Step-Heated Single-Pan Scanning Calorimeter for the Measurement of Specific Heat of Low Density Materials

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Abstract

A single-pan step-heating differential scanning calorimeter (SPSH DSC) for the measurement of specific heat is presented. It has three advantages over the two-pans DSC: larger sample and hence higher sensitivity, simplicity of construction and ease of use. The proposed step-heating mode of operation is investigated numerically and experimentally. Specific heat measurement of metals as iron, stainless-steel and molybdenum, are within 2%-5% compared with literature data. Low density materials as PTFE and FR4, fit within 2-7% to literature data. The comparison of PVC measured specific heat to literature data is questionable since material exhibits large increase in Cp due to glass transition phenomenon and the available data is not consistent. Measurement of extremely low density insulation materials like silicon and polyurethane foams exhibits large errors, compared to specific heats derived from measurements of thermal conductivity and thermal diffusivity.

1. Introduction

Differential scanning calorimeters (DSC) have become the most popular means for measurement of specific heat of materials. Among the advantages of DSC are: the fast measurement of Cp versus temperature, the relative ease of use and the commercial availability of reliable instruments that handle wide range of temperature and material forms (solids, liquids, powders, films etc.). Although the small material weight (milligrams), typically required for a DSC instrument, is advantageous for rapid measurement, it has an adverse effect in increasing specific heat errors measurement of low density materials as plastics and foams. The small sample size poses another disadvantage for heterogeneous materials, which may not be properly represented, Richardson (1992). Other shortcomings of two-pans DSC, discussed by Dong and Hunt (2000), are related to measurement of enthalpy change during phase transition when the sample temperature and reference temperature change at different rates which lead to smearing of the temperature over the phase transition. Also, large temperature differences between sample and reference can result in heat flow between the two, causing error in the measured enthalpy change. Finally, in heat -flux DSC the thermocouples do not measure the actual sample temperature because of the thermal resistance between the sample and reference is comparable in magnitude to the thermal resistance between the thermocouples and surroundings.

A single-pan calorimeter design was recently introduced by Dong and Hunt (2000, 2001). The new design seems to eliminate some of the errors that are encountered in a conventional twopans DSC. The sample is positioned in a uniform temperature enclosure and has the largest possible thermal resistance to the surroundings. The instrument is made of two crucibles enclosed in an insulated tube shaped heater as depicted schematically in Figure 1. The inner and outer crucibles are separated by air gap to ensure as large as possible thermal resistance and maximum temperature difference during heating or cooling cycles. This arrangement permits the use of large samples, provided the sample is kept at a uniform temperature. Very low thermal conductivity samples may require slow enough heating (or cooling) rates to ensure temperature uniformity within the sample. In particular, the fact that a single-pan DSC can accommodate very large samples, compared to two-pans DSC, can result in higher sensitivity for the measurement of heat capacity. This is an important advantage for the present study, aimed at the measurement of heat capacity of low density materials.

The preferred method of heating in conventional two-pans and the new single-pan DSC is a controlled constant heating rate or a constant temperature difference between sample and reference, Dong and Hunt (2000). In this work a simpler uncontrolled step-heating (or step-cooling) sequence is introduced, instead of a controlled ramped-heating sequence. The main effort in this study is aimed at a more accurate measurement of low density materials.



Figure 1. Schematic view of a single-pan differential scanning calorimeter.

2. Step-heating calorimetry

Similar to two-pans DSC, a single-pan calorimeter requires three runs, an empty pan run, a second run with reference material and a third run with the measured sample. The major thermal relations of the calorimeter assembly are depicted in Figure 2. The dashed line encloses the elements directly involved in the calorimetry. The heater and the insulation only control the maximum temperature that can be attained with a specific design. The sample (or reference) inner crucible and outer crucible are interacting thermally via two thermal resistances: sample to inner crucible, R_{si} , and inner crucible to outer crucible, R_{io} .



Figure 2. Heat transfer relations of single-pan DSC.

