# SIMPLIFICATION OF DIFFERENTIAL TEMPERATURE CALIBRATION AND EMITTANCE MEASUREMENTS IN SCANNING CALORIMETRY

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(Received September 7th, 1971)

ABSTRACT

The energy emitted by the two sample holders of a Perkin–Elmer Differential Scanning Calorimeter (DSC) can be balanced quickly at any temperature by observing instrument signal as a function of differential temperature control setting. This balance point, depending on the emittance characteristics of the individual sample holders, will correspond closely to the point at which the temperatures of the two sample holders are the same, making rapid differential temperature calibration possible. Deterioration in the characteristics of the sample holders can be detected, and emittance measurements can be greatly simplified.

INTRODUCTION

The Perkin–Elmer Differential Scanning Calorimeter (DSC)[1,2] is designed to partition energy between a sample and a reference material in such a way that the two temperatures remain the same while the average temperature of the system is controlled. As long as the design criterion is achieved, there is no variable cell constant to contend with; however, the achievement of this criterion depends on the quality of the sample holder assembly and the calibration of the differential temperature ($\Delta T$) system of the instrument. It is important to recognize the fact that certain measurements that can be made with the DSC are difficult or inaccurate unless the differential temperature calibration is made properly.

Directions for differential temperature calibration are given in the Perkin–Elmer Differential Scanning Calorimeter Instruction Manual. Different weights of the same sharply melting material are placed on the two sample holders, and the differential temperature control is set to produce a single fusion curve. Examples of curves obtained while making a calibration by this method are shown in Fig. 1. This procedure assures that the temperatures of the two samples are identical at the fusion temperature; the temperatures of the sample holders will not be much different.

The thermal emission of a surface is a sensitive function of the temperature of the surface. Emittances can be measured with the DSC[3]. Conversely, emission effects can be used as a sensitive test for temperature identity. A new method for differential temperature calibration, based on emission balancing, has been developed, and it makes possible the simplification of emittance measurements. Since two calibration methods are now available, one based on temperature identity and the other based on emission identity, it is also possible to test DSC cell holder assemblies for quality.
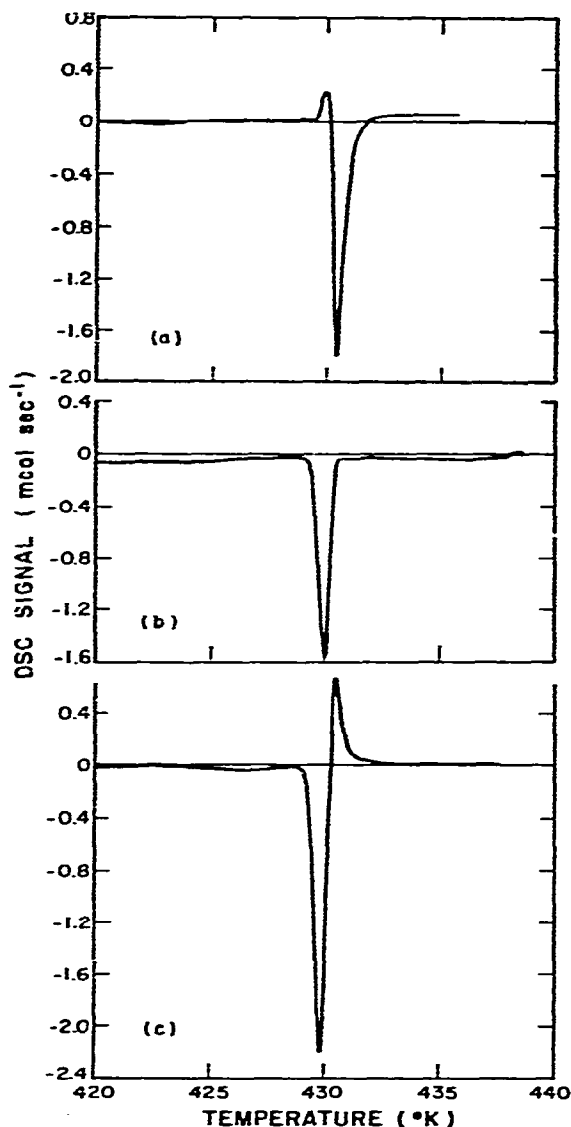
Fig. 1. Curves obtained during differential temperature calibration according to the Perkin–Elmer method. The sample, 2.458 mg In, and the reference, 1.460 mg In, were run at $10°K$ $min^{-1}$ on R8 under 5 ml $min^{-1}$ $N_2$ with aluminum covers. (a) $\Delta T$ control set at 489, reference melts first; (b) $\Delta T$ control set at emission balance, 493, sample and reference melt at same temperature; and (c) $\Delta T$ control set at 495, sample melts first.

