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CALIBRATION AND ACCURACY OF THERMAL MECHANICAL ANALYZERS

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ABSTRACT

A study has been carried out to evaluate the accuracy of thermal expansion coefficients (TEC) data obtained from two commercial thermomechanical analyzers. The potential sources of error in the technique have been identified, and the methods of reducing their impact are proposed. The standard ASTM procedure using thermomechanical analyzers restricts the applicability to materials with TEC $> 5 \times 10^{-6} \,^{\circ}C^{-1}$; the accuracy being reported as $\pm 61\%$ when TEC $= 1\text{–}5 \times 10^{-6} \,^{\circ}C^{-1}$. Using our correction procedures, the accuracy has been improved to about $\pm 2\%$ on a borosilicate sample of TEC $= 4.7 \times 10^{-6} \,^{\circ}C^{-1}$. More importantly, our correction procedures allow ultra-low expansion materials (TEC $\approx 0\text{–}1 \times 10^{-6} \,^{\circ}C^{-1}$) to be studied with reasonable confidence.

INTRODUCTION

Thermomechanical analysis (TMA) is a technique in which the deformation of a substance is measured under non-oscillatory load as a function of temperature as the substance is subjected to a controlled temperature program [1]. In practice, deformation is monitored as the linear dimensional change, e.g. length, and most commercial instruments operate in the −180 to 700 °C temperature range. The related technique, dilatometry, is traditionally considered to involved volume change as a function of temperature but again, commercial instruments monitor the linear dimensional change of a material over a wider temperature range of 25 to 2200 °C. Thus, both TMA and dilatometry instruments measure the change in length of a material as it is heated or cooled. This is usually achieved by monitoring the change in position of a probe, or push-rod, which is held against one face of the sample, typically using a linear variable differential transformer (LVDT) (Fig. 1).

The use of TMA for measuring thermal expansion coefficients (TEC) is widespread; the only other technique is fairly specialized and is based on laser interferometry. The LVDT measuring device is not absolute and is factory calibrated. In addition, system variables such as the expansion of the

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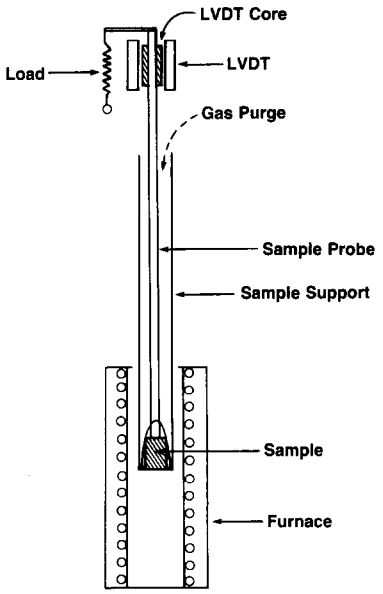

Fig. 1. Schematic of thermal mechanical analysis system.

push-rod and the sample support system, introduce unique individual instrument response factors. The aim of this study is to examine the various factors influencing calibration, precision, and accuracy for two commercial TMA units. Particular emphasis is placed on the study of low TEC materials (i.e. TEC $\leq 5 \times 10^{-6\circ} C^{-1}$) and of samples of varying lengths.

ERRORS AND CALIBRATION

Errors in TMA systems can mainly be ascribed to one of three reasons.

(a) Inaccuracies in the original length measurement. For example an error of $\pm 0.10\%$ in TEC is obtained for a sample length of 10 ± 0.01 mm and a TEC of $25 \times 10^{-6\circ} C^{-1}$ (Appendix A). Similarly the error is $\pm 1.0\%$ for a length of 10 ± 0.01 mm and a TEC of $5 \times 10^{-6\circ} C^{-1}$. It should be noted that the ASTM Method E831-81 [2] describing the operation of TMA units requires the initial sample length to be determined to an accuracy of ± 0.25 mm for a length of 10 mm. This is much less accurate than the ± 0.01 mm achieved by commonly available commercial micrometers such as that used in this study. Considering an accuracy of ± 0.01 mm in length measurement and a TEC of $2.5 \times 10^{-6\circ} C^{-1}$, it follows that the error decreases with longer initial lengths e.g. 0.01% (100 mm), 0.1% (10 mm), and 1% (1 mm).

