Thermochimica Acta, 62 (1983) 187–196
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

AN AUTOMATED DATA COLLECTION SYSTEM FOR DSC ENABLING CALCULATION OF SPECIFIC THERMAL CAPACITY AND ENTHALPY

T. FEARN, R. LAWSON, P.I. MARIS and P.L. RUSSELL

Flour Milling and Baking Research Association, Chorleywood, Rickmansworth, Herts. WD3 5SH (Gt. Britain)

(Received 19 August 1982)

ABSTRACT

An analogue to digital converter is described for the connection of a Perkin-Elmer DSC-2 differential scanning calorimeter to a Research Machines 380Z microcomputer. Programs have been developed to enable data acquisition from the DSC, and calculation of sample specific thermal capacity and enthalpy as a function of temperature, from sample, reference and calibrant data. Experimental data are given and the best way of operating the system is discussed.

INTRODUCTION

Differential scanning calorimetry (DSC) is a technique by which a difference in absorption or emission of heat between a sample and reference can be measured as a function of temperature. Differential heat supply is displayed as the ordinate on a chart recorder, while the time elapsed (or the temperature, since this is linear with time), is plotted as the abscissa. The ordinate value on such a plot (over the range B to F, Fig. 1a) is proportional to the thermal capacity of the material. Any chemical or physical change involving absorption or emission of heat is detected as a difference between the power supplied to the sample and the reference, and results in a peak (CDE, Fig. 1a), the area of which is proportional to the amount of heat associated with the change. In many applications of DSC the thermal changes are small — of the order of 2–3 J g^{-1}. Before the advent of modern methods of data acquisition and handling, the usual procedure was to employ high recorder sensitivity to give a large peak, and obtain the peak area by weighing, planimetry or the use of a mechanical integrator attached to the recorder. Under these circumstances the true baseline and all information about thermal capacity were lost. As has been pointed out, such a

0040-6031/83/0000-0000/$03.00

system was less than ideal [1]. Our aims were therefore to measure peak areas rather less laboriously than before, and to express these areas directly in terms of heat units (J g^{-1} sample).

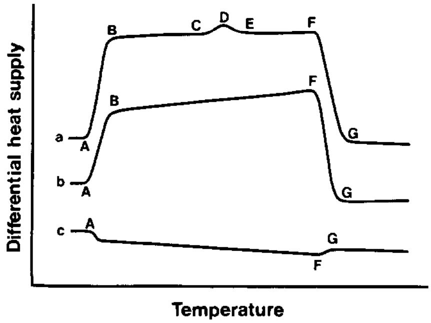

Fig. 1. Schematic diagram of DSC traces for (a) sample; (b) calibrant; and (c) reference.

Some earlier studies have described the application of computers to the analysis of DSC data; thus a general method has been described for the use of a digital voltmeter for the conversion of analogue data to digital form and a paper tape to transfer these signals to a mainframe computer for later analysis [2–4]. Other workers have used similar methods, but carried out data analysis using a calculator [5]. Paper tape is a bulky and expensive means of data storage, when compared with magnetic tape, and a more direct approach is to transfer analogue data directly from the DSC machine to a computer, via an analogue to digital converter. Magnetic tape or discs may then be used as storage media for both data and processed results. Different groups of workers have described interfacing of DSC equipment to either mainframe [6] or minicomputers [7]. This method enables considerable sophistication and flexibility in programming, and allows the use of magnetic storage, but the equipment cost is high. When this work began, some DSC instrument makers supplied analogue to digital converters interfaced to calculators, now updated to dedicated microcomputers. This enables the operation of a number of resident programs but again, is a relatively expensive option. Also, such systems are generally rather inflexible and the user does not necessarily have access to the program being used. We therefore set out to design and construct an analogue to digital converter (A to D) to enable the connection of a Perkin-Elmer DSC-2 to an inexpensive, commercially available microcomputer. The design criteria for the system were that it should

(1) combine computing power with flexibility, i.e. it should enable the user to modify programs as required;

(2) enable magnetic data storage and retrieval on either cassette tape or disc; and

(3) be inexpensive.