PROCEDURES

*Differential temperature calibration*

Set the recorder to a center zero, and set the DSC at the desired temperature. It is desirable to make calibration settings with sample, reference, and covers (if used) in position. Mark the pen position of the recorder with the DSC range control in the "standby" position, and switch to the 64 mcal $sec^{-1}$ range setting. The recorder pen

may move in either direction. Use the differential temperature ($\Delta T$) control to return the pen to its original "standby" position. After making the adjustment at R64, continue switching to the next more sensitive range and returning the pen to the original "standby" position with the $\Delta T$ control. The $\Delta T$ control is extremely sensitive, and it may be impossible to obtain a perfect balance on the most sensitive range, but adjustment should be made as closely as possible. Fig. 2 shows an example of observed pen positions *versus* $\Delta T$ settings for a specific sample holder assembly at a specific temperature and sensitivity. When little or no signal is obtained on the most sensitive range, very nearly the same amount of energy is being delivered to each of the sample holders, and their temperatures should be nearly identical.
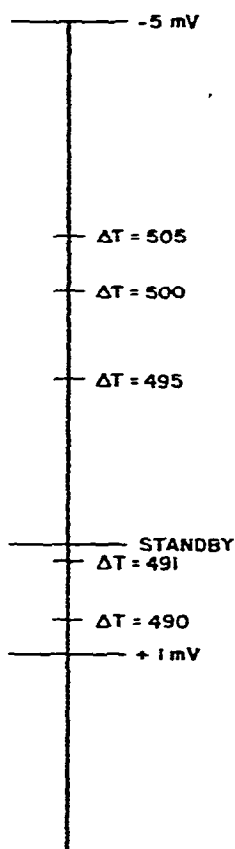


Fig. 2. Recorder deflection obtained with 10-inch, 10-mV recorder as a function of $\Delta T$ control settings at a DSC range setting of 2 mcal sec$^{-1}$ and 323 °K indicated and measured. Emission balance is achieved at a $\Delta T$ setting slightly above 491.

*Cell assembly quality test*

Place two indium samples of different weights on the sample holders, and determine the position of the melting endotherm. Set the $\Delta T$ control, by the method

described, at the indicated temperature of the endotherm. Program the two samples through the melting range, and observe the resulting fusion curve shape. Reference and sample should melt at the same temperature; a single peak, similar to Fig. 1b, should be obtained. If the points of equal energy emission and equal temperature do not coincide, the thermal characteristics of the two sample holders do not match. A larger area, corrosion, char formation, oxidation, or deposition on one sample holder will cause it to emit more energy than the other holder at the same temperature. New cell holder assemblies should match nearly perfectly; however, it is doubtful that a perfect match can be obtained at high temperatures. What constitutes a "high" temperature will depend on the surface finish of the sample holders. Emission from a metal surface is a 4.5–5.5 power function of the temperature; emission from a nonmetal surface is approximately a fourth-power function of the temperature. Therefore, small differences in emittance are amplified at higher temperatures. For example, the curve obtained at the melting point of lead, with an excellent assembly and with emission balanced, is shown in Fig. 3. The small upscale peak following the main endotherm indicates that the sample melted slightly before the reference, i.e., the temperatures were not exactly the same. Cell holder assemblies that
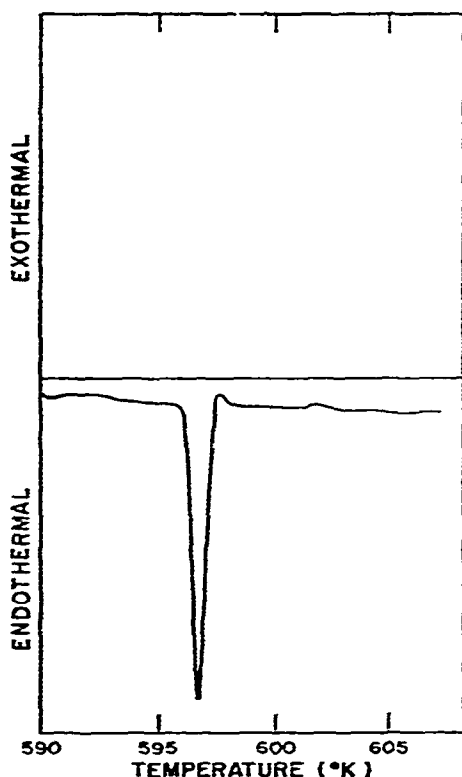


Fig. 3. Curve obtained by programming emission balanced samples of lead of different weights through the melting point at 10°/min on DSC range 8.

cannot be balanced reasonably well at the melting point of indium and the melting point of lead should not be used for quantitative work, heat capacity measurements, or emittance measurements. Obviously, an assembly will be totally useless when all of the available energy must be delivered to one of the holders to keep the two temperatures the same.