(b) Probe/sample support length differences. These can best be understood by reference to Fig. 2 which indicates that the probe and sample support within the furnace hot zone are unequal in length by an amount

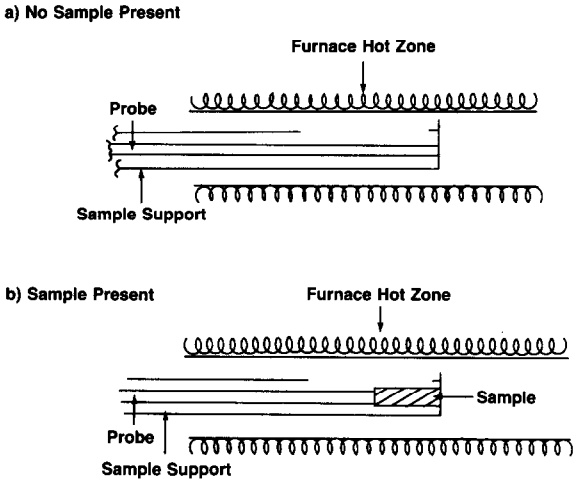

Fig. 2. Probe/sample support error.

equal to the sample length. Thus for a 10 mm sample in a quartz system there will be a reduction in the observed sample expansion, resulting in an error of -1.8% for a TEC of $25 \times 10^{-6} \circ C^{-1}$ (Appendix B). This gives rise to an error of -9% for a TEC of $5 \times 10^{-6} \circ C^{-1}$.

(c) Instrumental effects. These include thermal gradients within the furnace hot-zone and non-linearity of the detection system, and are not readily calculable. The ASTM Method E831-81 [2] states that no detectable increase in imprecision is observed for specimen sizes from 2 to 10 mm, for heating rates of $2–10 \circ C\ min^{-1}$ and for thermal conductivities of 0.2–400 W $m^{-1} \circ C^{-1}$. Our own preliminary studies confirm that heating rates of up to $10 \circ C\ min^{-1}$ do not detectably alter data obtained using a Perkin–Elmer TMA system [3].

The latter two sources of error are those most commonly addressed by practitioners in this field. The ASTM method requires correction of the observed expansion for the difference in expansion between the probe and sample support [2]. Interestingly, the commonly available commercial TMA units do not include this correction as part of their available data-handling software. The less well defined errors, described in (c) above, can be estimated from either a blank run or using a sample of the material of the construction of the probe/sample support [2]. An alternate method of calibrating is to measure a standard of known TEC and so generate a calibration curve. This method has been described by several workers [4–6] and is used by some commercial TMA manufacturers. It has the advantage that, if the standard is run under the same conditions as the samples, most forms of error will be corrected for. However, the limits of this technique are not well understood and so it is not clear how different the sample and standard can be before errors become unmanageable.

EXPERIMENTAL

Two TMA units were employed for this study. The first was the Perkin–Elmer TMS-2 fitted with a TADS data station and low temperature furnace (-150 to $325\,^{\circ}C$). This was mounted on an anti-vibration table and operated in flowing helium with the quartz expansion probe. Temperature calibration was checked using a short length of indium wire in the fiber probe. This indicated instantaneous infinite extension at $156.5 \pm 1\,^{\circ}C$ (literature m.p. $= 156.6\,^{\circ}C$). The system has no built-in method of calibrating the thermal expansion response.

The second TMA unit used was the Netzsch dilatometer 402ES/3, fitted with the $1600\,^{\circ}C$ air-cooled furnace. This was operated in flowing helium with the 0–25 mm quartz measuring system. Temperature calibration was checked using a small piece of gold which indicated instantaneous 'shrinkage' at $1064.5 \pm 1\,^{\circ}C$ (literature m.p. $= 1064.4\,^{\circ}C$). Data can be corrected by analyzing a known standard material. A 10th-degree polynomial is fitted to the expansion/temperature data and this is then subtracted from a stored polynomial describing the standard material. The resulting polynomial is used to corrected subsequent 'unknown' sample runs.

A range of standard materials was employed. These were an aluminum cylinder 7 mm long supplied by Perkin–Elmer, a borosilicate glass (NBS SRM731), and a single crystal sapphire cylinder 25 mm long (NBS SRM732).

