

INTRODUCTION

Since the introduction of the first commercial (temperature servo) device for quantitatively measuring heat flow into (or out of) a sample as it undergoes a transition, there has been considerable confusion about what name should be used to describe this analytical measurement (1). A wide variety of labels has been applied including Quantitative Differential Thermal Analysis (QDTA) (1,2,3), Dynamic Differential Calorimetry (DDC) (4), Dynamic Enthalpic Analysis (DEA) (5,6,7,8) and, of course, Differential Scanning Calorimetry (DSC) (1,9,10). DSC has been the most accepted name largely because instrument manufacturers have used the term. With the introduction of other commercial devices, which also measure differential heat flow (11,12) but are not based on the temperature servo approach (13), the confusion has increased. This confusion has been aggravated by the instrument manufacturers themselves who have often claimed unspecified advantages for their particular instrument. The manufacturer of the original commercial device, understandably, has attempted to limit the DSC definition exclusively to his design. He continues to claim that his instrument is the only "true DSC".

We believe that DSC should be defined in terms of what is measured (i.e., heat flow) rather than how a particular type of instrument makes the measurement. In this sense we believe that DSC is generic in definition. This is the position recently adopted by the International Confederation of Thermal Analysis (40). TA Instruments, almost all of the instrument manufacturers, and the vast majority of thermal analysis users have chosen to define DSC in the generic sense. The former position, we believe, is very much like the makers of front wheel drive automobiles claiming that only front wheel drive automobiles are "true automobiles" because some of the first models operated in that fashion. In practice it makes little difference whether the vehicle is front or rear wheel driven. What is important is how it makes the trip.

We intend to show that a generic definition of DSC is the only acceptable definition. This position will be supported by equivalency of results obtained, general usage in the open literature, by comparison of temperature excursions of the sample, and by comparison to classical calorimetry.

DEFINITION OF DSC

In a generic sense then, Differential Scanning Calorimetry is a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature while the substance and the reference

material are subjected to a controlled temperature program. (Note: This definition is that approved by the International Confederation for Thermal Analysis in August 1977.)

All DSC instruments possess similar features which differentiate them from classical Differential Thermal Analyzers (DTA) with which they are sometimes confused.

- They use temperature sensors as their primary transducer. There is no such device as a "heat flow" transducer. All DSC instruments use temperature sensors as the primary transducer. In all cases the heat flow output to the recorder is derived from the differences in temperature between sample and reference taken from these temperature sensors. In differential temperature type devices, the sensors are thermocouples or thermopiles. Since thermocouples are also used in DTA devices, it is often implied that DSCs which use thermocouples are really QDTA instruments. In temperature servo systems, the sensors are platinum resistance thermometers.
- They have their temperature sensors located external to the sample. Boersma, in his famous theoretical paper, points out that this is a condition which must be met in order to make calorimetric measurements (14). Non-calorimetric classical DTA, in which the temperature sensor is imbedded in the sample, can be made semi-quantitative simply by separating the thermocouple from the sample. This can be easily demonstrated with the TA Instruments High Temperature DTA cell which is capable of operating in either mode. With no sample cup liners it performs as a classic, non-quantitative DTA, but with liners (and consequently removal of the thermocouple from the samples) accuracies and precision of calorimetric measurements of $\pm 5\%$ can be obtained (41). These levels are insufficient to qualify this device as a DSC, however, since DSC devices characteristically provide calorimetric accuracies and precision better than $\pm 1\%$.

While removing the temperature sensor from the sample is a necessary condition for DSC (and quantitative calorimetry), removal of the temperature sensor alone is insufficient to produce a quantitative device. Advocates of the temperature servo definition of DSC have seized on this point and disparagingly refer to all devices whose thermocouple temperature sensors are external to the sample as "Boersma DTA's" regardless of their calorimetric performance.

- They have an instrument output proportional to heat flow (i.e. power). All DSC instruments display heat flow as their primary output. This is a condition for DSC and is met by all instruments carrying the DSC label.

