Thermochimica Acta, 33 (1979) 281—291

AN IMPROVED TECHNIQUE FOR PRECISE MEASUREMENTS OF SPECIFIC HEAT OF A LIQUID USING DUPONT 990 DSC

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(Received 18 December 1978)

ABSTRACT

Precise measurement of specific heat of liquid using the DuPont-990 DSC is not an easy matter, although the modular system has many desirable features for its determination. It was found that pan placement by the best human judgement was not sufficient to warrant accurate and reliable results. A technique which is based on a centering device has been established. The device, which consists of a plexiglas centering cylinder and a vacuum-operated sample loading probe, permits accurate positioning of either the Dupont or the Perkin-Elmer hermetic aluminum pans on the calorimeter. With the aid of the device, specific heats of demineralized water and phenyl ether were obtained with an accuracy and precision of better than 2% on a DuPont-905 standard DSC cell. The technique also enables measurements to be performed on the -902 standard DSC cell, and with a little sacrifice in accuracy, on the PDSC cell as well. The improved technique has many advantages over the silver disc/heat sink compound method reported by the manufacturer.

INTRODUCTION

One major application of differential scanning calorimetry (DSC) in industry is the determination of specific heats (C_p) of materials, solids and liquids. Liquids, because of their volatility and lower density, are much more difficult to handle and often become a challenge to the design of the calorimeter.

DuPont 990 DSC system, with its high sensitivity, improved baseline performance and thermograms printed on an XY recorder, is convenient for specific heat measurements. However, the calorimeter design of the instrument presents several difficulties for obtaining C_p of liquids with good precision and accuracy. A technique which involves using a heat sink compound on silver discs and hermetic gold pans has been published by the manufacturer [1—3]. In addition to the high cost of the gold containers, the technique is useable only for a limited temperature range within which the heat transfer agent is thermally stable. We have established an alternate and much improved technique with which precise C_p data on volatile liquids can be obtained regularly without the above drawbacks. This paper will describe the technique in detail together with our early experience in C_p measurements with the system.

EXPERIMENTAL

The DuPont-990 DSC system was composed on a -990 thermal analyzer equipped with an XYY' recorder, and a cell base module II. Specific heat measurements were obtained with a pressure (model -902), a standard (model -902) and an area thermocouple standard (model -905) DSC cell.

Demineralized water and phenyl ether (DPO) were the two reference materials used in the experiments. The former had a typical purity of about 17 $M\Omega$ cm^{-1} and was obtained by passing deionized water through an ultrapure cartridge, an organic removal Barnstead type HN cartridge, and a Corning ultra-high purity demineralizer cartridge in series. The phenyl ether was of Fisher certified grade from Fisher Scientific Co. The DPO was warmed slightly to above its melting temperature before use.

The DSC sample containers used were coated aluminum, and aluminum of the hermetic type from DuPont Co. We have also performed some measurements with the Perkin-Elmer hermetic aluminum pans. The DuPont sample encapsulating press and the Perkin-Elmer volatile sample sealer were used for sealing the respective sample containers. Sample transfer to the DSC pans was by means of a micro-syringe. In each C_p determination, the weight of the sample before and after the measurement was carefully checked with a Perkin-Elmer AD-2 Autobalance to ascertain that no sample loss was experienced.

The method for specific heat measurements using the DuPont system was described fully in the instrument's operational manual. In short, it involved comparing the thermal lag between the sample and the reference under "blank" and "sample" conditions. Calibration of the system for each $C_p(T)$ determination was accomplished by substituting the sample with a sapphire standard whose specific heats were known. In all cases, the blank, the sample and the sapphire were measured under identical conditions. The calibration constant E and the specific heat C_p of the sample were calculated according to

$$C_p = \frac{60E\Delta q\Delta Y}{H_r m} \tag{1}$$

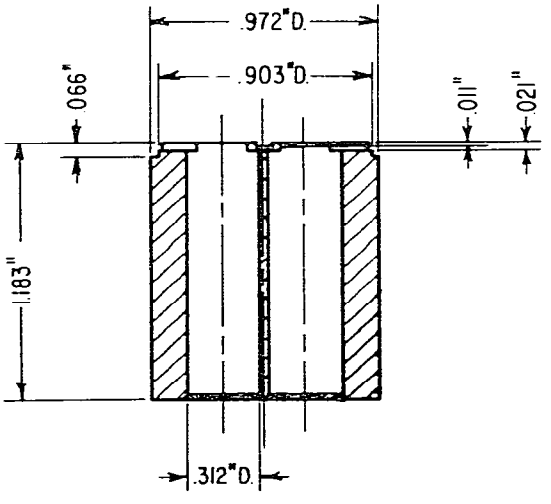
where C_p = specific heat of sample (or sapphire); E = calibration constant; Δq = Y-axis range (mcal sec-in^{-1}); ΔY = difference in Y-axis deflection between sample (or sapphire) and blank curves at temperature of interest (in); H_r = heating rate (deg min^{-1}); m = sample (or sapphire) mass (mg).

