Better Heat Capacity Data with the Power Compensated DSC

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One important aspect of a DSC instrument is its ability to measure heat capacities (Cp) which are both accurate and precise. The heat capacity – temperature response of a material is an important thermodynamic and physical characteristic.

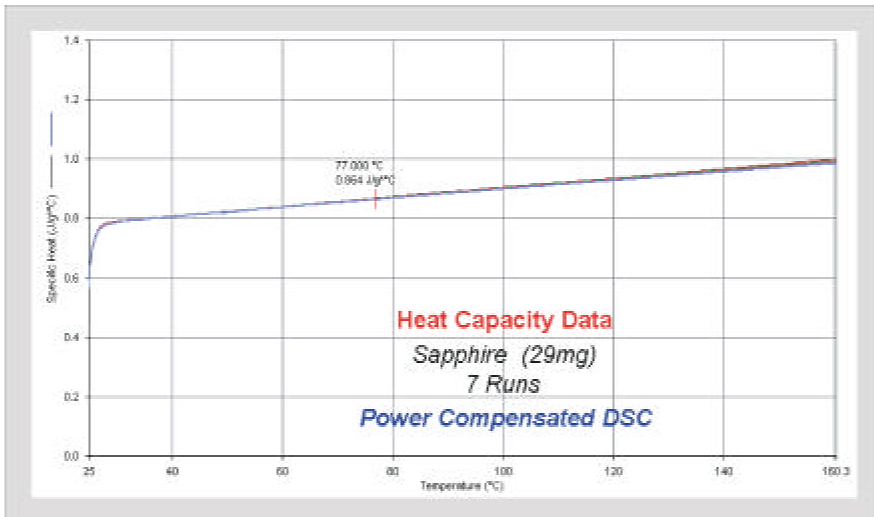
The heat capacity refers to the ability of a material to store heat and is given by the following expression:

$$Cp = dH/dT$$

In this expression, Cp is the sample's heat capacity (J/g°), dH is the change in heat absorbed (J/g) and dT is the change in temperature (°C). The heat capacity is a mass independent property. The Cp response is a fundamental thermodynamic characteristic of a sample and is generally considered to be more meaningful and far more quantitative than the simple presentation of the sample's heat flow versus temperature. The DSC heat flow is a relative and generally meaningless number whereas heat capacity is a well-defined and absolute quantity.

The PerkinElmer power compensated DSC instruments yield the most accurate and precise heat capacities of any DSC currently on the market. This is because of a number of hardware design factors:

Figure 1. Heat capacity results (7 runs) on 29.7 mg sample of sapphire.



- The use of the power compensated design of the DSC cell, which fundamentally measures the heat flow differential between the sample and reference. The sample side and reference side each have their own independent, very low mass furnaces to permit this direct measurement of heat flow. In contrast, heat flux DSC instruments have a single, common, and large mass furnace for the sample and reference. The fundamental measurement with a heat flux DSC is the temperature differential between the sample side and reference side rather than the actual heat flow.
- Use of the platinum resistance thermometer (PRT) for the measurement of sample temperature with the PerkinElmer DSC. The PRT is considered to be the best means of experimentally measuring temperature. It offers the highest possible precision and accuracy and is a standard temperature measurement device. In contrast other DSC instruments utilize the less expensive, and lesser performing thermocouples, such as the chromel-alumel system. The thermocouples used with heat flux DSC instruments are

Figure 2. Heat capacity results (7 runs) on large mass (129 mg) sapphire sample.

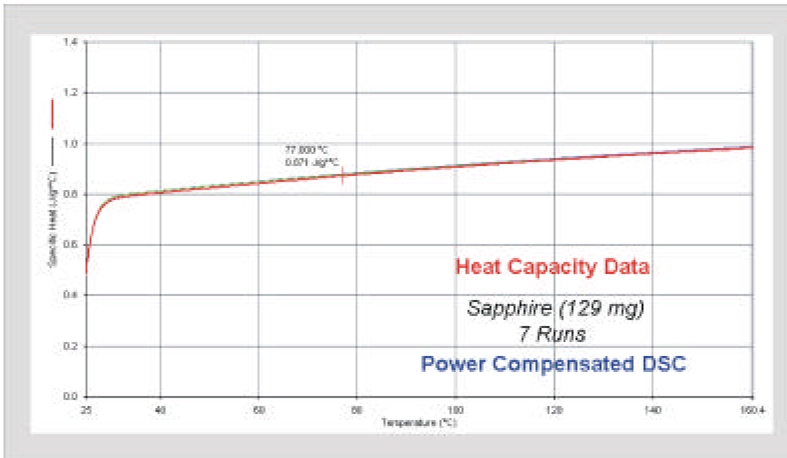
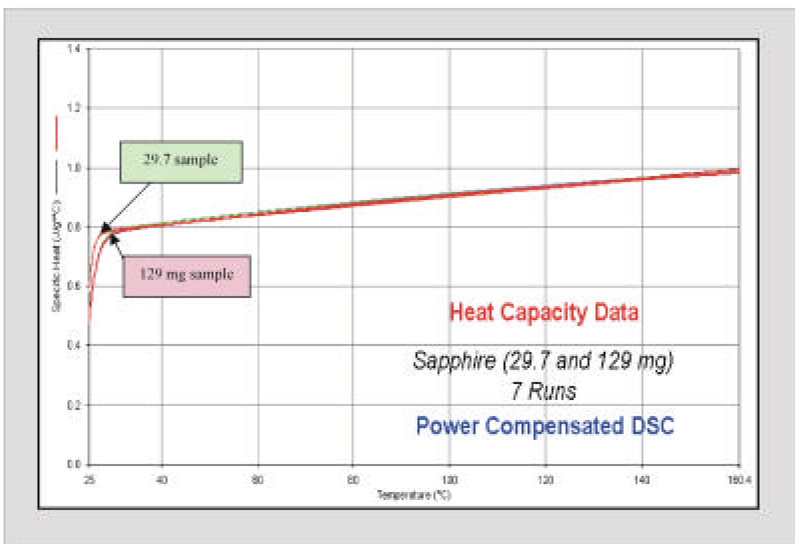


