

Uncertainties in the Measurements in Differential Scanning Calorimeter and Thermomechanical Analyser

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Abstract : Reproducibility of the output signal in Differential Scanning Calorimeter has been examined in detail. The ordinate calibration factor has been found to diminish at higher temperatures. Calibration factor for enthalpy output has also been evaluated. A procedure for calibrating the area by the proper selection of the base-line for both scanning and isothermal modes of operation has been described. This factor has largely been ignored in the papers published so far. And also the assessment of the performance of Thermomechanical analyser has been done by using *Al* as expansion standard varying heating rate, sensitivity and load. A simple method for the determination Youngs modulus at room temperature using TMA is also given.

Introduction

The use of commercial Differential Scanning Calorimeter (DSC) has grown considerably since its inception. For studying the kinetics and thermodynamics of a process, it is desirable to have accurate knowledge about the ordinate signal and its reproducibility. The advent of commercial Thermomechanical Analyser (TMA) is quite recent. TMA is a valuable technique for the thermal characterization and quality control of materials. It measures the dimensional changes (expansion and extension modes) or viscoelastic changes (penetration and compression) and properties such as coefficient of thermal expansion, modulus, heat distortion temperature, softening point, shrinkage etc. precisely over the required temperature range on small samples in any form : pellet, film, fiber or moulded part. The reliability of data in TMA depends upon the reproducibility of the instrument. The present paper deals with the assessment of reproducibility of output signal of DSC and TMA and the uncertainties involved in various measurements, so that the reliable data could be obtained. In the present case the instrument used was Dupont 943 TMA provided with a quartz penetration probe with a small flat tip projection of 0.635 mm diameter.

Experimental

The present work was done on Perkin-Elmer DSC-1B instrument and the details of the operation are given elsewhere¹. Manufacturers' instructions² were closely followed

during the setting of the instrument. Temperature axis was calibrated by melting the metals indium, tin and lead. The bottom of the aluminium pans were pressed flat to have a proper contact with the holder. Identical pans and lids were used for reference and sample holders. The sample and the reference pans were positioned at the center of the holder cells and were covered with aluminium doms. Weighings were done on a microelectrobalance. Samples used for DSC studies were two sapphire discs of mass 36.9 mg and 128.4 mg supplied by the manufacturer. For sapphire samples open aluminium pans were used.

Sapphire samples were used for calibrating the output signals and for this purpose heat capacities were measured under various conditions. For the measurement of heat capacities, two thermograms were obtained. First with the empty pan and then with the same pan containing the sapphire disc. Each thermogram can be described in three parts. For example, if the scanning is done between temperature T_1 and T_2 then the first part consists of the isothermal signal at T_1 followed by scanning part between T_1 and T_2 , and finally isothermal signal again at T_2 .

The description of Dupont 943 TMA and its operation has been given elsewhere³. *Al* sample provided with the instrument was kept on the sample holder platform, near the thermocouple tip. Probe position control was adjusted such that the probe and weight tray just rest on the sample. Load is placed on the weight tray and the probe position displacement (ΔL) is recorded as a function of temperature.

Results and Discussion

The change of melting point of tin with heating rate is shown in Table 1. The temperature lag of the sample with respect to heating rate can thus be approximated under given scanning conditions. It was necessary to check the reproducibility of the signal by removing and placing the pan again in the calorimeter. The results of such reproducibility test are shown in Table 2. Table 2 shows that although the signal changes to some extent due to the above mentioned operation, the error is small and is within the acceptable limits.

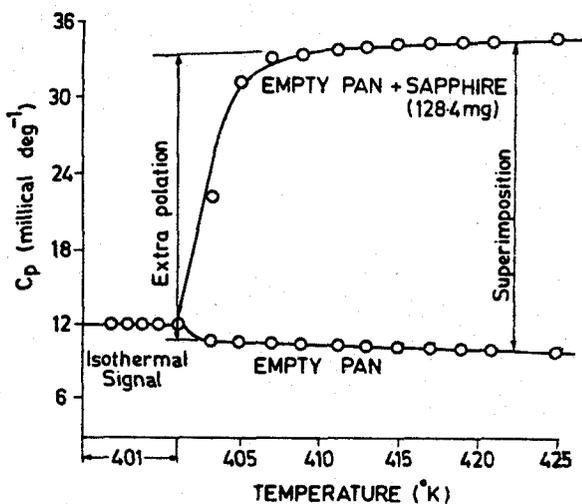
The heat capacity measurements of the sapphire samples were carried out by two methods viz. 'extrapolation and superimposition'. The methods of estimation are shown in Fig. 1, which is self explanatory. The results are given in Table 3. The

Table 1. Change of melting temperature of tin with heating rate.