In order to keep the conditions identical, the blank, the sapphire and the sample were measured either with the same DSC pan or three different pans of the same kind with weights matching each other to 0.01 mg. The pans were all sealed in the latter but was so in the former only when it contained the sample. As the sapphire specimen provided with the instrument was too large for the DuPont hermetic pans, a similar piece supplied by Perkin-Elmer corporation was used instead.

The DuPont DSC cell was designed with the temperature sensors for the sample and reference on two raised platforms stamped from a constantan disc. Since the diameter of the sample container, sealed or unsealed, is much

greater than that of the raised platform, precise sample loading onto the sensors is a practical impossibility if human judgement only is exercised. Sample placement is a crucial factor for accurate and precise specific heat measurements.

To assure the sample and reference were placed accurately and reproducibly on their respective platform, a centering device was designed and used. The device could be used with the hermetic pans from DuPont (sealed) and Perkin-Elmer (sealed and unsealed) and consisted of a plexiglas cylinder machined to the inside diameter of the furnace of the DSC cell and a sample loading probe. Through the plexiglas cylinder, two holes were drilled along the axes of the platforms' centers which were precisely determined with a Scherr-Tumico optical comparator (Fig. 1). The face of the cylinder in contact with the constantan disc was milled to an exact counterpart of the disc. Thus, when the cylinder was placed into the cell cavity, it was keyed to the grids and rim of the constantan disc with its two holes concentric with the sample and reference platforms (Fig. 2). The sample loading probe which was lathed to fit exactly and smoothly with the two holes in the plexiglas cylinder was used to place the hermetic pans into the calorimeter. It consisted of a piece of stainless steel high pressure tubing machined to mate to the top of the pan with the aid of a rubber insert on one end and connected to a house vacuum (adjusted to about 200 torr) on the other end (Fig. 3). A bleed hole drilled at right angle to the tubing permitted easy pick up and release of the pan with the manipulation of the index finger. To avoid distorting the pan when it was positioned on the constantan disc, a stop (steel collar) was set at proper depth on the probe. Once the pans were properly placed, the plexiglas cylinder was removed carefully from the DSC furnace chamber. Due attention was paid to assure the pans were not dis-



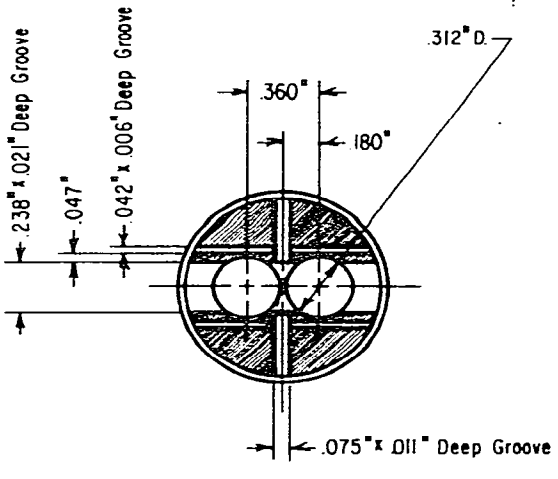


Fig. 1. Drawing of the plexiglas centering cylinder — vertical section.

Fig. 2. Drawing of the plexiglas centering cylinder — a view of the face in contact with the constantan disc of the DSC cell.