The DSC equations are derived from energy balance corresponding to the three runs, and assuming each element is in uniform temperature (lumped capacitance model), Empty pan:

$$m_i C p_i \frac{dT_E}{dt} = \frac{1}{R_{ioE}} \left(T_o - T_i \right)_E \tag{1}$$

Pan with reference:

$$\left(m_i C p_i + m_R C p_R\right) \frac{dT_R}{dt} = \frac{1}{R_{ioR}} \left(T_o - T_i\right)_R$$
(2)

Pan with sample:

$$\left(m_i C p_i + m_s C p_s\right) \frac{dT_s}{dt} = \frac{1}{R_{ios}} \left(T_o - T_i\right)_s \tag{3}$$

where m is mass, Cp is specific heat and R is thermal resistance. Subscripts o, i, E, R, S stand for outer-pan, inner-pan, empty-pan, pan with reference and pan with sample, respectively. Since thermal resistance between the inner and outer crucibles is very large and the positioning of the two crucibles is similar for the three runs, we can assume,

 $R_{ioE} = R_{ioR} = R_{ioS} \equiv R_{io}$. In general R_{io} is non-linear function of temperature and temperature difference between two crucibles, $R_{io}(T, \Delta T)$.

Defining $\Delta T = (T_o - T_i)$ and rearranging equations (1) to (3) we eliminate R_{io} and $m_i C p_i$ to derive the basic DSC equation,

$$Cp_{s} = Cp_{R} \frac{m_{R}}{m_{s}} \frac{\Delta T_{s} \frac{dT_{E}}{dt} - \Delta T_{E} \frac{dT_{s}}{dt}}{\Delta T_{R} \frac{dT_{E}}{dt} - \Delta T_{E} \frac{dT_{R}}{dt}}$$
(4)

All the parameters and variables in (4) are known. Although, Dong and Hunt (2000) performed measurements while keeping either dT/dt or ΔT as constant during a test run, it seems that in general, equation (4) pose no specific requirements of these kind.

We propose a step heating procedure, in which the heater in Figure 1 is turned on while the power is held constant throughout a test run, and the temperatures of inner and outer crucibles are recorded.

To check the validity of this procedure, the system presented in Figure 2 is numerically modelled to create simulated DSC test runs. Figures 3a, 3b and 3c show the simulated temperature response to heating power of 15 watts (for 3 DSC runs - empty-pan, reference and sample), and the respective temperature-difference between inner and outer crucibles, and the rate of temperature change (temperature-time-derivative) for a 4.04g stainless steel empty pan, 6.99g copper reference sample, and a 0.785g 'polymer' type material with constant specific heat of 1200 $Jkg^{-1}K^{-1}$. It is apparent that both ΔT and dT/dt change substantially during the three test runs. The estimated sample specific heat is presented in Figure 4. Except for a small temperature interval of $20^{\circ}C$ at the beginning of the scanned temperature interval, the estimated specific heat converges very well to the simulated specific heat. This convergence interval corresponds to a time interval of about five minutes that should be ignored in actual measurements. Figure 5 presents simulated C_p measurement of a material with variable specific heat, increasing linearly from 1000 $Jkg^{-1}K^{-1}$ at 0°C to 2000 $Jkg^{-1}K^{-1}$ at $100^{\circ}C$. Again, the reconstruction of C_p is very good. The 'noise' in the estimated specific heat is attributed to truncation errors, since the temperature was introduced with only three significant digits to simulate actual measurement situation. This is not an inherent problem of the method since it can be overcome by proper filtering, faster sample rate and averaging.



a) Temperature response to step heating

b) Temperature difference between crucibles



c) Temperature rate of inner crucible

Figure 3. Thermal simulation of a single-pan step heating DSC run for an empty pan, for reference material and for sample material.



Figure 4. Estimated specific heat for simulated single-pan step heating DSC for constant Cp=1200 J/kg/K.



Figure 5. Estimated specific heat for simulated single-pan step heating DSC for linearly variable specific heat $C_p=1000 + 10T$.

3. Experimental Setup

A laboratory prototype of a single-pan calorimeter was designed and built to study the proposed single-pan step-heating DSC (SPSH DSC). The sample size is up to 10 millimetres in diameter and length. It is encapsulated in a stainless-steel or aluminium pan, and both are enclosed in a larger crucible separated by a small air gap. As mentioned before, the gap serves to increase thermal resistance that plays important role in increasing DSC measurement sensitivity. The crucibles assembly is positioned inside a cylindrical insulated heater, also separated by a small air gap. In practice the air gaps are maintained by small diameter stainless steel holders and by the thermocouples, this can introduces non-ideal effects that should be handled carefully during the instrument design.