Materials of ultra-low thermal expansion used were Zerodur (glass ceramic, Heraeus–Schott), ULE 7971 (titanium silicate, Corning), and Unispan (LR-35 Invar, Universal Cyclops).

RESULTS AND DISCUSSION

Perkin–Elmer TMS-2

Thermal expansion data for aluminum showed that for a series of six consecutive experiments the TEC was $21.77 \pm 0.08 \times 10^{-6}\,^{\circ}C^{-1}$ between -55 and $95\,^{\circ}C$. This translates to a variation of 0.37% in the precision of measurement. Aluminum is recommended by Perkin–Elmer [7] as a standard although published data cover a range of values (Table 1). The result obtained here is on the low end of that range.

As-observed thermal expansion data (i.e. no correction) for borosilicate glass (NBS SRM731) of lengths 3.19, 7.25, and 9.90 mm are shown in Table 2. These data indicate an error of up to 18.5% relative to the NBS value of $4.743 \times 10^{-6}\,^{\circ}C^{-1}$ across the temperature range -55 to $95\,^{\circ}C$.

The observed data were then corrected (a) for the difference in expansion between the probe and sample support. The correction was achieved by using a 5th-order polynomial expression, describing the expansion of fused

TABLE 1

Published thermal expansion coefficients for aluminum

Temperature range (°C)	TEC ($\times 10^{-6}$ °C^{-1})	Ref. no.
−50– 20	21.8	7
−50–100	23.3	8
20–100	23.6	7
20–100	23.5	8
20–100	23.6	9
20–200	24.5	7
20–300	25.5	7
−73	20.2	10
−23	22.0	10
20	23.0	10
77	24.1	10
127	24.9	10
−50	22.1	2
0	23.0	2
50	23.7	2
100	23.8	2

silica NBS SRM739 over the range −103–727 °C, to calculate the expansion of that material during the TEC determinations. This gave a $\Delta l/l$ value of 67.701×10^{-6}, (−55 to 95 °C) which, when used to correct the expansion of the aluminum (Appendix C), results in a value of 22.22×10^{-6} °C^{-1}. Similarly, data for the borosilicate glass are corrected to within 9% of the NBS data using this process (Table 2). A second correction (b) was performed

TABLE 2

Thermal expansion coefficients for borosilicate glass (NBS SRM731) as a function of sample length, obtained using the Perkin–Elmer TMS-2

Run	TEC ($\times 10^{-6}$ °C^{-1}) −55 to 95 °		
	Sample length (mm at RT)		
	9.90	7.25	3.19
1	4.24	4.00	3.87
2	4.10	4.24	3.87
3	4.31	4.45	3.87
Average	4.22 ± 0.11	4.23 ± 0.23	3.87 ± 0.00
Corrected (a) [a]	4.67 ± 0.12	4.68 ± 0.25	4.32 ± 0.00
Corrected (b) [b]	4.79 ± 0.12	4.85 ± 0.25	4.70 ± 0.00
NBS Value		4.743	

[a] Correction (a) for the expansion of the length of probe displaced by the sample.

[b] Correction (b); as (a) plus a constant instrumental error of 1.8×10^{-6} mm expansion.

TABLE 3

Thermal expansion coefficients for ultra-low expansion materials, obtained using the Perkin–Elmer TMS-2

Sample	Comment	TEC ($\times 10^{-6}$ °C^{-1}) −55 to 95 °C		
		Observed	Corrected (a) [a]	Corrected (b) [a]
Unispan	x direction 1	0.66		
LR-35	2	0.66		
	average	0.66	1.11	1.23
	y direction 1	−0.53		
	2	−0.66		
	average	−0.60	−0.14	0.07
	z direction 1	−0.13		
	2	−0.39		
	average	−0.26	0.19	0.31
Zerodur	1	−0.35		
	2	−0.89		
	average	−0.62	−0.26	−0.05
ULE 7971	1	−0.19		
	2	−0.31		
	average	−0.25	0.20	0.32

[a] See Table 2 footnotes.

using data obtained for a quartz sample (length 7.032 mm). This gave an instrumental error of -1.80×10^{-4} mm in Δl across the temperature range of interest. When this is added to the experimental data for the borosilicate glass, and then the correction for the displaced fused silica is applied, the data are closer to the expected values. In the case of the borosilicate glass, the maximum observed error is now 2.26%.