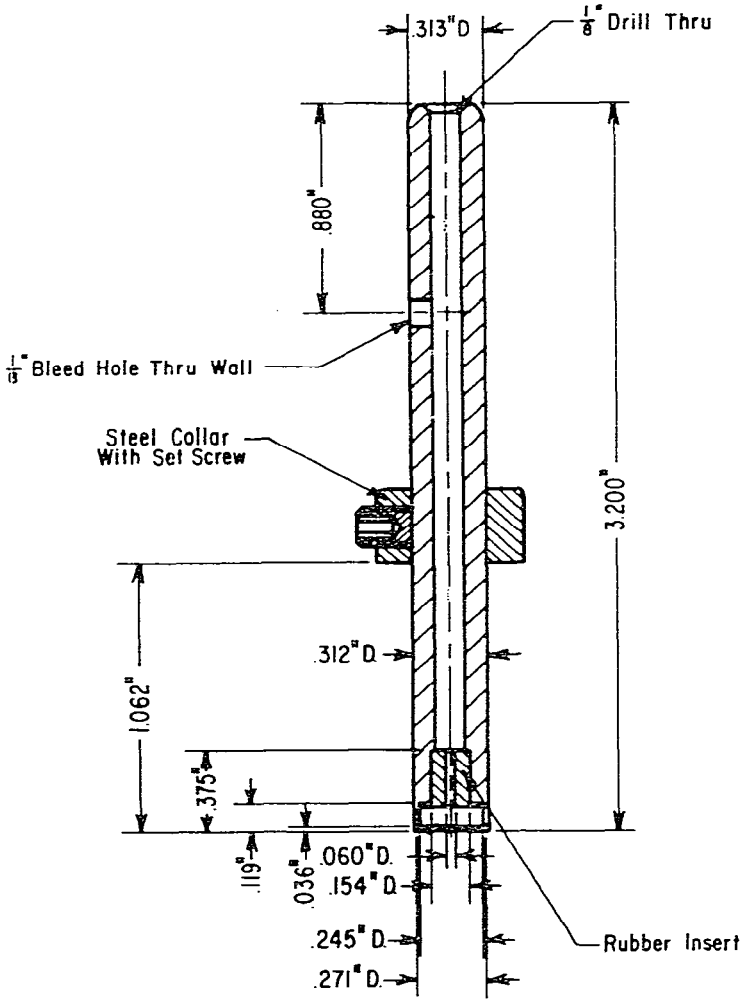


Fig. 3. Drawing of the sample loading probe — vertical section.

turbed. With the cell assembled, measurements were performed when the recorder pen stabilized, indicating equilibration had been reached.

RESULTS AND DISCUSSION

Although the importance of sample placement to specific heat measurements is not emphasized in the DuPont-990 operation manual, its relevance to the determination is explicit in the following equation by Baxter [4] describing the operation of the DSC system.

$$\frac{dH}{dt} = \frac{T_{SH} - T_{RH}}{R_D} + (C_S - C_R)\frac{dT_R}{dt} + \frac{R_D + R_C}{R_D} C_S \frac{d(T_{SH} - T_{RH})}{dt} \qquad (2)$$

where dH/dt is the rate of heat evolution of an exothermic transition; $(T_{SH} - T_{RH}) = \Delta T = [R_D/(R_D + R_O)](T_S - T_R)$ is the temperature difference between the sample and reference containers; R_D is the thermal resistance

between furnace and sample or reference container; R_C is the thermal resistance between sample (reference) container and sample (reference) and is determined by the sample (reference) container, atmosphere and the contact of the sample with container, and container with detector; C_S and C_R are the heat capacity of sample and reference, respectively; and dT_R/dt is the heating rate.

Tables 1 and 2 show the results obtained in nitrogen (0.05 SCFH) at 10°C min^{-1} on demineralized water with the pressure and the standard DSC cell, respectively, when sample placement was achieved by best human judgement. Each trial represents a new sample sealed in a DuPont hermetic-coated aluminum pan which previously was also used to obtain the blank and the sapphire curves. With the PDSC cell, the results at each temperature averaged to 22% higher than the literature value. There was also considerable scattering in the results ($\sigma = \pm 3$ to 5%). The five trials with the standard DSC cell indicated a closer agreement with the literature value (5 to 7%), but the precision was worse ($\sigma = \pm 6$ to 7%). A similar experience with the instrument had been published by Yip et al. [7]. The authors used a PDSC cell in their study and placed the pans with the aid of a 14 power cathetometer.