For some DSC devices, the calorimetric sensitivity changes with temperature and thus a calibration constant (which is a function of temperature) must be applied to each calorimetric measurement. For such devices the output from the DSC is expressed as voltage to the recorder and an empirically determined calibration factor is applied to obtain heat flow data. Such instruments, while increasing the amount of effort required to obtain calorimetric data, are still calorimetrically quantitative and properly part of the generic DSC family.

- It is desirable then, but not a necessary condition for a DSC instrument to have constant calorimetric sensitivity. In instruments possessing this capability the calibration constant is not a function of temperature permitting the instrument output to be directly calibrated in heat flow units of milliwatts.

OPERATION

As discussed above, Differential Scanning Calorimeters operate on one of two principles—differential temperature measurement and temperature servo measurements. Let us first examine the TA Instruments DSC 910 System as an example of the differential temperature type DSC.

A cross sectional diagram of the DSC cell is shown in Figure 1. The cell employs a constantan disc as its primary means of heat transfer to the sample and reference positions, and as one element of the temperature measuring thermoelectric junctions. The sample of interest and a reference are placed in pans which sit on raised platforms on the constantan disc. Heat is transferred through the disc and up into the sample and reference via the sample pans. The differential heat flow to the sample and reference is monitored by chromel-constantan area thermocouples formed by the junction of the constantan disc and a chromel disc which covers the underside of each platform. The ΔT output from these series opposed sample and reference thermocouples, is fed to a variable high gain amplifier where the signal is amplified, electronically scaled to read directly in heat flow units and finally displayed on one Y-axis. Chromel and alumel wires are connected to the underside of the chromel disc, and the resultant chromel-alumel thermocouple is used to directly monitor the sample temperature.

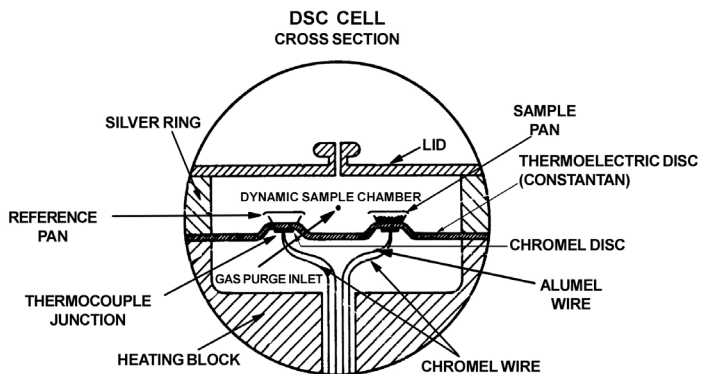


Figure 1: DSC Cell cross-section

When a sample is programmed at a constant heating rate through its melting point, the heat capacity of the sample increases to infinity (in theory) and the sample temperature becomes essentially invariant; thus, a ΔT is developed between it and the constantly rising reference temperature. This ΔT signal is proportional to the heat flowing into the sample as part of this transition. (The mathematical verification of this fact is provided in the "Theory" section of this paper). When the amplified and scaled signal presented to the computer in milliwatts is integrated over time, a value for the heat in millijoules associated with the transition is obtained.

The inherent simplicity of this design affords the scientist an easy grasp of its operating principles. Several manufacturers offer DSC devices based on this principle including TA Instruments and Mettler.

Let us now turn our attention to the second type of instrument, that of the temperature servo system shown in Figures 2 and 3 (9). In this design the sample and reference pans are placed in close contact with platinum resistance thermometers which are used to measure their temperature at any given moment. In addition, the unit has two individual heaters which control the heat flow to these samples.