Scan speed ($^{\circ}\text{C min}^{-1}$)	Melting point ($^{\circ}\text{K}$)
2	598.3
4	599.2
8	600.4
16	602.2
32	604.3
64	607.9

Table 2. Reproducibility due to the removal and placement of an empty pan in the calorimeter.Scan speed = $8^{\circ}\text{C min}^{-1}$; Range setting = 2 millical sec^{-1} ; Zero setting = 0.0001.

	Signal (millical, sec^{-1}) at 401 $^{\circ}\text{K}$	Signal (millical, sec^{-1}) at 601 $^{\circ}\text{K}$
First time	0.19	0.30
Pan removed and placed for second time	0.21	0.31
Pan removed and placed for the third time	0.20	0.30
Standard deviation	0.01 (5%)	0.01 (3.3%)

**Figure 1.** Calculation of C_p from extrapolation and Superimposition methods from DSC plots.

order of uncertainty in both the methods are same and therefore any of them could be followed for the purpose. In the present work the extrapolation method has been adopted all over. It may be noted that for the superimposition method the temperature selected should be such that signals should get stabilised at that particular temperature. It necessitated the measurement of time required for the stabilisation of the signal at a particular temperature. For this purpose empty pan and pan containing two sapphire samples were scanned separately at $8^{\circ}\text{C min}^{-1}$ starting at 401°K . The runs were stopped at 425°K after 3 minutes and then the isothermal signals were recorded. The plots are shown in Fig. 2. The time between the stoppage of scanning and the appearance of the isothermal signal was calculated from Fig. 2. The results are recorded in Table 4 for a heating rate of $8^{\circ}\text{C min}^{-1}$. This happens

Table 3. Comparison of the evaluated heat capacities by using the method of extrapolation and superimposition.

Scan speed = $8^{\circ}\text{C min}^{-1}$; Range settings = 2, 4 and 8 millical sec^{-1} ; Zero-knob position = 0.0001, 2.0004.

Sample	Heat capacity, C_p , (millical deg^{-1})					
	Superimposition					
	422 °K		622 °K		722 °K	
	C_p	% error	C_p	% error	C_p	% error
Sapphire (<i>l</i>)	5.10	6.2	6.00	5.1	7.65	5.3
Sapphire (<i>h</i>)	17.25	3.6	19.88	2.9	27.00	1.8
Sapphire (<i>l</i> + <i>h</i>)	21.75	2.7	27.90	1.4	33.75	2.5
Sample	Extrapolation					
	401 °K		601 °K		701 °K	
	C_p	% error	C_p	% error	C_p	% error
	Sapphire (<i>l</i>)	4.88	6.0	5.72	2.5	7.2
Sapphire (<i>h</i>)	16.40	3.1	19.50	2.5	26.25	1.5
Sapphire (<i>l</i> + <i>h</i>)	21.00	2.4	27.45	1.4	32.86	1.4

$l = 36.9 \text{ mg}$; $h = 128.4 \text{ mg}$

Note : For each sample at a particular temperature and at a particular zero-knob position, six runs were obtained by changing the range.

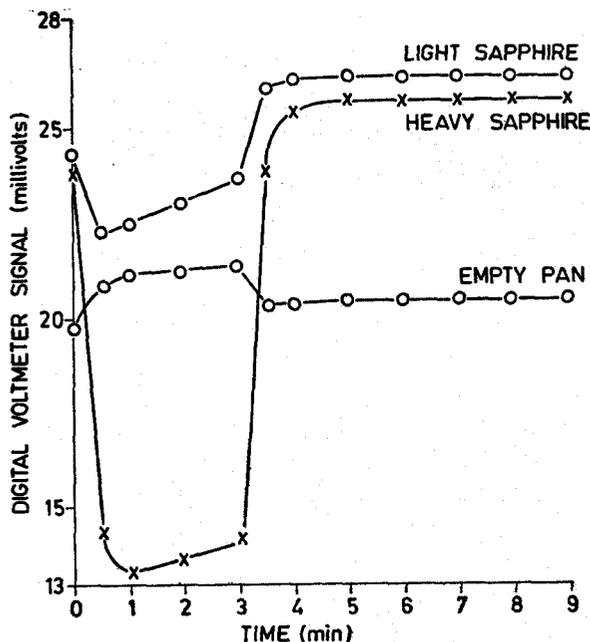


Figure 2. Millivolts vs time plot at 401°K for the calculation of the time required for the signal stabilization.