Baker [2,3] reported that accurate specific heats could be measured with a standard DSC cell if a silver disc (11/32 inch in diameter) was put onto the sample and reference platform with a Dow-Corning 340 silicone heat sink compound before the pans were placed. Using gold hermetic pans for the sample and non-hermetic gold pans for the sapphire calibration, in five trials with a -905 DSC cell, the author obtained an average specific heat for water at 80°C which agreed with the literature value to 0.2% (standard deviation, 1.0%). We evaluated the Baker technique and found that it was usable only with gold pans and within a narrow temperature range. This is illustrated in Tables 3 and 4 which summarize our results on demineralized water and phenyl ether (DPO) obtained with a standard 902 DSC cell. The procedure we used differed from Baker's only in flow rate of nitrogen (24 vs. 50 cc

TABLE 1

Specific heats of demineralized water (cal $g\text{-}deg^{-1}$) with a -902 PDSC cell [5]

Pan placement by best human judgement

Trial	Temp. (°C)		
	30	40	50
1	1.25	1.24	1.21
2	1.22	1.23	1.25
3	1.32	1.33	1.34
4	1.31	1.30	1.34
Mean	1.28	1.28	1.29
σ (% about mean)	0.05 (3.4)	0.05 (3.7)	0.07 (5.1)
Lit. [6]	0.998	0.998	0.999
Deviation from lit. (%)	22.0	22.0	22.6

TABLE 2

Specific heats of demineralized water (cal g-deg^{-1}) with a -902 standard DSC cell [5]

Pan placement by best human judgement

Trial	Temperature (°C)				
	30	40	50	60	70
1	0.984	0.985	0.983	0.986	0.986
2	0.964	0.964			
3	1.06	1.05	1.05	1.06	1.06
4	1.10	1.10	1.09	1.11	1.11
5	1.14	1.12	1.13	1.14	1.13
Mean	1.05	1.04	1.06	1.07	1.07
σ (% about mean)	0.07 (7.1)	0.07 (6.6)	0.06 (5.9)	0.07 (6.3)	0.06 (6.0)
Lit. [6]	0.998	0.998	0.999	0.999	1.001
Deviation from lit. (%)	5.0	4.0	5.8	6.6	6.4

TABLE 3

Specific heats of demineralized water (cal g-deg^{-1}) with a -902 standard DSC cell, silver disc and Dow-Corning 340 silicone heat sink compound [8]

Trial	Temp. (°C)				
	30	40	50	60	70
1	0.970	0.979	0.991	0.978	0.971
2	1.08	1.08	1.08	1.08	1.09
3	1.05	1.05	1.05	1.05	1.05
4	1.05	1.04	1.05	1.05	1.05
Mean	1.04	1.04	1.04	1.04	1.04
σ (% about mean)	0.05 (4.6)	0.04 (4.2)	0.04 (3.7)	0.04 (4.2)	0.05 (4.8)
Lit. [6]	0.998	0.998	0.999	0.999	1.001
Deviation from lit. (%)	4.0	4.0	3.9	3.9	3.8

TABLE 4

Specific heats of phenyl ether (cal g-deg^{-1}) with a -902 standard DSC cell, silver disc and Dow-Corning 340 silicone heat sink compound [8]

Temp. (°C)	Trial		Mean	σ (% about mean)	Lit. [9]	Deviation from lit. (%)
	1	2				
75	0.321	0.314	0.318	0.005 (1.6)	0.408	22.1
100	0.335	0.326	0.331	0.006 (1.9)	0.423	21.7
125	0.345	0.342	0.344	0.002 (0.6)	0.439	21.6
150	0.358	0.353	0.356	0.004 (1.0)	0.455	21.8
175	0.371	0.370	0.371	0.001 (0.2)	0.471	21.2
200	0.381	0.389	0.385	0.006 (1.5)	0.486	20.8
225	0.390	0.408	0.399	0.01 (3.2)	0.502	20.5
250	0.400	0.422	0.411	0.02 (3.8)	0.518	20.7

min^{-1}) and type of pan (aluminum vs. gold). The 4% error and ±5% precision for the water surely represented only a slight improvement on our previous results obtained without the silver disc and heat sink compound. The main concern on the Baker technique, however, was the 22% error observed with the DPO (Table 4). The huge discrepancy from the literature value and the strange appearance of the thermograms (Fig. 4) were due to the continuous change of heat transfer property of the heat sink compound with temperature. Thermogravimetry showed that the compound started losing its heat transfer agent at a temperature as low as 63°C (Fig. 5), while differential thermal analysis (Fig. 6) indicated onset of an endotherm at 120°C (peak minimum 238°C). Both the TG and DTA experiments were performed in nitrogen with a Mettler Thermoanalyzer-1.