The reference sample in the present study is made of pure copper. The temperatures is measured with chromel-alumel thermocouples (type-K).

The temperature difference between the two crucibles is either calculated from temperature measurements or measured directly (connecting the two thermocouples as thermopile) for improved resolution. The temperatures are recorded by a PC controlled data acquisition system at a rate of 0.2Hz to 2Hz.

The data reduction procedure starts with calculation of the temperature derivatives and temperature differences (averaged over pre-selected time interval to reduce noise) and continuous with the conversion of these variables from a time domain to a temperature domain. This step is considered very important in making the data of the three separate runs consistent, and is also believed to minimize errors relate to temperature variation of thermal resistance, R_{io} . Finally, the specific heat is derived from equation (4) using pure copper specific heat based on recent work by White and Minges (1997).

4. Results and discussion

Three metals were measured using SPSH DSC, Iron, 303L stainless-steel and Molybdenum. The measurements are presented in Figures 6, 7 and 8, respectively, along with specific heats reported in the literature. Pure iron is compared to data from TPRC thermophysical properties of matters, Touloukian (1970), based on measurements by Wallace et al (1960), and measurements by TPRL, Nabi and Taylor (1992). Stainless-steel is compared with data from Touloukian (1970) for type 301 and with TPRL measurements for type 303, Nabi and Taylor (1992). The Molybdenum is compared with data from CINDAS (1999) and Touloukian (1970) which are almost identical for the temperature range in the present study. Above 100°C, the measured specific heat of Iron by SPSH DSC is in good agreement with TPRC and TPRL data. Below 100°C, the deviation between measured and literature data is between 5% and 8% of the measured value. Stainless-steel SPSH measurements within 4% with literature data. The Molybdenum specific heat measurement exhibits very good agreement with CINDAS and TPRC data within less than 2% for temperatures above 50°C.



Figure 6. Specific heat of pure Iron measured by step-heating DSC (red open circles) compared with other measurements.



Figure 7. Specific heat of 303L Stainless Steel measured by step-heating DSC (red open circles) compared with other measurements.



Figure 8. Specific heat of pure molybdenum measured by step-heating DSC (red open circles) compared with other measurements.

Measurement of specific heat of relatively low density materials was demonstrated with three types of polymers, Polytetrafluoroethylene (PTFE), Glass-epoxy (FR4) and Polyvinylchloride (PVC). The measured heat capacities are presented in Figures 9, 10 and 11, respectively. The PTFE measured C_p agrees within 2% to 5% with the data in reference CINDAS (1999), where FR4 Cp is lower by 3% to 7% compared with data in reference CINDAS (1999). Finally, the measured specific heat of PVC exhibit large increase over 55°C. This may correlate with glass transition of PVC at about 87°C. The specified C_p in Goodfellow (2005) website ranges from 1000 to 1500 J/kg-K (temperature is not mentioned) is similar to SPSH measurement around 30°C, and is much lower than C_p in Tangram (2005) website, 2150 to 2600 J/kg-K. This inconsistency may be explained by measurements done on both sides of the glass transition.



Figure 9. Specific heat of PTFE measured by step-heating DSC (red open circles).



Figure 10. Specific heat of FR4 measured by step-heating DSC (red open circles)



Figure 11. Specific heat of PVC measured by step-heating DSC (red open circles)

Finally, measurement of extremely low density insulation materials, Silicon foam with density of 190 kg/m^3 and Polyurethane foam with density of 65 kg/m^3 was attempted. The measured specific heat presented in Figure 12, exhibit large errors and poor repeatability, compared with measurements done by alternative approach. The specific heat of the two foams was estimated based on measured thermal diffusivity by step heating technique, Nabi et al (2000), and measured thermal conductivity by planar source heating. The specific heat was calculated by:

$$C_p = k / (\rho \alpha) \tag{5}$$

Table 1 summarizes the measured parameters. The estimated errors for the measurement of the thermal conductivity and thermal diffusivity are 8% and 5%, respectively. Near room temperature, the specific heat of the Silicon foam is estimated by this approach, as 840 ± 75 J/kg-K, and for the Polyurethane foam, as 1170 ± 110 J/kg-K.