*Emittance measurements*

The present procedure is a simplification of the previously reported method[3]. Using the new calibration method, it has been possible to eliminate all instrument correction terms. However, the large difference between the total hemispherical and normal emittances of metals and nonmetals would still require correction terms, if a single reference material were used. Therefore, a further simplification has been made: metals are compared with a metal reference, and nonmetals are compared with nonmetal references.

*Metals*

Place two flat, clean, 1/4-inch disks of aluminum foil in sample pans. Do not crimp. Place an aluminum reference on each sample holder of the DSC, and balance $\Delta T$, as described, at the desired temperature. Replace the aluminum disk in the sample side of the assembly with a pan containing a 1/4-inch disk of the metal to be measured. Measure recorder deflection (in cm) on a suitable sensitivity range, and calculate emittance as follows:

$$\varepsilon = \frac{SD + R_r}{W} \qquad (1)$$

$S$ is a sensitivity factor for the instrument, calculated from the full-scale width of the recorder and the range setting used for the measurement. For example, $S = 3.15 \times 10^{-4}$ cal sec$^{-1}$ cm$^{-1}$ for a 10-inch, 10-mV recorder with the DSC on the 8 mcal sec$^{-1}$ range setting. $R_r$ is the emission of the reference surface at the specified temperature. For the 0.3167 cm$^2$ aluminum foil reference between 273 and 500°K, $R_r$ can be calculated from the following expression:

$$R_r = 1.282 \times 10^{-3} - 9.019 \times 10^{-6}T + 3.307 \times 10^{-7}T^2 \text{ cal sec}^{-1} \qquad (2)$$

Values used to derive this expression were obtained from Ref. 4. $D$ is the recorder deflection measured in centimeters. $W$ is the black body emission of a 0.3167 cm$^2$ surface at the specified temperature, and it can be obtained between 273 and 500°K from the following expression:

$$W = 0.0208 - 1.57 \times 10^{-4}T + 3.31 \times 10^{-7}T^2 \text{ cal sec}^{-1} \qquad (3)$$

Measurements should be made with the cell holder assembly cover in place to prevent convection currents, and a slow flow (10–15 ml min$^{-1}$) of inert gas helps to prevent oxidation of metal surfaces.

*Nonmetals*

In order to eliminate correction terms, nonmetals must be compared with nonmetal reference surfaces. Ideally, the reference surface should have nearly the same emittance as the surface to be measured. Nonmetal references are difficult to find, because published emittances vary widely and some nonmetal surfaces tend to change with time and heating. For making quick estimates, a heavily sooted aluminum disk can be used, assuming an emittance of 0.95. An aluminum surface with a 1-micron electrolytic oxide coating has an emittance of 0.3–0.4 at 400°K ($R_r \approx 0.004$ cal sec$^{-1}$). A 5-micron electrolytic oxide coating on aluminum has an emittance of 0.7 at 400°K ($R_r \approx 0.0077$ cal sec$^{-1}$). Other data can be obtained from Ref. 4. Using a suitable reference material, the procedure for nonmetals is exactly the same as for metals.

DISCUSSION

The Perkin–Elmer calibration method requires a standard material for each temperature calibrated, but it is important to note that calibrations at widely spaced temperatures are not sufficient for all purposes. It is stated in the Instruction Manual that "This differential temperature calibration should be optimized over the temperature range of interest. If more than one calibration point is used, it may not be possible to achieve complete cancellation at every point". This is true; deviation from an exact temperature match between sample holders normally increases with increased distance from the calibration point. One important and easily observable consequence of this fact is an increase in baseline drift with increased distance from the calibration point.

The proposed calibration method, involving emission balancing, does not require standard materials, and it can be used at any temperature. An assembly that has deteriorated to such an extent that emission balancing cannot be used to make the $\Delta T$ calibration will cause difficulties in the application of the instrument.

Fewer measurements are required in the simplified emittance method, and a temperature-controlled cover is not required; therefore, precision is improved. Speed has been improved even more; measurements can be made by the simplified method in 1–3 min. Accuracy is hard to determine, because "primary standard" surfaces do not exist; however, previously measured surfaces[3] were remeasured, and the results matched the reported values perfectly. The sensitivity of the method for comparing closely related surfaces is excellent. Emittance differences between the different crystal faces of the same material can be measured. For example, the emittance of pyrolytic graphite at 400°K cut parallel to the planes was found to be 0.67; cut perpendicular to the planes it was found to be 0.85. The values had been assumed[5] to be approximately 0.7 and 0.9.

We believe that the methods for $\Delta T$ calibration, sample holder quality testing, and emittance measurement can contribute significantly to the simplicity, accuracy, and utility of the Differential Scanning Calorimeter.

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