The disadvantages of the Baker's method were eliminated completely with our centering device technique. Demonstrated in Tables 5 and 6 are results measured on our two reference materials with a -905 standard DSC cell. In each trial, the sample was sealed in a Perkin-Elmer hermetic aluminum pan which was also used in calibration of the cell previously. The accuracy and precision of the determinations were remarkable, even at high temperatures. Similar results were also obtained using the DuPont hermetic aluminum pans (Table 7). In this case, three individually sealed pans ("Experimental" section) were used for each sample.

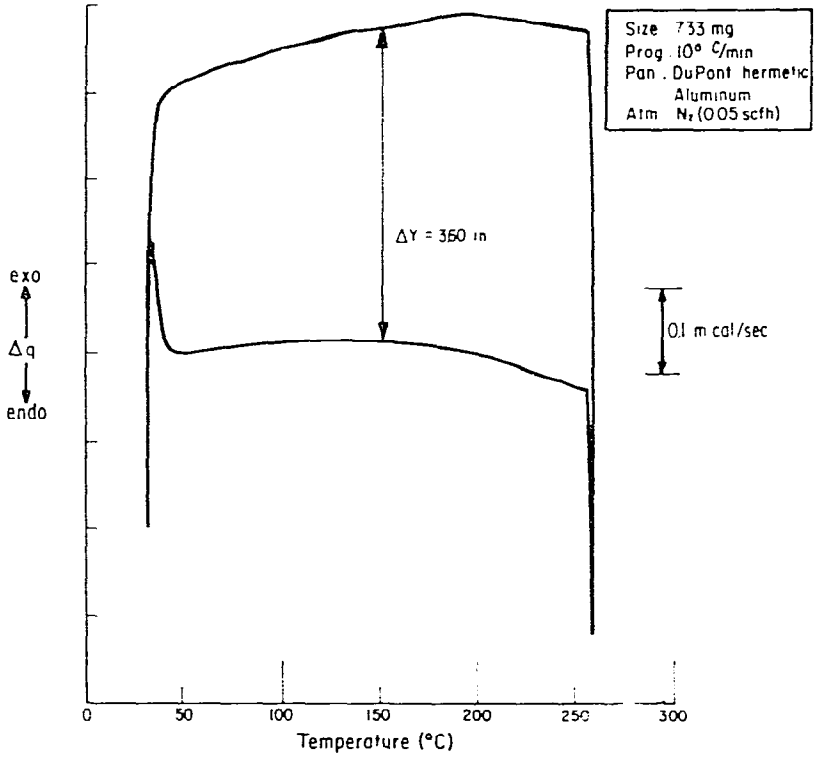


Fig. 4. Typical specific heat determination curves of phenyl ether obtained with a -902 standard DSC cell, silver disc and Dow-Corning 340 silicone heat sink compound.

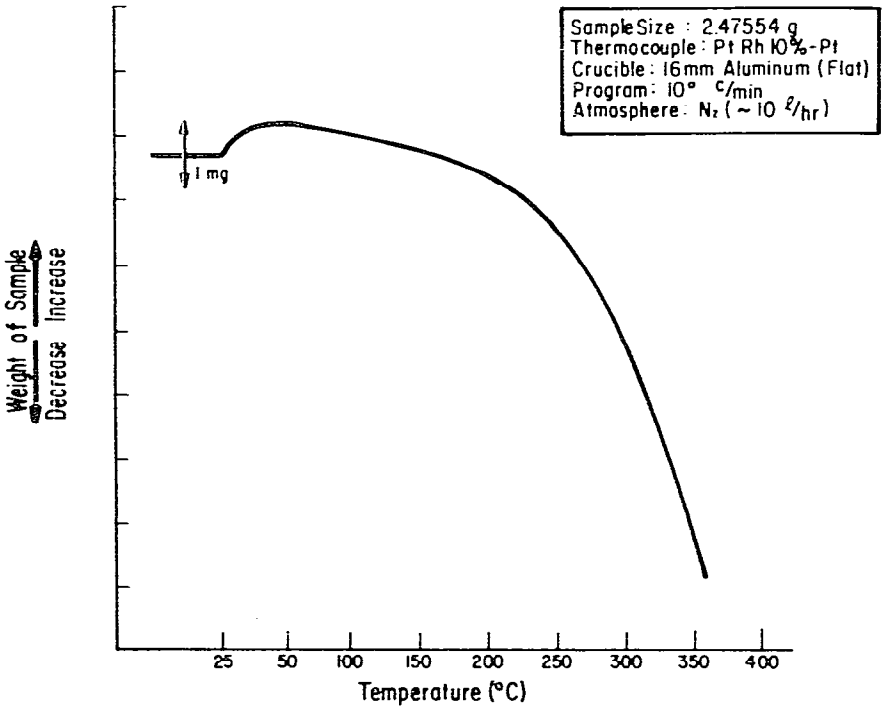


Fig. 5. Thermogravigram of Dow-Corning 340 silicone heat sink compound showing weight loss was first detected at 63°C.

