

## DEVELOPMENT TOWARDS A SINGLE-RUN DSC FOR HEAT CAPACITY MEASUREMENTS

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It is shown that it should be possible to construct a single-run heat conduction type DSC that records heat capacity directly, eliminating the present need for three separate runs. A simplified mathematical derivation of the needed computation is given and some suggestions about improved DSC construction are presented.

Heat capacity  $C_p \equiv (\partial H/\partial T)_{p,N}$ , expressed in  $\text{J K}^{-1} \text{mol}^{-1}$ , should be the basic results of differential scanning calorimetry (DSC) [1, 2]. Despite the existence of many thousand DSC installations world-wide, there have been, however, only few (hundreds) reports about the heat capacity of materials over the last 20 years. The main reason seems to be that the initial output of a typical DSC measurement is a relative, uncalibrated differential temperature signal that is close to proportional to the differential power input between reference and sample ( $\text{J s}^{-1}$  or watt). To extract the heat capacity of the sample from this signal it is not only necessary to establish the zero baseline by making a measurement of the differential temperature signal over the same temperature region of two identical empty calorimeters (empty aluminium pans), but, in addition, the differential power and the temperature axes must be calibrated point by point by measuring  $C_p$  of a reference substance, usually sapphire ( $\text{Al}_2\text{O}_3$ ), and by fixing a series of well-known transition temperatures to perhaps  $\pm 0.1$  K. Typical temperature ranges that can be covered with a single, continuous run are limited by the isotherm baseline-curvature with temperature. Within the acceptable error limit, the shift in the isotherm baseline with temperature must be linear. For typical, present-day instrumentation this temperature range may vary from 20 to perhaps 200 K, depending on symmetry of construction, care of calibration, and technique of operator. Over the chosen temperature range it is thus necessary to carry out three successive runs: 1. both calorimeters empty to establish the zero; 2. one calorimeter empty, one with sapphire for calibration; and 3. one calorimeter empty, one with the unknown.

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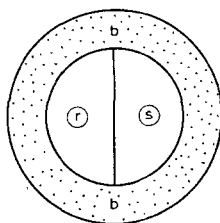
Besides the tedium of triple runs, it was found that the three runs can only be combined for one measurement if the thermal history of the overall instrument is compatible and no systematic change occurred in the experimental set-up during the time of the three runs [3]. The latter is easily detected by a mis-match of initial or final isothermal baselines somewhere during the three runs. Often one finds thus that the two calibration runs must be done at least once a day.

With all calibrations properly carried out, most present day instruments are able to measure easily to  $\pm 3\%$  precision [4]. Adding a sufficient computer-averaging of the short-time fluctuations eliminates much of the statistical error and may increase reproducibility of measurements to  $\pm 0.3\%$  [3, 5] or better.

In this paper it will be shown that it should be possible to reduce such triple-run calorimetry to a single run, i.e. to construct a calorimeter that records data directly in  $\text{J K}^{-1}$ , without separate amplitude calibration and independent of heating rate. First, the basis of the triple-run DSC will be reviewed, then the single-run calorimeter described, and finally, some general remarks about its construction and suggestions about possible advances in DSC construction will be given. All discussions concern the standard heat-conduction or Newton's Law type DSC [2].

### Triple-run DSC

Schematically a "triple-run DSC" is shown in Figure 1. The use of such DSC is based on a series of six assumptions that can be summarized as follows [6].



**Fig. 1** Schematic of a Triple-Run DSC,  $b$ : constant block temperature increasing or decreasing at constant rate  $q = dT_b/dt$ ;  $r$  and  $s$  positions of reference (empty calorimeter, usually aluminium pan) and sample (aluminium pan with to be analyzed sample) at temperatures  $T_r$  and  $T_s$ , respectively

#### *1. There should be no temperature gradient within the sample*

Since the heat flow from the heater block  $b$  to the sample (or reference) is dependent on the thermal diffusivity (in  $\text{m}^2 \text{s}^{-1}$ ) and geometry of the arrangement, the unknown thermal conductivity (in  $\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$ ) of the sample would enter into the calculation. By making the temperature gradient within the sample negligible

(ideally = zero) relative to the rest of the conduction path, the temperature difference between  $r$  and  $s$  is only dependent on the heat capacity of the sample (see Fig. 1).

2. *The thermocouples are inert*

The thermocouples are assumed to have no influence on the heat flow.

3. *Contacts are perfect*

The contact resistance to heat-flow between the aluminium pans (calorimeters) and the heat-conduction disc are assumed to be small and identical for  $r$  and  $s$ . In fact, it is not a good technique to account even for differences in mass of the  $r$  and  $s$  aluminium pans by correcting with the known Al heat capacity [7]. It is better to match pan weights within the required accuracy. The pans may act to some degree as an integral part of the heat conduction disc.

4. *Heat capacity and thermal conductivity change so slowly with temperature (except during transitions) that steady state is practically maintained throughout the measurement*

If this condition cannot be met, the mathematical description of DSC becomes much more complicated [1].