TEMPERATURE SERVO CELL Schematic Diagram

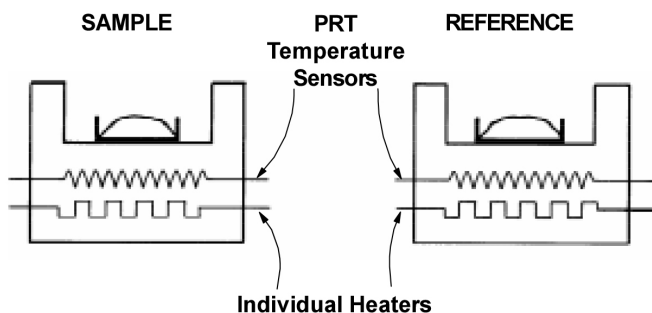


Figure 2: Temperature Servo Cell Schematic Diagram

TEMPERATURE SERVO Schematic Diagram

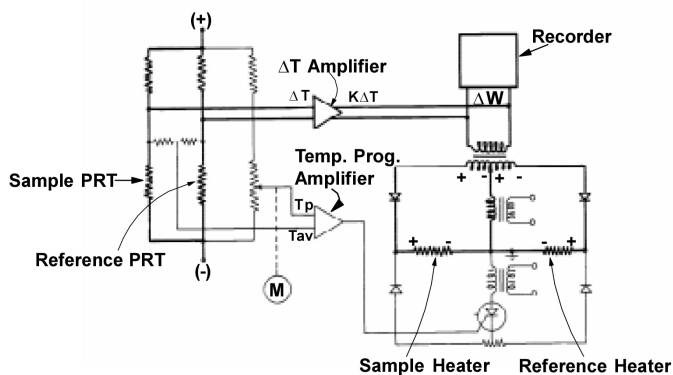


Figure 3: Temperature Servo Schematic Diagram

When a sample is temperature programmed through its melting point and the sample temperature becomes essentially invariant, the ΔT signal developed between it and the reference is amplified, scaled and displayed as the output from the device, as shown in Figure 3 (9, 13). In addition, differential power is supplied back to the sample heater attempting to reduce the temperature difference between the sample and reference. The operating principle of a servo system, however, requires the restoring signal (here a voltage signal to the differential heater) to be proportional to the offset (here the temperature difference). If the temperature difference is really zero, no differential power could be supplied by the servo system. An actual zero temperature difference can exist only if the servo amplifier gain is infinite, which, of course, it is not.

SAMPLE TEMPERATURE DIFFERENCE

Many users believe, that the temperature servo system reduces the temperature differences between sample and reference to zero during a transition (1,15). The very nature of a servo system belies this. Indeed, the recorder output is directly proportional to the temperature difference between sample and reference as can be seen in both the patent covering such devices shown in Figure 3, and electronic schematic of such instruments (13,16). The manufacturer states "... (the temperature difference between sample and reference) is never really zero, because in any such control system there must always be some small 'error signal'" (17). Let us examine how small this error signal really is.

The error signal (S , in K/cm of chart) can be calculated from the maximum sensitivity of instrument output (G , in mV/cm of chart), the ΔT amplifier gain (A) and the differential response of the transducer (E , in mV/K change in temperature).

$$S = \frac{G}{EA}$$

Since the 13 ohm (at room temperature) platinum resistance

thermometers used in the instrument in question do not generate a voltage output themselves, their response depends upon the 23 mA current (i) passing through them and the temperature sensitivity (R). R can be obtained from standard tables; a value of 0.24% /K at 157°C, (the calibration temperature of most DSC instruments) can be used (18).

$$E = \frac{i\Delta R}{\Delta T} = (23 \text{ mA}) (16\Omega) (0.0024 / \text{K}) = 0.88 \text{ mV} / \text{K}$$

Using this value, 0.5 mV/cm for G , and an amplifier gain of 2500 we get:

$$S = \frac{G}{EA} = \frac{(0.5 \text{ mV} / \text{cm})}{(71 \mu\text{V} / \text{K}) (30,000)} = 0.23 \text{ mK} / \text{cm}$$

At maximum sensitivity of 21mW/cm (0.01 mcal/sec in), each centimeter of chart deflection corresponds to 0.23 millikelvin difference in temperature between sample and reference. Put in other words, a modern, second generation temperature servo type DSC generates an 11 millikelvin sample temperature excursion for each milliwatt of heat flow. (In traditional units this is 0.046 degrees per mcal/s). This is despite the attempts of the system's temperature servo to minimize this temperature excursion. This temperature difference between sample and reference is easily verified by measurement with a differential thermocouple pair.