The centering device technique was also used to evaluate the performance of the -902 standard and pressure DSC cells for specific heat measurements. The results obtained on four water samples with the standard cell are summarized in Table 8. It was observed that the precision was about the same, although the accuracy was slightly inferior (~2%). The centering device tech-

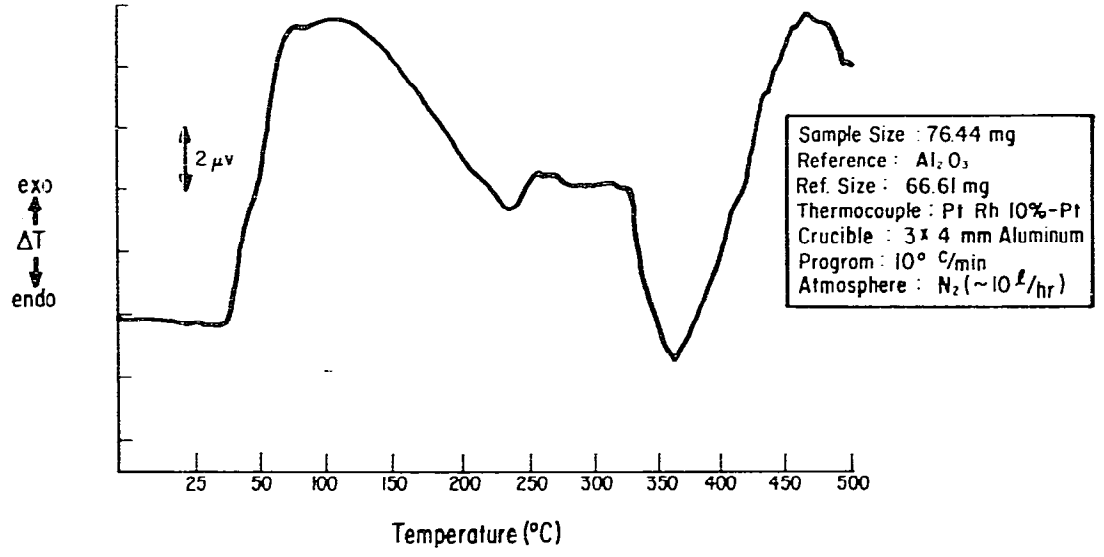


Fig. 6. DTA thermogram of Dow-Corning 340 silicone heat sink compound.

TABLE 5

Specific heats of demineralized water (cal g-deg^{-1}) with a -905 standard DSC cell [10]

Pan placement by centering device technique

Trial	Temp. (°C)		
	50	60	70
1	1.014	1.018	1.018
2	0.991	1.001	1.000
3	0.960	0.976	0.966
4	0.966	0.965	0.980
5	1.022	1.014	1.014
6	0.988	0.983	0.998
7	0.987	0.998	0.993
8	1.007	1.011	1.015
9	0.985	0.998	1.000
Mean	0.991	0.996	0.998
σ (% about mean)	0.02 (2.1)	0.02 (1.8)	0.02 (1.7)
Lit. [6]	0.999	0.999	1.001
Deviation from lit. (%)	0.8	0.3	0.3

TABLE 6

Specific heats of phenyl ether (cal g-deg^{-1}) with a -905 standard DSC cell [10]

Pan placement by centering device technique

Temp. (°C)	Trial		Mean	σ (% about mean)	Lit. [9]	Deviation from lit. (%)
	1	2				
50	0.398	0.395	0.397	0.002 (0.5)	0.392	1.3
70	0.414	0.407	0.411	0.005 (1.2)	0.404	1.7
90	0.421	0.421	0.421	0 (0)	0.417	1.0
110	0.434	0.440	0.437	0.004 (1.0)	0.429	1.8
130	0.453	0.449	0.451	0.003 (0.6)	0.442	2.0
150	0.462	0.467	0.465	0.004 (0.8)	0.455	2.2
170	0.473	0.482	0.478	0.006 (1.3)	0.467	2.3
190	0.486	0.489	0.488	0.002 (0.4)	0.480	1.6