This work describes the construction, programming and operation of such a system.

EXPERIMENTAL

Materials

Indium (thermal analysis grade), and gold and aluminium pans were supplied by Perkin-Elmer Corporation. Aluminium pans were also supplied by Du Pont.

DSC instrumentation and operation

A Perkin-Elmer DSC-2 differential scanning calorimeter was used. For measurements of the specific thermal capacity of gold and aluminium thermograms were obtained at a heating rate of 10 K min^{-1} from 240 to 323 K. A measurement frequency of ~ 45 readings min^{-1} and a sensitivity of 0.5 mcal s^{-1} were used. Calibrant and reference scans were made under the same conditions. The gold or aluminium pans were run as samples, against empty reference platforms.

For measurements of the latent heat of melting of indium, thermograms were obtained at the same heating rate between 400 and 450 K, again using a measurement frequency of ~ 45 min^{-1}, but employing a sensitivity of 1.0 mcal s^{-1}. The indium samples were run against empty pans of the same weight as the sample pans (within 0.05 mg).

Hardware

A number of ordinate output signals were available at the DSC at different voltages. The 10 mV filtered signal was taken from the DSC-2, amplified (gain 148) and fed to an ICL 7109 12-bit binary analogue to digital converter. This chip was operated with a bipolar differential input of 4 V. Signal averaging was carried out at the hardware level by using the chip as an integrating converter, integrating the signal over the sampling interval, which was around 1/7th of a second. The chip had a 13th (polarity) bit so that 13-bit resolution was achieved. The buffered output from the chip was fed to a parallel input–output board (PIO) of a Research Machines 380Z microcomputer, fitted with twin 5-in. mini floppy discs, with 56 K bytes storage in core. Two eight-bit ports on the PIO were used for the 14 lines from A to D to PIO. The chip was organised in such a way that information could either be taken out in two sequential bytes or as a parallel word of 14 bits. For simplicity in both software and hardware, data were led out in parallel. The data valid bit was a bit in one of the ports: it was tested by software. Connections to the PIO were soldered, not wirewrapped.

Data processing method

The method of data processing was based on that described by Richardson [2–4]. Measurements were made under identical conditions of a sample (Fig. 1a), a calibrant whose thermal characteristics are well known (synthetic sapphire, Fig. 1b) and a reference (a pair of empty DSC pans). The horizontal regions (A and G) of such traces, before and after heating, correspond to the steady signal under isothermal conditions. The method consisted in aligning the initial and final isothermals of the digitised calibrant and reference traces, subtracting reference from calibrant on a point by point basis, and dividing each reading by calibrant mass. The ordinate values thus obtained were proportional to calibrant specific thermal capacity. The temperature axis was corrected to allow for both static and dynamic effects [3], and the area under the normalised traces calculated using the trapezium rule. Using literature data for the specific thermal capacity and enthalpy of sapphire, a calibration constant was calculated to convert area measurements directly into heat units ($J\ g^{-1}$). The processed calibrant data and calibration constant were then written to disc. The sample and reference data were processed in an analogous manner to obtain ordinate values/mg sample and the area under the normalised trace. Using the processed calibrant data and literature data for the specific thermal capacity of sapphire, these values were converted into thermal units. The end result was a three-column file listing corrected temperatures, and the corresponding specific thermal capacity and enthalpy of the sample. This file was also written to disc.

Software

A number of computer programs were developed to handle the acquisition, processing and display of data, and results (Fig. 2). Only two of these will be dealt with in any detail. Programs were written in BASIC using Research Machines BASIC interpreter (DBAS9 version 3.0B and later versions).