We can compare this error signal with that of the TA Instruments DSC 910 for which G is also 0.5 mV/cm and A is 30,000. The value for E for chromel/constantan of 71, $\mu\text{V}/\text{K}$ can be obtained from the same source as that above (19).

$$S = \frac{G}{EA} = \frac{(0.5 \text{ mV} / \text{cm})}{(71 \mu\text{V} / \text{K}) (30,000)} = 0.23 \text{ mK} / \text{cm}$$

This comparison points out that *at maximum sensitivity the temperature servo instrument and the TA Instruments DSC 910 generate approximately the same sample temperature excursion per centimeter of chart deflection.* Most DSC work is not done at maximum sensitivity, however, and values 1000 times greater are likely to be encountered in ordinary work. For example, O'Neill has published scans for real life indium samples in which the maximum heat flow during freezing was 71 mW (19). This value, multiplied by the instrument differential temperature sensitivity calculated above, yields, for this so-called temperature null device, *a peak temperature excursion of 0.8 kelvin (0.8°C).* While this value is not large, it is certainly not zero and certainly is not isothermal.

It is clear from the comparison above, that practical temperature servo type instruments do not maintain the sample and reference materials at the same temperature even if the instrument is of high sensitivity.

COMPARISON TO CLASSICAL CALORIMETRY

Calorimetry is the scientific field dealing with the

measurement of the heat or energy content of various chemical and physical reactions. In a typical classical adiabatic calorimetric experiment, a chemical reaction may be carried out in a sealed container insulated from heat losses to the outside world. From the known heat capacity (C_p) of the insulated container and its contents, and the small measured change in temperature (ΔT) of that system, the heat content of the chemical reaction (ΔH) can be calculated:

$$\Delta H = \Delta T C_p$$

The experiment is usually designed so that the change in system temperature is kept small, usually several Kelvin. Under such conditions C_p is a constant.

Such experiments have given rise to the definition of the calorie as the unit of measurement for heat content or energy: calorie—the amount of heat necessary to raise the temperature of 1g of water at 15°C, 1°C.

In DSC, the temperature excursion of a sample seldom exceeds a few tenths of a degree. It is clear, then, that DSC instruments operate well within the conditions of classical calorimetry from which thermodynamic data is almost exclusively obtained.

This comparison of DSC to classical calorimetry needs one other amplification. In classical adiabatic calorimetry, heat losses from the sample to the environment are kept to a minimum. This concept is most nearly met in differential temperature DSC instruments since the sample is totally surrounded by a uniform temperature environment. It is the temperature of this environment which is programmed during the course of the experiment. Thus the sample “sees” only an environment whose temperature is very near that of its own, thereby reducing to a minimum emissivity, atmosphere thermal conductivity, and other potential heat losses. This produces the remarkably stable baseline performance of the instruments of this type.

On the other hand, temperature servo instruments suffer from thermal conductivity and emissivity losses, thermal gradients and thermal atmosphere convection because the sample chamber (in which the sample and reference materials are located) is thermostated at constant temperature (20). This means that the sample sees a constantly changing environmental gradient during the course of an experiment. Obviously this is far afield from the standard adiabatic calorimeter and can lead to poor baseline performance of temperature servo instruments if not corrected for by electronic baseline compensation.