TABLE 7

Specific heats of demineralized water (cal g-deg^{-1}) with a -905 standard DSC cell [11]

Pan placement by centering device technique

Trial	Temp. (°C)		
	50	60	70
1	0.985	0.998	1.000
2	0.998	1.000	0.992
3	1.000	1.004	1.014
4	1.005	1.007	1.010
Mean	0.997	1.002	1.004
σ (% about mean)	0.009 (0.9)	0.004 (0.4)	0.01 (1.0)
Lit. [6]	0.999	0.999	1.001
Deviation from lit. (%)	0.2	0.3	0.3

TABLE 8

Specific heats of demineralized water (cal g-deg^{-1}) with a -902 standard DSC cell [10]

Pan placement by centering device technique

Trial	Temp. (°C)		
	50	60	70
1	0.953	0.961	0.967
2	1.006	1.006	1.014
3	0.981	0.984	0.993
4	0.964	0.973	0.973
Mean	0.976	0.981	0.987
σ (% about mean)	0.02 (2.4)	0.02 (2.0)	0.02 (2.2)
Lit. [6]	0.999	0.999	1.001
Deviation from lit. (%)	2.3	1.8	1.4

TABLE 9

Specific heats of demineralized water (cal g-deg^{-1}) with a -902 PDSC cell [10]

Pan placement by centering device technique

Trial	Temp. (°C)		
	50	60	70
1	1.028	1.034	1.038
2	1.031	1.041	1.045
Mean	1.030	1.038	1.042
σ (% about mean)	0.002 (0.2)	0.005 (0.5)	0.005 (0.5)
Lit. [6]	0.999	0.999	1.001
Deviation from lit. (%)	3.0	3.8	3.9

TABLE 10

Specific heats of phenyl ether (cal g-deg^{-1}) with a -902 PDSC cell [10]

Pan placement by centering device technique

Temp. (°C)	Trial		Mean	σ (% about mean)	Lit. [9]	Deviation from lit. (%)
	1	2 [a]				
50	0.403	0.403	0.403	0 (0.0)	0.392	2.7
60	0.416	0.410	0.413	0.004 (1.0)	0.398	3.6
70	0.422	0.417	0.420	0.004 (0.8)	0.404	3.8
80	0.431	0.423	0.427	0.006 (1.3)	0.410	4.0
90	0.440	0.430	0.435	0.007 (1.6)	0.417	4.1
100	0.442	0.437	0.440	0.004 (0.8)	0.423	3.9
110	0.452	0.447	0.445	0.006 (1.5)	0.429	3.6
120	0.460	0.452	0.456	0.006 (1.2)	0.436	4.4

[a] Obtained also with silver discs but no heat sink compound.

nique also greatly improved the data obtained with a 902 PDSC cell (Tables 9 and 10). Instead of an error of 22% and a standard deviation of 3 to 5% as discussed previously when human judgement was used to place the pans, our two trials on demineralized water and DPO indicate an accuracy and precision of about 4 and 2%, respectively.

CONCLUSION

Accurate and precise measurements of specific heat of liquids can be obtained with the DuPont-990 DSC system using the centering device technique. This new technique has many advantages over the Baker's and they are summarized as follows.

(1) Use of aluminum pans rather than gold — lower analysis cost.

(2) An equilibrium time of 1—2 min between sample loading and thermogram recording rather than 10—15 min — shorter analysis time.

(3) Restoration of starting point (Y axis) between blank, calibration and sample scans — greater assurance of proper pan placement and equilibration.

(4) No additive to the calorimeter — higher confidence in results and full temperature range of instrument available for measurement.

(5) Observed about 2% error with the 902 standard DSC cell and 4% with the 902 PDSC cell with good precision — full functionality to earlier users.

ACKNOWLEDGEMENTS

The authors are grateful to Mr. E. Seiber, Monsanto Company, for the machining of the centering device, and to DuPont Company for its full cooperation and donation of the -905 cell during the course of this project.

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11 Blank, sapphire and sample measured with three individually sealed DuPont hermetic aluminum pans in nitrogen (0.05 SCFH) at 10°C min^{-1}. The pans matched one another in weight to 0.01 mg.