An assembly language routine, READMAD.COM (Read Mean from Analogue to Digital converter), was patched onto the BASIC Interpreter to handle the data acquisition from the DSC machine. Operation began in a companion BASIC program, READMAD.BAS, which requested values of various machine parameters, sample and pan weights, the frequency at which readings were to be stored, and the total number of readings to be taken, all of which were later put out to disc as headers to the data set. The program then passed control to the patched routine READMAD.COM carrying down with it the required number of points. After a specified interval, transmitted earlier to READMAD.COM via a POKE from the BASIC program, and based on the required frequency for returning numbers, the mean reading during that interval was calculated and stored in core, occupy-

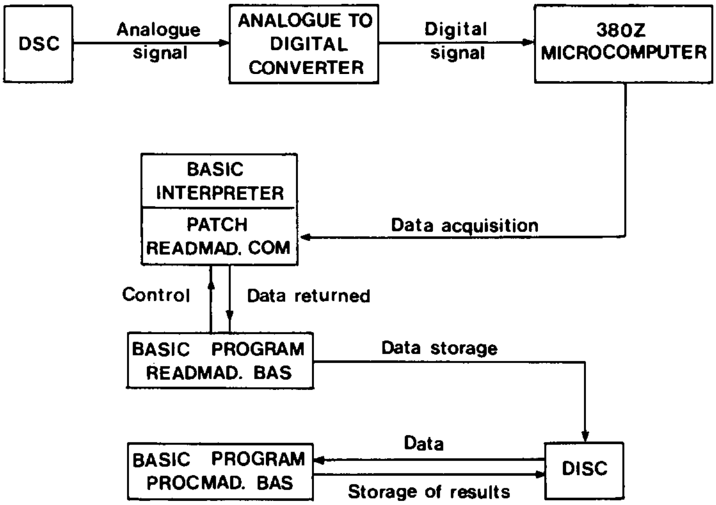

Fig. 2. Schematic diagram showing data flow.

ing two bytes/number. Since the chip cycled seven times a second, the accessible time interval was 1/7th of a second upwards. So far measurement frequencies of ~ 45 and ~ 60 min^{-1} have been used. When the requisite total number of readings had been obtained control returned to READMAD.BAS. The experimental setup was passive, that is, the microcomputer exercised no control functions over the DSC. Heating of the calorimeter was commenced when around 20 readings had been taken, so that the data set began with a steady initial reading corresponding to the initial isothermal. Readings were stopped some time after the final isothermal had been reached. The data stored in core was put into an array and the take-off point (A, Fig. 1, where heating commenced and the isothermal reading changed) was found. The data were displayed on a TV screen, indicating the take-off point. Excess points at the start of the data were deleted, leaving an initial isothermal of exactly five points, and the remaining data written to disc as a single file of ordinate values occupying typically 7–10 Kbytes. The abscissae could be calculated later when required, since the indicated initial and final temperatures were known, as well as the heating rate and frequency of reading. All this information was contained in the headers to the data set.

Another program, PROCMAD.BAS, was written to carry out the data processing. It implements in BASIC the methods of Richardson [2–4] described above. The program is a large one and it would not be appropriate to describe it in detail here. Listings of this or any of the other programs mentioned may be obtained from the authors (P.L.R.) on request. The processing is completely automatic: it requires no user interaction when finding isothermals, for example, and uses fitted equations to reproduce the necessary literature data on enthalpy and specific heat for the calibrant.

Other programs were also written to handle smoothing of calibrant and reference data, plotting of both raw data and results on either screen or printer, peak area (enthalpy) calculations and the modelling of the results. None of these will be described in more detail here. They are all, however, in routine operation.

RESULTS

The digitised output signal from the A to D converter to the computer was plotted against input voltage (from known standard voltages); a satisfactory linear plot was obtained. For a given input voltage some variation in A to D output signal occurred with time due to variation in laboratory temperature. This was not a serious drawback, because in normal operation the DSC runs lasted for not more than 30 min, much too short a period for significant differences in laboratory temperature to become apparent. In the normal method of operation described above, the absolute values of A to D output were not important, only the change with respect to the steady initial and final voltages at the initial and final isothermals.