EQUIVALENCY OF RESULTS

Perhaps no stronger claim can be made for a generic definition of DSC, than the fact that results from instruments of the temperature servo type and instruments of the differential temperature type are indistinguishable from each other. This has been pointed out in a previous treatise on the subject;

“It is not possible by inspection of an unlabeled thermal analysis peak to determine which sort of apparatus was used...”(17). Moreover, there are almost no applications where one instrument obtains data and the other does not. Articles abound in the open literature on the ability of a variety of equipment, based on differing operating principles, to make equivalent measurements (21,22,23,24). Outstanding research (21,23,25) has testified to the equivalency of results obtained on instruments of both types. In addition, such respected institutions as the Drug Standards Laboratory and American Society for Testing and Materials (ASTM) have stated the equivalency of results obtained on both instrument types (22,26,27).

GENERIC USE OF DSC

Despite attempts to limit the definition of DSC to devices based on the temperature servo technique, DSC is used in the open scientific literature as a generic phrase. All other titles have faded into historical interest although one occasionally still sees QDTA used. C. B. Murphy's biennial review of thermal analysis uses the phrase DSC generically without differentiating the type of instrument used and includes DSC under the DTA heading as a quantitative technique (28,29,30,31,32).

Virtually all thermal analysis manufacturers who make quantitative calorimetric measurements, market their instruments under the title of Differential Scanning Calorimetry even though operating under different principles. These include: TA Instruments, Mettler, Perkin-Elmer, and others.

SUMMARY

We have shown that all Differential Scanning Calorimeters, regardless of method of measurement, measure the same quantity, namely, heat flow into (or out of) a sample. It follows that the name should be used generically and applied to all measurements of this type rather than limited to measurements made on a particular instrument. This position is supported by:

- equivalence of measurement
- general usage in the open literature
- similar temperature excursions of the sample
- comparison to classical calorimetry

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APPENDIX THEORY

The theoretical basis for the TA Instruments DSC 910 is well documented in Baxter's work on the subject (11). A portion of his work is reproduced and expanded here for the sake of completeness:

The essential parts of the DSC are a sample at temperature T_S , its container at temperature T_{SH} and a temperature programmed source at temperature T_B . Heat will flow between these positions at a rate di/dt depending on the temperatures involved and the thermal resistances connecting the positions. The sample and its container have a heat capacity C_S . Since the calorimeter operates differentially, a similar description can be developed for the reference side of the cell. Figure 4 illustrates this description schematically.

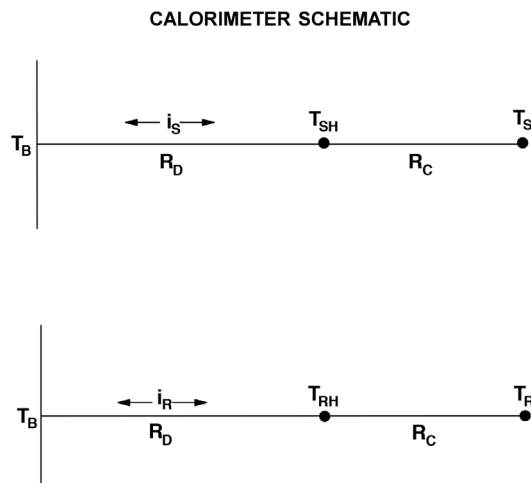


Figure 4: Calorimetric Schematic

If we make the simplifying assumptions that the calorimeter is symmetrical and that thermal resistances are identical on the reference and sample sides at any given temperature; that the temperatures of the sample, reference, and their containers are uniform; and that the flow of heat from sample to reference can be neglected, then the response of the calorimeter can be described with the aid of heat balance equations and thermal ohm's law relationships.

If we assume a sample undergoing an exothermic transition giving up heat energy at a rate dH/dt , then the appropriate equations are:

$$(1) \quad \frac{di_S}{dt} = \frac{T_{SH} - T_B}{R_D} = \frac{T_S - T_B}{R_C + R_D}$$

and

$$(2) \quad \frac{di_R}{dt} = \frac{T_{RH} - T_B}{R_D} = \frac{T_R - T_B}{R_C + R_D}$$

$$(3) \quad 0 = \frac{C_R dT_R}{dt} + \frac{di_R}{dt}$$

$$(4) \quad \frac{dH}{dt} = \frac{C_S dT_S}{dt} + \frac{di_S}{dt}$$

Equation (4) indicates that the heat evolved by the sample goes either into heating the sample or is dissipated to the surroundings.