5. *All heat transfer occurs by conduction or by radiation*

Of the various heat conduction mechanisms only conduction and radiation can be described by Newton's Law (for small temperature differences) [6]. Particularly conduction by turbulent gas flow must be avoided since it would destroy the symmetry of heat conduction to  $r$  and  $s$ .

6. *No cross-flow of heat between reference and sample*

Since  $r$  and  $s$  have slightly different temperatures, an additional gradient is set up between them with its accompanying heat flow. This secondary heat flow must be negligible. It limits the total sample mass in an experiment.

With these six assumptions, and, furthermore, assuring that the instrument is perfectly symmetric (equal  $K$  for  $r$  and  $s$ , see below), one can write two simple Newton's Law expressions for reference (empty calorimeter) and sample [8]:

$$T_b - T_r = (W/K) (dT_r/dt) \quad (1)$$

$$T_b - T_s = [(W + C_{ps})/K] (dT_s/dt), \quad (2)$$

where the temperatures  $T$  are defined in Fig. 1,  $W$  is the "water value" i.e. the apparent heat capacities of the (matched) empty calorimeters, and  $K$  is the remaining part of the Newton's Law constant after separation of the heat capacity contribution, i.e.  $K$  contains only geometry and thermal conductivity terms that are assumed to be equal for reference and sample. It is now useful to recognize that at

steady state the heating rate  $q = dT_b/dt = dT_r/dt$  and, if  $\Delta T$  is taken as  $T_r - T_s$ , then one can write:

$$d\Delta T/dT_r = 1 - (dT_s/q dt). \quad (3)$$

Combining equations 1-3 one finds easily that

$$T = \frac{C_{ps}q}{K} - \frac{Wq d\Delta T}{K dT_r} - \frac{C_{ps}q d\Delta T}{K dT_r} \quad (4)$$

or

$$C_{ps} = K \frac{\Delta T}{q} + \left[ \left( \frac{K\Delta T}{q} + W \right) (d\Delta T/dT_s) \right], \quad (5)$$

where  $\Delta T$  is directly accessible from the DSC recordings of the sample and baseline runs and  $K$  is determined by comparison with the separate  $\text{Al}_2\text{O}_3$  run. The term in brackets is small, not recorded in standard DSC, and usually neglected. It represents the change in steady-state and is approximately the total heat capacity  $C_{ps} + W$  (sample + water value) multiplied with the slope of the DSC curve when plotted versus  $T_s$ . For a horizontal recording (no change in steady state,  $d\Delta T/dT_s = 0$ ) the heat capacity is exactly equal to  $K\Delta T/q$ . Since the  $T$ -scale is usually 100 times as sensitive as the  $T_s$ -scale, a slope of about 0.5 K on a DSC graph may introduce an error of about 1% in amplitude. A calibration with similar slope would, however, have the same error and largely correct the measurement.

For transitions, similar unrecorded portions exist for the heat of transition if initial and final baseline are not identical [6].

### Single-run DSC

The "single-run DSC" is shown schematically in Figure 2. As in the triple-run, one expects the same six assumptions to hold and the symmetry to be perfect. Analogous to equations 1 and 2 one can write now

$$T_b - T_e = (W/K)(dT_e/dt), \quad (6)$$

$$T_b - T_r = [(W + C_{pr})/K](dT_r/dt), \quad (7)$$

$$T_b - T_s = [(W + C_{ps})/K](dT_s/dt), \quad (8)$$

where all temperatures are defined in Fig. 2 and other terms are defined analogous to equations 1 and 2. As before, one can assume that at steady state the heating rate  $q = dT_b/dt = dT_e/dt$ . Setting now  $\Delta T_r = T_e - T_r$  and  $\Delta T_s = T_e - T_s$  one can write:

$$d\Delta T_r/dT_e = 1 - (dT_r/q dt) \quad (9)$$

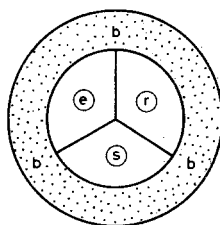


Fig. 2 Schematic of a Sing-Run DSC; b: constant block temperature increasing or decreasing at constant rate  $q = dT_b/dt$ ; e, r, and s positions of empty, reference ( $\text{Al}_2\text{O}_3$ ) filled, and sample filled calorimeters at temperatures  $T_e$ ,  $T_r$ , and  $T_s$ , respectively

and

$$d\Delta T_s/dT_e = 1 - (dT_s/q dt). \quad (10)$$

In analogy to equations 4 and 5 the expressions for the single-run DSC become

$$\Delta T_r = \frac{C_{pr}q}{K} - \frac{Wq d\Delta T_r}{K dT_e} - \frac{C_{pr}q d\Delta T_r}{K dT_e} \quad (11)$$

$$\Delta T_s = \frac{C_{ps}q}{K} - \frac{Wq d\Delta T_s}{K dT_e} - \frac{C_{ps}q d\Delta T_s}{K dT_e} \quad (12)$$

and

$$C_{pr} = K \frac{\Delta T_r}{q} + \left[ \left( \frac{K\Delta T_r}{q} + W \right) (d\Delta T_r/dT_r) \right] \quad (13)$$

$$C_{ps} = K \frac{\Delta T_s}{q} + \left[ \left( \frac{K\Delta T_s}{q} + W \right) (d\Delta T_s/dT_s) \right] \quad (14)$$

