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Note

Calibration of a thermomechanical analyser

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Thermomechanical analysers (TMA) which operate with a quartz probe and a linear variable differential transformer as the transducer, require calibration of the transducer output as a function of probe displacement. The most convenient method of calibration is to use a metal specimen of known coefficient of thermal expansion as a standard. The expansion of the standard over a given temperature range can be related to observed TMA output to provide the instrument calibration factor. The usual method[1] is to measure the response of the instrument to the expansion of the standard over a temperature range in which it is an approximately linear function of temperature. This requires multiple experiments to determine the calibration over a wide temperature range.

A method is now proposed for processing the results from a single calibration run over a wide temperature range, which provides an internal check on the linearity of the TMA response.

THEORY

The coefficient of linear thermal expansion (α) for the standard can be accurately related to temperature (T) by the polynomial expression

$$\alpha = a_1 + a_2T + a_3T^2 \cdots + a_nT^{n-1} \tag{1}$$

where a_1 to a_n are constants.

The expansion coefficient is given by

$$\alpha = \frac{dl}{dT} \cdot \frac{1}{l_0} \tag{2}$$

where l is the length of the specimen at temperature T, and l_0 is the length at some reference temperature T_0.

From eqn. (2) it follows that

$$\int_{l_0}^{l} \frac{dl}{l_0} = \int_{T_0}^{T} \alpha \, dT \tag{3}$$

and the right-hand side of this expression gives

$$F = \left(a_1 T_d + \tfrac{1}{2} a_2 T_d^2 \cdots + \frac{1}{n} a_n T_d^n \right) \tag{4}$$

where $T_d = T - T_0$.

From the left-hand side of equation (3)

$$F = \left(\frac{l}{l_0} - 1 \right)_T \tag{5}$$

and from eqn. (5)

$$\frac{dF}{dl} = \frac{1}{l_0} \tag{6}$$

The instrument calibration constant is given by

$$C = \frac{dl}{dY} = \frac{dl}{dF} \cdot \frac{dF}{dY} \tag{7}$$

where Y is the instrument output in mV corresponding to a displacement l.

From eqns. (6) and (7)

$$C = l_0 \Big/ \frac{dY}{dF} \tag{8}$$

It follows that a plot of Y against F should be linear if C is a constant, and the slope of the plot is l_0/C.

EXPERIMENTAL, RESULTS, AND DISCUSSION

The instrument used was the Du Pont 943 TMA, with a quartz probe having a flat end with a cylindrical cross-section of 0.607 cm diameter. The expansion standard was an aluminium cylinder supplied with the instrument, 0.7607 cm in height and 0.6363 cm in diameter.

The α values used for the aluminium standard were those of Kirby[2], and they were fitted by computer to polynomial equations of the form of eqn. (1), with n = 3, 4 and 5. The second order polynomial gave a maximum error between observed and calculated α of 3.5%, while the third order polynomial gave values within $\pm$ 0.5% of those observed, and for the fourth order polynomial the corresponding values were all within $\pm$ 0.1%. Since $\pm$ 0.5% is within the usual experimental error for TMA measurements, the third order solution was considered satisfactory for the calibration. The polynomial coefficients corresponding to eqn. (1), with n = 4, together with the observed and calculated expansion coefficients are given in Table 1.

TABLE 1

POLYNOMIAL REGRESSION FOR α AGAINST TEMPERATURE

$a_1 = 22.52503$
$a_2 = 0.28044 \times 10^{-1}$
$a_3 = -0.94856 \times 10^{-4}$
$a_4 = 0.19413 \times 10^{-6}$

Temperature (°C)	$10^6\alpha$ (K^{-1})	
	Observed[2]	*Calculated*
−123	17.20	17.28
+ 73	20.00	19.90
23	21.90	21.83
27	23.20	23.22
77	24.10	24.21
127	24.90	24.95
227	26.40	26.27
327	28.30	28.34