The reproducibility of the equipment was tested in various ways. A computer program SHCOMP.BAS was written to compare experimental data for specific thermal capacity with quadratic interpolations to literature data for aluminium, gold, indium and water [8]. Although water is not normally used as a thermodynamic standard in DSC experiments, it was included because it was intended to use the instrument routinely to scan samples containing significant quantities of water, and it was wished to confirm that satisfactory results were obtained under these circumstances. Tests were carried out as follows.

(1) A number of DSC scans were made using the same sapphire sample in the same pan. Values of K, the area to enthalpy conversion factor, were obtained by processing these runs as calibrants. In any one day K varied little, usually less than 1%. However, the range of K values obtained if calibrant scans were measured over a number of days was ~ 5% (Table 1).

(2) DSC scans were also made using a single gold sample, run on different occasions against different references. These data were processed using calibrant runs on a single sapphire sample, but also run at different times against different references. The derived specific thermal capacity data for gold were compared point by point with literature data, as indicated above (Table 2). The mean differences over the whole scan for these data sets, obtained from SHCOMP. BAS, exhibited a range of ~ 10%. This figure was in line with expectations, since it was clear that opportunities exist for variation in all three runs associated with any single experimental measurement of the specific thermal capacity of a sample. For the sapphire calibrant

TABLE 1

Determination of area to enthalpy conversion factor, *K*, from DSC scans of synthetic sapphire

Sample: sapphire calibrant	DSC calibrant scan no.	Day	DSC ref. scan no.	Day	Area to enthalpy conversion factor *K*
SAP1	CAL1	1	REF1	1	1.77
SAP1	CAL2	2	REF3	2	1.68
SAP1	CAL5	4	REF7	4	1.76
SAP1	CAL5	4	REF3	2	1.78
SAP1	CAL6	4	REF9	4	1.75

there was only the opportunity of variation in two runs.

(3) DSC scans were obtained using two different aluminium samples (AL1 and AL2). The same reference and calibrant runs were used to process these data (Table 3, Nos. 1 and 2). Duplicate scans were run of AL1 and AL2, but in this case another reference and calibrant, common to AL1 and AL2, were used (Table 3, Nos. 3 and 4). The mean differences for either pair of samples AL1 and AL2 exhibited a range of ~ 3% (Table 3, Nos. 1 and 2 or 3 and 4). However, for all four runs taken together a larger range of mean differences (8.2%) was obtained. This increased discrepancy was due to the comparison of data using two different calibrants: if the four scans were analysed using the same calibrant and reference the range of total mean residuals was reduced again to ~ 3% (Table 3, Nos. 3–6).

(4) To check the reproducibility of latent heat of melting experiments, a number of DSC scans were made over the temperature range spanning the melting of indium (Table 4).

TABLE 2

Comparison of measured specific thermal capacity of gold with literature values [8]

Sample: gold	DSC sample scan no.	Day	DSC ref. scan no.	Day	DSC calibrant scan no.	Day	DSC ref. scan no.	Day	Mean difference (%) [a]
GOL1	G1	2	REF3	2	CAL2	2	REF3	2	−6.3
GOL1	G2	2	REF4	2	CAL2	2	REF3	2	−2.6
GOL1	G3	4	REF7	4	CAL5	4	REF7	4	4.3
GOL1	G4	8	REF8	4	CAL5	4	REF7	4	3.0

[a] % Deviation from literature value averaged over the effective temperature range scanned.