Figure 3. Overlay of heat capacity results on lighter (29.7 mg) and heavier 129 mg) sapphire specimens.



not as accurate, linear and precise as the PRT and this can affect the reproducibility of the heat capacity measurements.

- With the power compensated DSC device, sample placement is not as critical as it is with the heat flux DSC. This is because the PerkinElmer power compensated device has separate, independent furnaces for the sample and reference sides. In this case, sample placement is not critical. In contrast, the heat flux DSC device has a single furnace which provides the heat to the sample and reference. In this case, uniform sample placement does become critical, especially for heat capacity measurements. The heat transfer path from the single furnace to the sample and the reference must remain symmetrical (or constant) for best results and this is difficult to accomplish in reality. With the separate sample and reference furnace design of the power compensated DSC, constancy is always guaranteed.
- The sample and reference platforms with the power compensated DSC are self-contained and closed and this provides for more accurate and reproducible heat capacity results. There is little 'thermal leakage' from the power compensated DSC. If the sample mass is changed with the PerkinElmer DSC, the heat capacity results will not be significantly affected, as should be the case. The heat capacity is a mass-independent quantity. In contrast, the Cp results obtained from the heat flux DSC (with the single furnace and open pathway between sample and reference sides) can be significantly affected by 'thermal leakage' from the sample side. If the sample mass is significantly increased, the measured Cp values will exhibit a significant decrease with the heat flux DSC. It should be noted that temperature modulated DSC (TMDSC) suffers from this

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problem as well, when applied to a heat flux DSC.

To demonstrate the accuracy and reproducibility of heat capacity values generated using the PerkinElmer power compensated DSC instrument, a sample of sapphire (aluminum oxide disk) was analyzed multiple times. The sample was analyzed using the following conditions:

Instrument:	Power compensated DSC
Heating rate:	20 C/min
Initial temperature:	22 C
Final temperature:	160 C
Sapphire sample mass:	29.7 mg
Sample pan:	Crimped aluminum pan
Purge gas:	Nitrogen at 30 mL/min

The DSC instrument was calibrated for its temperature and enthalpic responses using high purity indium metal. A baseline experiment (empty cell with no pans) was performed and this data was subtracted from the sample results.

Displayed in Figure 1 are the DSC heat capacity results generated on the 29.7 mg specimen of sapphire. The plot shows the Cp curves (J/g°) as a function of sample temperature.

The data is excellent in terms of both reproducibility and accuracy. At a temperature of 350 K, the measured Cp is 0.864 J/g° which is within ±1% of the literature value of 0.8713 J/g° [Reference: D.A. Ditmars, *et al*, J. Res. Nat. Bur. Standards, Vol. 87, No. 2, pp 159-163 (1982)].

The heat capacity results on a much larger specimen of sapphire (129 mg) were determined using the same experimental conditions as for the 29.7 mg sample. The ability to obtain accurate and precise results on significantly varying sample masses is a hallmark of the power compensated DSC. The very low heat losses from the sample, because of the power compensated design, makes this possible. With the heat flux DSC, larger sample masses generally result in significantly lower values of Cp, due to loss of the heat flow from the sample. This is true with temperature modulated DSC (TMDSC) as well.

Displayed in Figure 2 are the heat capacity results generated on a large mass (129 mg) of sapphire.

These results demonstrate that the PerkinElmer power compensated DSC yields excellent heat capacity results even on very large mass samples.

Displayed in Figure 3 is an overlay of the Cp results generated on the lighter sapphire specimen (29.7 mg) and the much heavier sapphire material (129 mg).

These results demonstrate the excellent reproducibility of the power compensated DSC for the measurement of heat capacity values.

Summary

The power compensated design of the PerkinElmer DSC provides a fundamentally sound measurement of the heat flow. The use of the PRT and the separate sample side and reference side low mass furnaces yield very accurate and reproducible heat capacity values. In contrast, the heat flux DSC has a single, large mass furnace and employs the lesser performing thermocouples to measure the sample response. The heat capacities obtained from this type of DSC are less accurate and less reproducible.

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