We can combine equations (2) and (3), and (1) and (4)

$$(5) \quad 0 = \frac{C_R dT_R}{dt} + \frac{T_R - T_B}{R_C + R_D}$$

$$(6) \quad \frac{dH}{dt} = \frac{C_S dT_S}{dt} + \frac{T_S - T_B}{R_C + R_D}$$

The equation for the reference side (5) is subtracted from that for the sample side (6) to obtain:

$$(7) \quad \frac{dH}{dt} = \frac{T_S - T_R}{R_C + R_D} + \frac{C_S dT_S}{dt} - \frac{C_R dT_R}{dt}$$

Since

$$(8) \quad \frac{dT_S}{dt} - \frac{dT_R}{dt} = \frac{d}{dt} (T_S - T_R)$$

Solving equation (8) for dT_S/dt and substituting into (7) yields:

$$(9) \quad \frac{dH}{dt} = \frac{T_S - T_R}{R_C + R_D} + (C_S - C_R) \frac{dT_R}{dt} + \frac{C_S d(T_S - T_R)}{dt}$$

Since the quantity measured is the difference in temperature between the sample and reference holders, not the sample and reference themselves, this equation can be modified by the relationships in equations (1) and (2).

$$(10) \quad \Delta T \equiv T_{SH} - T_{RH} = \frac{R_D}{R_D + R_C} (T_S - T_R)$$

The final relationship is arrived at by combining Equations (9) and (10) to obtain:

$$(11) \quad \frac{dH}{dt} = \frac{T_{SH} - T_{RH}}{R_D} + (C_S - C_R) \frac{dT_R}{dt} + \frac{R_D + R_C}{R_D} C_S \frac{d(T_{SH} - T_{RH})}{dt}$$

Equation (11) indicates that the rate of heat evolution is made up of three terms (Figure 5):

1. The instrument response divided by a constant which is proportional to the difference in heat flow between sample and reference.
2. A constant term depending on the heat capacity of the sample and the heating rate.
3. A term involving a time constant and the rate of change of the recorded quantity.

It is useful to define a term Δq to be the difference in heat flow to the sample and reference as illustrated in Figure 4.

$$(12) \quad \Delta q \equiv \frac{di_S}{dt} - \frac{di_R}{dt}$$

Substituting the temperature values from equations (1) and (2) for the individual heat flow yields:

$$(13) \quad \Delta q = \frac{T_{SH} - T_{RH}}{R_D} = \frac{\Delta T}{R_D}$$

The temperature difference sensed by the detectors is directly proportional to the difference in heat flow into or out of the sample and reference.

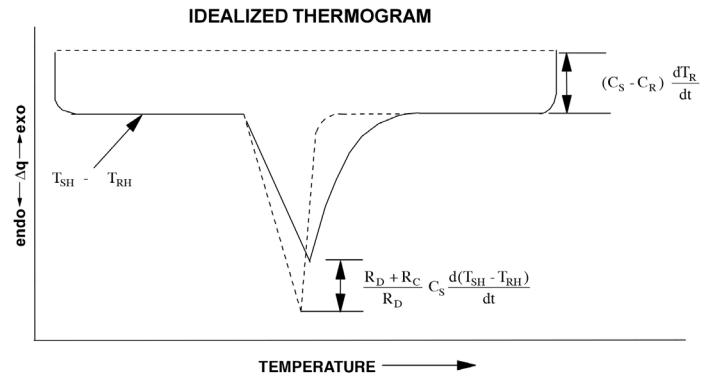


Figure 5: Idealized Thermogram

Prepared by Roger L. Blaine

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