Assuming, as before, that the terms in brackets are small, one gets as a first approximation

$$C_{ps} = C_{pr} \Delta T_s / \Delta T_r \quad (15)$$

With the approximation of the normal triple-run DSC, the single-run DSC is capable to determine  $C_{ps}$ , the heat capacity of the sample, directly from the two  $\Delta T$  recordings, a knowledge of the heat capacity of the reference substance and a calibration of the symmetry by an all-empty-cups DSC-run. The latter will critically assess the DSC and may be needed only at infrequent intervals. Note also, that equation 15 is independent of the heating rate, and that one expects most effects causing symmetric changes during a run to be eliminated.

As with the triple-run DSC, one can naturally go beyond the first approximation of equation 15 by making use of the full expression for the heat capacities:

$$C_{ps} = C_{pr} \frac{(K\Delta T_s/q) + [(K\Delta T_s/q + W)(d\Delta T_s/dT_s)]}{(K\Delta T_r/q) + [(K\Delta T_r/q + W)(d\Delta T_r/dT_r)]} \quad (16)$$

By dividing by  $K\Delta T_r/q$  and approximating  $K\Delta T_r/q$  by  $C_{pr}$  one can eliminate  $q$  and  $K$ :

$$C_{ps} = C_{pr} \frac{(\Delta T_s/\Delta T_r) + [(\Delta T_s/\Delta T_r + W/C_{pr})/d\Delta T_s/dT_s]}{1 + [(1 + W/C_{pr})/d\Delta T_r/dT_r]} \quad (17)$$

Since typically the water values, are less than 25% of the heat capacities  $C_{ps}$  and  $C_{pr}$ , one may, as a second approximation to the full expressions 16 or 17, neglect  $W/C_{pr}$  relative to 1.0 and write:

$$C_{ps} = C_{pr} (\Delta T_s/\Delta T_r) (dT_r/dT_s) \quad (18)$$

Equation 18 contains, as before, only easily accessible and measurable quantities.

## Discussion

A single-run DSC seems feasible based on equations 15, 18, or 17. Especially with computer based data-handling and full elimination of statistical error, it should be possible to use the most accurate equation 17.

The advantage of such a single-run DSC should not be the increase in productivity by going to single runs with infrequent symmetry calibrations, but also an overall increase in precision of DSC. Interpretation of data should be helped when the now frequently used arbitrary baseline-method can be abolished and absolute values of heat capacity produced. This is of particular importance for broad transitions, as are often observed in polymers and have been a frequent research topic at our ATHAS Laboratory [9].

Possible problems for such an instrument are connected with the six assumptions listed above for handling any DSC. Items 1–5 should give no additional difficulties over the triple-run DSC. Item 6, concerning the cross-flow of heat between  $e$ ,  $r$ , and  $s$  of Fig. 2 may need special attention in the DSC design. It may be of advantage, for example, to decrease the conductivity along the lines separating the three parts of the heat-conduction disc. This can be accomplished by, either, separating the disc (fully or partially) into thirds, reducing its thickness along the lines marked, or by using insulating barriers.

Overall, development of such a "new" DSC would offer the chance of experimentation with better designs. Some possible improvements may come from heat flow from the inside of the DSC-disc to the outside with controlled cooling (or reduced heating) on the outside. Such arrangement may permit closer approach to standard calorimeter design.

Finally, it should be mentioned, that there exists a commercial instrument in

form of the "DuPont 912 Dual Sample Differential Scanning Calorimeter" which could permit testing of the above equations.

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## References

- 1 For basic references on DSC see, for example, E. A. Turi, ed. "Thermal Characterization of Polymeric Materials", Academic Press, New York, N.Y., 1982.
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**Zusammenfassung** — Es wird gezeigt, daß es möglich sein müßte, ein single-run DSC vom Wärmeleitertyp zu konstruieren, mit dessen Hilfe man anstelle der bisherigen drei separaten Durchgänge die Wärmekapazität direkt registrieren kann. Es werden für die notwendigen Berechnungen eine vereinfachte mathematische Ableitung und für den Bau des verbesserten DSC einige Anregungen gegeben.

**Резюме** — Показано, что представляется возможным построить дифференциальный сканирующий калориметр с тепловым потоком, позволяющий единственным измерением непосредственно определять теплоемкость, исключая тем самым три отдельные стадии измерения, как это требовалось до сих пор. Приведено упрощенное математическое дифференцирование требуемых вычислений и представлены некоторые предложения по улучшению конструкции ДСК.