Data for the ultra-low expansion materials are summarized in Table 3. The TEC for the Zerodur material is the lowest, i.e. -0.05×10^{-6} °C^{-1} Berthold and Jacobs [11], using an optical technique (based on a laser interferometer), report that, for this temperature range, Zerodur has a TEC in the range -0.05–0.05×10^{-6} °C^{-1}, ULE has a TEC of −0.15 to 0.05, and for Unispan, TEC varies between around 0.48 and 0.65×10^{-6} °C^{-1}. Their precision of measurement is given as 0.001×10^{-6} °C^{-1}. O'Donnell and Rowe [12] report values of 2.21 and 2.16×10^{-6} °C^{-1} for Unispan between 0 and 70 °C in the machine direction, again using an optical technique. Wolff [13] found that the TEC of Zerodur was around -0.05–0.03×10^{-6} °C^{-1} and for ULE the TEC was about 0.05 to -0.01×10^{-6} °C^{-1} between −55 and 95 °C. Thus, it appears that the system of data correction used here, i.e. correction for the difference in expansion between the probe and sample support, and subtraction of instrumental errors, enables ultra-low expansion materials to be ranked using this instrument.

Netzsch 402ES/3

The Netzsch system is designed less as a TMA for precise measurement of TEC over a narrow temperature range and more as a versatile high temperature system for studying larger dimensional changes such as those occurring during sintering. In addition, the use of large sample sizes (up to 50 mm) means that it is more important to correct for probe/sample support length differences than is the case for the Perkin–Elmer unit. However, to enable some comparisons to be made between the units, a similar series of experiments were performed. Using sapphire as a standard in flowing helium, a series of six consecutive analyses of aluminum gave a TEC of $22.77 \pm 0.73 \times 10^{-6} \circ C^{-1}$ between 50 and 250 °C. As was found with the Perkin–Elmer result for aluminum, the obtained value of TEC appears to be low in comparison with the published values (Table 1).

There is a concern when using a system that automatically generates calibration data that the choice of standard and operating conditions will influence the data. Again, using aluminum as an example of a high TEC sample, thermal expansion data for this material using a range of standards and conditions is summarized in Table 4. The data clearly demonstrate that the choice of standard and experimental conditions do influence the data, giving a range in the TEC of $22.77–26.94 \times 10^{-6} \circ C^{-1}$ between 50 and 250 °C.

A second concern is that the furnace hot zone may contain temperature gradients in the sample zone (25 mm length). In order to check this, the aluminum standard was run in the presence of two quartz cylinders (each of length 7 mm) such that the three samples were placed in line with each other in the unit. Three scans were made, with the aluminum being at either end and in the center. The TEC values obtained were 22.46, 22.72, and 22.25 ×

TABLE 4

Effect of experimental conditions on the thermal expansion coefficients for aluminum, obtained using the Netzsch 402ES/3 system

Run	Comment	Standard, length	TEC $\times 10^{-6} \circ C^{-1}$ 50–250 °C
1	Flowing air 5 °C min^{-1}	Fused silica, 7.032 mm	26.85
2	Static air 2 °C min^{-1}	Fused silica, 7.032 mm	26.94
3	Flowing air 5 °C min^{-1}	Vacronium, 25 mm	25.40
4	Flowing helium 2 °C min^{-1}	Sapphire, 25 mm	22.77

TABLE 5

Thermal expansion coefficients for borosilicate glass (NBS SRM731) as a function of sample length obtained using the Netzsch 402ES/3 system

Run	TEC ($\times 10^{-6}\,°C^{-1}$), 50–250 °C		
	Sample length (mm at RT)		
	24.40	9.89	3.18
1	4.686	4.651	4.544
2	4.713	4.580	4.450
Average	4.700	4.616	4.497
Corrected (Netzsch)	5.059	4.975	5.220
Corrected (a) [a]	5.310	5.226	5.107
Corrected (b) [a]	5.367	5.367	5.544
NBS value		5.155	

[a] See footnotes for Table 2.