The possible sources of errors are currently under study. Probably, the major source of errors and the degraded sensitivity can be related to the relatively heavy inner crucible, about 1.5 grams, compared with the weight of low density samples, only 0.20 to 0.05 grams. Additional source of errors can be related to non-ideal heat transfer interference between inner and outer crucibles caused by the stainless-steel holder and thermocouple attached to the inner crucible, which has larger effect with samples with very low thermal conductivity. The present instrument design needs to be slightly modified in order to overcome the two suspected sources of errors.

Table 1. Thermal properties measurement of extremely low density insulation materials, k is measured by planar source heating and α is measured by step heating technique, Nabi et al (2000).

	Properties at 300 K			
Material	$\rho/ \text{ kg m}^{-3}$	$k/Wm^{-1}K^{-1}$	$\alpha/m^2 s^{-1}$	$C_p = k(\rho \alpha)^{-1}$
				$J kg^{-1} K^{-1}$
Silicon foam	195	0.053	3.23e-7	840 ± 75
Polyurethane foam	65	0.026	3.42e-7	1170 ± 110



(a) Polyurethane foam

(b) Silicon foam

Figure 12. Specific heat of Polyurethane foam and Silicon foam measured by step-heating DSC, compared with measurements done by alternative approach (green plus sign).

5. Conclusions

We have demonstrated in this study a new and simple mode of operation for a single-pan DSC using step-heating. The method does not require active control of heating rate. The proposed mode of operation was studied numerically and was consistent in retrieving the specific heat of constant or temperature-depended specific heat of low density materials.

Specific heat measurement with a laboratory prototype of a single-pan demonstrated that reliable Cp measurement of high to low density material was feasible. Measurements of extremely low density materials produced large measurements errors. We believe that these errors are related to limitations in the instrument present design, in particular, in the mass of the inner pan. It has to be reduced substantially, in order to perform measurements of extremely low density materials.

The test setup and the newly proposed step-heating sequence were validated by measuring specific heat of several well characterized metals, i.e. Iron, Stainless-steel and Molybdenum. The measurements compared well, within 5% deviation, with published data.

Measurement of relatively low density materials was demonstrated with two types of polymers: Glass-epoxy (FR4) and PVC. The measured specific heats were in good agreement, within 7%, compared to published data. In addition, the specific heat of the two polymers was evaluated by a different method, using measured thermal diffusivity by step heating technique, and measured thermal conductivity by planar source heating.

Finally, measurement of extremely low density insulation materials, for example Silicon foam, exhibits larger errors, compared to measurements using the alternative approach mentioned above. The possible sources of errors are currently under study.

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References

- CINDAS, 1999 in Microelectronics Packaging Materials Database, CINDAS (under sponsorship of SRC), Purdue Univ., V.2.11
- Dong H B and Hunt J D, 2000 High Temp.-High Pres. 32 pp 311-319

Dong H B and Hunt J D, 2001 J. Therm. Anal.Cal. 64 341-350

Goodfellow, 2005, <u>www.goodfellow.com/csp/active/gfHome.csp</u>

- Nabi A, Taylor R E, 1992 High Temp.-High Pres. 24 pp 135-143
- Nabi A, Cohen Y and Hazan N, 2000 High Temp.-High Pres. 32 pp 589-598

Richardson M J, 1992 in Compendium of Thermophysical Property measurement

Methods, Eds K D Maglic, A Cezairliyan, V E Peletsky (NY Plenum) pp 519-545 Tangram Technology Ltd., 2005, <u>www.tangram.co.uk/</u>

Touloukian Y S, Powell R N and Clemence P G, 1970 in *Specific heat, Vol. 4 of thermophysical properties of matter*, Eds Y S Touloukian, C Y Ho (New York IFI/Plenum), 102-109 and 693-695 and 135-139

Wallace D C, Sidles P H and Danielson G C, 1960 J. Appl. Phys., **34** pp 168-176 White G K and Minges M L, 1997 Int. J. Thermophysics 18 pp 1269-1327