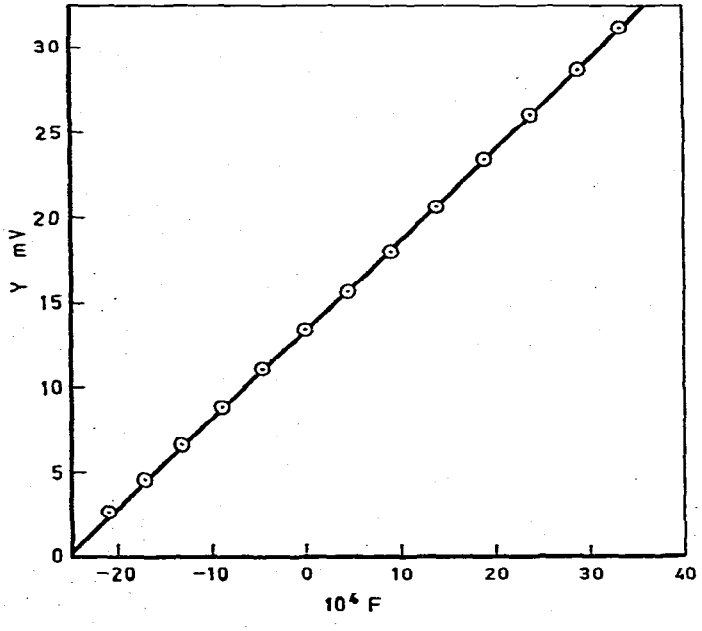

Fig. 1. Plot of TMA output against F (calculated from eqn. (4)) for the thermal expansion of the aluminium standard.

The results of a typical calibration run are illustrated in Fig. 1 as a plot of the TMA Y axis output in mV against F, calculated from eqn. (4) using the regression coefficients from Table 1. The experiment was between −80 and +160°C at a heating rate of 10 K min^{-1}, and the reference temperature T_0 was 20°C.

TABLE 2

SUMMARY OF CALIBRATION RUNS

Run No.	*Heating rate (K min^{-1})*	*Temperature range (°C)*		*Calibration constant 10^4 C (cm mV^{-1})*
		Min	*Max*	
1	5	+60	+220	1.560
2	2	+60	+220	1.629
3	10	+60	+220	1.466
4	5	+60	+220	1.546
5	5	+60	+220	1.517
6	5	+60	+220	1.499
7	10	−80	+160	1.446
8	5	−60	+ 40	1.457
9	10	−80	+ 60	1.494
10	10	−80	+100	1.498

The linear regression slope of the plot is 0.5259×10^4 with a correlation coefficient of 0.99980. This slope gives the calibration coefficient $C = 1.446 \times 10^{-4}$ cm mV^{-1}.

The plot indicates that the instrument response is linear over the experimental temperature range. The results of several calibration runs at various heating rates and over various temperature ranges are summarised in Table 2.

The mean value for the calibration constant is 1.511×10^{-4} cm mV^{-1}, the standard deviation is 0.055×10^{-4}, and the 95% confidence interval is $\pm$ 0.039 or $\pm$ 2.6%. This experimental scatter is of the same order as that reported[1] for the usual single point calibration over a smaller temperature interval (30–80°C).

The calibration could be further refined to include correction for the slight non-linearity of the baseline. For example, in the temperature range corresponding to Run No. 7 in Table 2 a blank run with no specimen in the TMA indicated a baseline correction varying between 0.05 mV at −80°C, 0 mV in the range 0 to 80°C, and 0.15 mV at 160°C. Applying these corrections gives a slight improvement in the regression correlation coefficient which becomes 0.99986, and provides a value for the calibration constant of $C = 1.453 \times 10^{-4}$ cm mV^{-1}, which is within 0.5% of the uncorrected value.

CONCLUSIONS

The proposed calibration method for a thermomechanical analyser is applicable over a wide temperature range, and demonstrates that the response to probe displacement is substantially linear for the instrument used. Baseline correction had only a small effect on the calibration constant, which showed a standard deviation of 3.6% in 10 successive runs at various heating rates and over various temperature ranges.

REFERENCES

1 R. Gaskill and E. M. Barrall, *Thermochim. Acta*, 12 (1975) 102.
2 R. K. Kirby, in *American Institute of Physics Handbook*, McGraw-Hill, New York, 2nd edn., 1963.