Table 4. Time required for the stabilisation of the signal.

Scan speed = $8^{\circ}\text{C min}^{-1}$; Range setting = 2 millical sec^{-1} ; Zero setting = 2.0015.

	Time taken at 401 °K (min)	Time taken at 601 °K (min)
Empty pan	0.50	0.50
Sapphire (<i>l</i>)	0.70	0.50
Sapphire (<i>h</i>)	1.30	1.00

l = 36.9 mg; *h* = 128.4 mg

because the calorimeter assembly takes some time (depending upon the heat capacity of the sample) to settle down at a particular temperature. For the sample of higher mass the time for the stabilization of the signal was more which may be due to the higher heat capacity of the sample. The time for the stabilisation of the signal may thus be determined at the heating rate at which the heat capacity measurements are to be carried out by superimposition method.

Table 5. Reproducibility of DSC signal on changing the zero-knob position and the range.

Scan speed = $8^{\circ}\text{C min}^{-1}$.

Sample	Changing the range ¹			
	401 °K		601 °K	
	Signal (millical sec^{-1})	% error	Signal (millical sec^{-1})	% error
Sapphire (<i>l</i>)	0.67 ± 0.04	6.0	0.80 ± 0.04	5.0
Sapphire (<i>h</i>)	2.21 ± 0.07	3.2	2.64 ± 0.04	1.5
Sapphire (<i>l</i> + <i>h</i>)	2.81 ± 0.06	2.1	3.72 ± 0.10	2.7

Scan speed = $8^{\circ}\text{C min}^{-1}$; Changing the zero-knob² position

Sample	401 °K		601 °K	
	Signal (millical sec^{-1})	% error	Signal (millical sec^{-1})	% error
Sapphire (<i>l</i>)	0.70 ± 0.04	5.7	0.81 ± 0.04	4.9
Sapphire (<i>h</i>)	2.21 ± 0.01	4.5	2.59 ± 0.01	3.9
Sapphire (<i>l</i> + <i>h</i>)	2.86 ± 0.07	2.5	3.74 ± 0.04	1.1

1. Range was changed to 2, 4 and 8 millical sec^{-1} while zero-knob was kept fixed at 0.0001.2. Zero-knob was changed to the position at 0.0001, 2.0004 and 3.3440 while the range 4 millical sec^{-1} was fixed at 2 millical sec^{-1} .*l* = 36.9 mg; *h* = 128.4 mg

The effect of altering the back off voltage (i.e., the change in zero adjustment) and also the range setting on the reproducibility of output signal was investigated. The output signals were recorded by changing the range setting while keeping the zero adjustment at a fixed level and vice versa. The results are given in Table 5. The combined effect of zero adjustment and the range setting is shown in Table 6. It may be seen that the output signals are reproducible upto 6%.

Table 6. Reproducibility of the DSC signal by changing both the range and zero-knob position.

Scan speed = $8^{\circ}\text{C min}^{-1}$; Range settings = 2, 4 and 8 millical sec^{-1} ; Zero-knob settings = 0.0001, 2.0004 and 3.4440.

Sample	DSCsignal (millical sec^{-1})					
	401°K		601°K		701°K	
	Signal	% error	Signal	% error	Signal	% error
Sapphire (<i>l</i>)	0.88 ± 0.03	4.4	0.80 ± 0.04	5.0	1.01 ± 0.06	5.9
Sapphire (<i>h</i>)	2.32 ± 0.12	5.2	2.65 ± 0.15	5.7	3.49 ± 0.12	3.4
Sapphire (<i>l + h</i>)	2.96 ± 0.13	4.8	3.90 ± 0.21	5.4	4.44 ± 0.18	4.1

l = 36.9 mg; *h* = 128.4 mg

Note : Nine readings were taken for each sample at each temperature by changing the range setting and zero-knob position.