$10^{-6}\,°C^{-1}$ (between 50 and 250 °C) respectively. This clearly demonstrates the absence of any significant temperature gradients.

As-observed thermal expansion data for three lengths of borosilicate glass (24.40, 9.89, and 3.18 mm) (NBS SRM731) are shown in Table 5. The data indicate an error of up to −10.5% relative to the NBS value of $5.155 \times 10^{-6}\,°C^{-1}$ across the temperature range 50–250 °C. The observed data were then corrected as per the Netzsch software using data for the sapphire standard run under identical conditions. This reduces the error to less than 3.5%. By only correcting (a) for the theoretical difference in expansion between the probe and sample support (taken to be $\Delta l/l = 122.023 \times 10^{-6}$, calculated as described earlier in this report) the largest error is 3.0%. A third correction (b) was made using data obtained for the quartz sample (length 7.032 mm). This gave an instrumental error of 2.78×10^{-4} mm in Δl across the temperature range of interest. When this value is added to the experimental data for the borosilicate glass, and then the correction for the displaced fused silica is applied, then the data fall more close to the expected values, with a maximum error of 7.5%. It should be noted that this is for the shortest sample length; for the larger lengths the error is 4.1%. The results clearly indicate that the correction of choice is the manufacturers' procedure involving a standard run under identical conditions. It also appears possible to vary the sample size considerably relative to the standard length and still ensure accuracy.

CONCLUSIONS

A calibration procedure has been developed to help determine TEC's more accurately than indicated by the suppliers of the TMA units used. This

involves subtraction of an instrumental error, obtained by running a sample of the material used in the units' construction, from the experimental data. This is followed by a correction for the length of probe displaced by the sample from the measuring zone. In the case of the Perkin–Elmer instrument, which does not incorporate a rigorous calibration procedure, this technique results in a definite improvement in the precision. However, for the Netzsch unit it appears that the manufacturer's calibration procedure gives accurate data. This has not been demonstrated for ultra-low thermal expansion data.

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APPENDIX A

$$\text{TEC} = \frac{\Delta l}{l \Delta T}$$

For $l = 10$ mm and TEC $= 25 \times 10^{-6} \,^{\circ}\text{C}^{-1}$ then

$\Delta l = 25 \times 10^{-6} \times 10 = 25 \times 10^{-5}$ mm

Now, if l was measured to ± 0.01 mm (i.e. 9.99 mm) then

$$\text{TEC} = \frac{25 \times 10^{-5}}{9.99} = 25.025 \times 10^{-6} \,^{\circ}\text{C}^{-1}$$

Thus the error in TEC $= (0.025/25) \times 100 = 0.1\%$.

APPENDIX B

If a 10-mm sample is present, then the support is 10 mm longer than the probe. Expansion of the 10 mm of support of TEC $= 0.45 \times 10^{-6} \,^{\circ}\text{C}^{-1}$ will be

$\Delta l = \text{TEC} \times l$

$= 0.45 \times 10^{-6} \times 10$ mm

$= 4.5 \times 10^{-6}$ mm

Now for a sample of 10 mm length and TEC $= 25 \times 10^{-6} \,^{\circ}\text{C}^{-1}$ then

$\Delta l = \text{TEC} \times l$

$= 25 \times 10^{-6} \times 10$ mm

$= 250 \times 10^{-6}$ mm

Corrected $\Delta l = (250 + 4.5) \times 10^{-6}$ mm
$= 254.5\text{–}0^{-6}$ mm
Corrected TEC $= (254.5 \times 10^{-6})/10\,^{\circ}\mathrm{C}^{-1}$

Error in TEC $= (0.45 \times 100)/25$
$= 1.8\%$.

APPENDIX C

TEC for aluminum $= 21.77 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$ over a 150 °C range, i.e. −55 to 95 °C

$$\frac{\Delta l}{l} = 3265.5 \times 10^{-6}$$

The corrected $\Delta l/l$ = observed $\Delta l/l + \Delta l/l$ of the support material

Corrected $\Delta l/l = (3265.5 + 67.701) \times 10^{-6}$
$= 3333.201 \times 10^{-6}$

Thus the corrected TEC of aluminum $= (3333.201/150) \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$ or
$= 22.22 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$

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