The force is continuously selectable in either the up or down direction. In general, if the sample is expected to soften, then a light force is called for (if the material softens and the force is too great, the sample may settle, causing error in CTE). If the sample is not expected to soften over the investigated temperature range, a more substantial probe force is appropriate.

Purge Gas. The purge gas is normally nitrogen or, if there is no danger of oxidation, air. The purge rate is normally 20 cc/min, but this rate is not critical. Helium is an even better purge gas because of its greater thermoconductivity. The sample equilibrates more quickly with helium, enabling the use of faster scan rates. However, the TMA 4000 was designed and optimized for use with nitrogen, which is much less expensive.

Heating Rate and Equilibration Time. The CTE calculation is based on the height difference between two temperatures, and for that calculation to be accurate the average temperature of the sample and the thermocouple should be very close to one another. This is best achieved by allowing full equilibration after loading the sample before starting the temperature scan portion of the program, and by allowing adequate time (and temperature) after starting the

scanning portion before using the data for the CTE calculation. The length of equilibration time depends upon the sample size, how well the sample is thermally coupled to the quartz platform, the sample's internal thermal conductivity, the temperature of the furnace and the purge type. One way to see how much time is required is to heat to a new isotherm and observe the time needed for the signal to become constant.

Procedures

Sample Preparation. The sample for CTE measurement should be cut to have flat and parallel surfaces top and bottom. It should be no thicker side-to-side than is necessary to stand freely on the platform; and it should have no burrs that support the sample or impinge the probe. The method of preparing the sample should not introduce stress into the sample, stress that might be relieved on heating, nor should preparation raise the temperature of the sample sufficiently to cause a physical change. A razor knife may be sufficient for plastics, and a lapidary system may be required for ceramics.

Temperature Calibration. The thermocouple, together with its built-in digital correction, provides accurate temperature readouts and reporting. The main reason for temperature calibration is to compensate for the temperature difference that develops between the thermocouple tip and the average temperature of the sample as the system is heated. This difference will be negligible for a thin film or fiber, and (at moderate scan rates) barely significant for a 1 mm high solid in good contact with the furnace tube floor. One can easily check the temperature difference between the tip of the thermocouple and platform floor by placing a small piece of a pure melting standard between the probe and the platform, then performing the temperature program that you would use for samples. This is the basis for temperature calibration.

Length Calibration. The length calibration is performed at installation and is independent of all operating conditions. It can easily be checked by measuring the apparent height of a disk of material which has been independently measured using a micrometer.

An alternate method of calibration sometimes used for CTE analysis is to measure the length change of a calibration sample (aluminum samples provided) using the temperature program and experimental conditions you will be employing to run samples. This method has the advantage of compensating for certain errors and also for correcting the expansion of fused quartz. This method works best when the standard sample most closely resembles the samples you will be testing.

Baseline Subtraction. When samples are run using the expansion probe and appropriately slow scanning rates it is not necessary to subtract a baseline. To confirm this, simply run a no-sample baseline under standard conditions and compare the displacement to that of your typical sample.

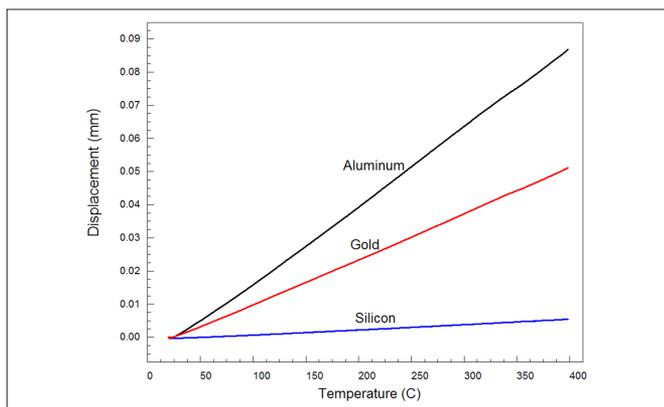


Figure 4. Expansion of pure elemental standards aluminum, gold and silicon

When that which is expanding with temperature includes more than the sample itself, for example, if the sample is enclosed in a capsule, sitting on a pedestal, in a dilatometer, or suspended in extension by clips, then a baseline should be subtracted from the expansion curve before CTE calculations are performed. Also, when heating rates greater than those suggested above are used, subtracting a baseline will reduce system error resulting from temperature gradients.

Results

One way to assess the capabilities of a new TMA is to run standard samples and compare the data to the results reported by highly respected laboratories. Standard Reference Material 731-L1, Borosilicate Glass, is a National Institute of Standards and Technology (NIST) primary reference for thermal expansion. The other samples measured were pure metals: gold, silver and aluminum, all of which have been measured by the National Physical Laboratory in England. These materials are standard thermal analysis melting point temperature calibration materials available from PerkinElmer. The figures below show the raw data which has been corrected in the table for the CTE of fused quartz. The experimental conditions are practical ones, namely, using a heating rate of 5 °C/min and a purge gas of nitrogen. The sample size was in the range of 5 to 10 millimeters.

Figure 4 shows the expansion data for the three pure materials. Figure 5 shows the expansion data for the NIST borosilicate glass standard together with the expansion data obtained on the TMA 4000. Table 1 summarizes the values of CTE at 227 °C for four standard materials comparing TMA results compared to NIST and NPL data¹. The glass plot shows data for both NIST and TMA 4000 data versus temperature.

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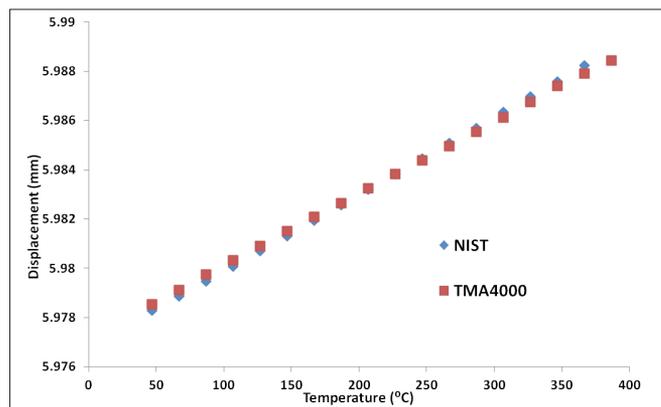


Figure 5. Expansion of Borosilicate glass

Table 1. CTE Results using standard materials

Material	CTE (um/mC) at 227 °C	
	TMA 4000	NPL/NIST Value
Aluminum (not same material)	25.08	26.4
Silver	19.15	20.6
Gold	15.24	15.4
Silicon	3.2	3.5
Borosilicate glass	4.5	4.33

Summary

The results show that the TMA 4000 is able to measure the coefficient of thermal expansion of several well characterized materials to within a few percent or better. The borosilicate glass is a particularly challenging sample because the CTE is low, and it is not a good thermal conductor. The ability of the TMA 4000 to achieve this level of results is due to the quality of the measuring electronics, the design of the probe/stage measuring system and the precision thermostating of the LVDT position sensor. The use of a damped suspension system is particularly important since small vibrations in the benchtop could otherwise produce noise in the sensitive position sensor. This level of accuracy and sensitivity is essential when measuring the dimensional changes of the low-expansion, undersized samples typically encountered in the electronics industry.

References

1. Kaye and Laby Online, Section 2.3.5 Version 1.1 updated 2 December 2010 (On-line physical constant data base maintained by National Physical Laboratory)