Table 7. Comparison of the experimental and reported heat capacity (C_p) data of sapphire at different temperatures.

Scan speed = $8^{\circ}\text{C min}^{-1}$; Range settings = 2, 4 and 8 millical sec^{-1} .

	C_p (millical deg^{-1}) chart paper out put					
	409 °K		609 °K		709 °K	
	Exptl	Known	Exptl	Known	Exptl	Known
Sapphire (<i>l</i>)	7.3 ± 0.3	8.41	9.2 ± 0.1	9.77	10.5 ± 0.2	10.15
Sapphire (<i>h</i>)	25.8 ± 1.0	29.28	33.4 ± 1.1	34.00	37.1 ± 0.8	35.32
Sapphire (<i>l + h</i>)	33.0 ± 0.2	37.69	42.6 ± 1.0	43.77	47.8 ± 1.5	45.48

	C_p (millical deg^{-1}) digital voltmeter output					
	409 °K		609 °K		709 °K	
	Exptl	Known	Exptl	Known	Exptl	Known
Sapphire (<i>l</i>)	5.0 ± 0.2	8.41	6.2 ± 0.2	9.77	7.4 ± 0.2	10.15
Sapphire (<i>h</i>)	17.2 ± 0.2	29.28	21.3 ± 0.3	34.00	25.1 ± 1.0	35.32
Sapphire (<i>l + h</i>)	22.4 ± 0.3	37.69	28.3 ± 0.2	43.77	32.3 ± 0.3	45.48

l = 36.9 mg; *h* = 128.4 mg; Known = Literature value

Note : For each sample at a particular temperature, six runs were taken by changing the range.

The calibration of the output signal was carried out by comparing the experimentally determined heat capacity with the literature value. The results are shown in Table 7, where the measurements have been done by using both the chart recorder and the digital voltmeter. The data presented in Table 7 have been used to compute the calibration factor $C_p(\text{known})/C_p(\text{exptl.})$ which is given in Table 8. $C_p(\text{known})$ refers to the heat capacity calculated from the standard Tables and $C_p(\text{exptl.})$ refers to the heat capacity of the sapphire discs derived from the present experiments. The mean value of the calibration factor (from Table 8) has been plotted as a function of temperature in Fig. 3. The calibration factor is quite significant in digital voltmeter results whereas the chart recorder gives satisfactory results. However, the similarity in the trend of both the results signifies the method of calibration. Since the instrument uses only chart recorder in usual practice, the seriousness of the digital output results may be neglected. Fig. 3 further shows that the calibration factor is temperature dependant and at higher temperatures the calibration becomes insignificant in view of the uncertainty in the results as shown earlier. The possible change in the calibration factor may be ignored while deriving the relative reaction-rates because the temperature ranges involved were small.

Table 8. Calibration factor $C_p(\text{Known})/C_p(\text{Exptl})$ at different temperatures.

Sample	$C_p(\text{Known})/C_p(\text{Exptl})$					
	Chart recorder output			Digital voltmeter output		
	409 °K	609 °K	709 °K	409 °K	609 °K	709 °K
Sapphire (<i>l</i>)	1.146	1.060	0.965	1.682	1.576	1.372
Sapphire (<i>h</i>)	1.133	1.018	0.961	1.702	1.596	1.402
Sapphire (<i>l</i> + <i>h</i>)	1.142	1.027	0.951	1.683	1.547	1.408
Mean Value	1.14 ± 0.06	1.03 ± 0.03	0.96 ± 0.01	1.69 ± 0.01	1.57 ± 0.03	1.39 ± 0.02

$l = 36.9 \text{ mg}; \quad h = 128.4 \text{ mg}$

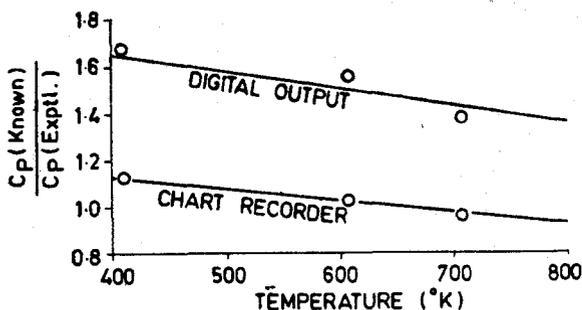


Figure 3. Dependence of calibration factor on temperature.

The typical TMA plot of ΔL vs temperature of *Al* sample is shown in the Fig. 4. The coefficient of linear expansion (α) of the sample can be calculated as follows :

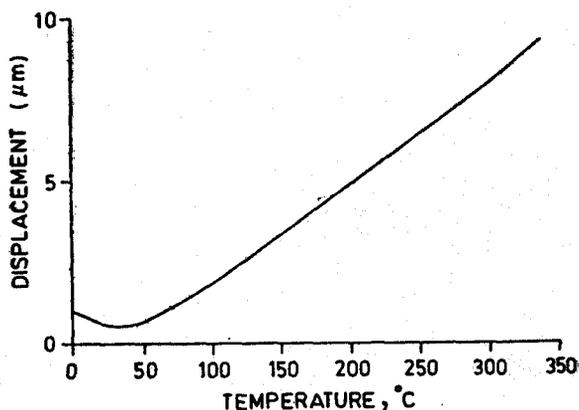


Figure 4. A typical TMA plot of *Al* expansion.

$$\alpha = \frac{\Delta L}{\Delta T} \times \frac{\Delta Y}{L}$$

where ΔL is the displacement (cm), L is the thickness of the sample (cm), ΔT is the change in temperature ($^{\circ}\text{C}$) and ΔY is the y -axis sensitivity. The experiment was repeated varying the heating rate, sensitivity and load and results are presented in Table 9. It may be seen that the error due to the change in heating rate and sensitivity is less than 2% and thus the results are not affected too badly. However when the measurements of α are carried out varying the load, the error is more than 3% it may be possible that this error could occur on account of change in load effecting the spring tension.

Table 9. Data showing the α value of *Al*, at different heating rates, sensitivity and load.

$l = 0.2680 \text{ cm}$, Time base setting = 1 min/cm					
α at different heating rates ($^{\circ}\text{C}/\text{min}$) load = 5 g sensitivity = $2\mu\text{m}/\text{cm}$		α at different sensitivity ($\mu\text{m}/\text{cm}$) load = 5 g heating rate = $10^{\circ}\text{C}/\text{min}$		α at different load (g.) Sensitivity = $5\mu\text{m}/\text{cm}$ heating rate = $10^{\circ}\text{C}/\text{min}$	
Heating rate	α	y -axis sensitivity	α	load	α
50	23.88×10^{-6}	1	23.88×10^{-6}	5	25.37×10^{-6}
20	24.63×10^{-6}	2	23.88×10^{-6}	10	23.88×10^{-6}
10	23.88×10^{-6}	5	23.13×10^{-6}	20	25.37×10^{-6}
5	24.37×10^{-6}			50	23.38×10^{-6}
Standard deviation	1.5%	Standard deviation	1.8%	Standard deviation	3.5%

TMA has been used to evaluate Youngs Modulus (E) of elastomers. Earlier³ we have reported a value of 2.8×10^5 at 190°C for carboxy terminated polybutadiene

(CTPB) polymer. But the method could not be used to determine E at room temperature. In the present work E of an elastomer (CTPB) at room temperature has been determined by a very simple procedure as follows. The sample was placed and the probe position was adjusted so that it just rests on the sample. Weights were placed on the weight tray and the extent of penetration (ΔL) was measured. The correlation coefficient of plot of load vs $\Delta L/L$ was found to be 0.9898, the slope of which gave $\Delta L/L$ per gram load. The data are presented in Table 10. E was calculated using the stress-strain relationship as follows :

$$E = \text{Stress/Strain} \\ = \frac{\text{load}_{(g.)} \times 980/\text{area of the penetrating tip}}{\Delta L/L}$$

Table 10. Table showing $\Delta L/L$ value at different load.

Load (g.)	$\Delta L/L$
0	—
5	0.122
10	0.218
20	0.301
50	0.532

Correlation coefficient of the plot of load vs $\Delta L/L$ is 0.9898 and slope is 0.00860.

$$E = \text{Stress/Strain} = \frac{980/0.03178}{\text{slope}} \\ = 3.587 \times 10^6 \text{ dynes/cm}^2$$

References

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3. Kishore, K. & Gayathri V., *J. Polym. Sci.* (letters accepted.)