TABLE 3

Comparison of measured specific thermal capacity of aluminium with literature values [8]

Sample: aluminium	Log no.	DSC sample scan no.	Day	DSC ref. scan no.	Day	DSC calibrant scan no.	Day	DSC ref. scan no.	Day	Mean difference (%) [a]
AL1	1	A1	2	REF3	2	CAL2	2	REF3	2	−6.2
AL2	2	A2	2	REF3	2	CAL2	2	REF3	2	−4.2
AL1	3	A3	4	REF7	4	CAL5	4	REF7	4	−0.7
AL2	4	A4	4	REF7	4	CAL5	4	REF7	4	2.0
AL1	5	A1	2	REF7	4	CAL5	4	REF7	4	−1.0
AL2	6	A2	2	REF7	4	CAL5	4	REF7	4	1.9

[a] % Deviation from literature value averaged over the effective temperature range scanned.

TABLE 4

Comparison of measured latent heat of fusion of indium with literature values [9]

Sample: indium	Latent heat of melting ($J\ g^{-1}$)
IND1	28.8
IND2	28.9
IND3	27.9
Lit. value [9]	28.5

From the data in Tables 1–3 several conclusions were drawn. Calibrants run at different times gave different values for K. These were presumably related to small changes in experimental variables such as gas flow rate through the DSC machine, pan placement, sample and reference holder cover alignments, and the amount of solid carbon dioxide in the cold sink. Visual inspection of the traces showed a variation in "drift" (Fig. 1, level at G-level at A) and in the curvature of the traces (most apparent on reference traces) from day to day. For a series of related measurements taken over several days, therefore, the procedure adopted was to use a single calibrant and matched reference run to analyse all the other runs during the course of the experiment. In this way the precision of the measurements was maximised. The choice of calibrant run to use was decided by obtaining K values from each calibrant run, calculating the mean K, and choosing the scan which had the nearest value of K to this mean value. This maximised the accuracy of the measurements.

As a consequence of these conclusions, a similar method was applied to the data obtained from experiments to measure the latent heat of melting. Scans were made over the temperature range spanning the melting of indium, using three different indium samples of different weights. Three reference scans and six calibrant scans were also made, all on one day. All the calibrant data were analysed using a chosen reference, values for K obtained, and a mean K value calculated. The indium data were then processed against the same reference, using the calibrant scan that gave the closest value of K to the calculated mean K. Good agreement was obtained between the measured latent heat and the literature value (within 2%). Such good agreement resulted from two factors:

(1) accurate calibration, by choice of calibrant in the manner described above; and (2) the fact that the peak area is effectively measured with reference to a "local" baseline, removing reference variability.

In conclusion, both hardware and software have been successfully developed to allow DSC data collection, storage and processing so as to give sample specific thermal capacity and enthalpy, as a function of true temperature. This system is in routine operation. Comparison of experimental data for specific thermal capacities (aluminium, gold) and enthalpy (indium) with literature values showed that the system as a whole was capable of satisfactory reproducibility and accuracy, and these experiments suggested a method of operation to achieve this.

ACKNOWLEDGEMENTS

The authors thank Dr. M.J. Richardson for helpful discussions, as well as Mr. C.F. Jeffreys and Mrs. S. Stone for technical assistance. This work forms part of a research project sponsored by the U.K. Ministry of Agriculture, Fisheries and Food to whom our thanks are due. The results of the research are the property of the Ministry of Agriculture, Fisheries an Food, and are Crown Copyright.

REFERENCES

1 M.J. Richardson, in J.V. Dawkins (Ed.), Polymer Characterisation, Vol. 1, Applied Science Publishers, Essex, 1979, p. 205.
2 M.J. Richardson, J. Polym. Sci., Part C, 38 (1972) 251.
3 M.J. Richardson and P. Burrington, J. Therm. Anal., 6 (1974) 345.
4 M.J. Richardson, Plast. Rubber Mater. Appl., 1 (1976) 162.
5 U. Gaur, A. Mehta and B. Wunderlich, J. Therm. Anal., 13 (1978) 71.
6 A. Doelman, A.R. Gregges and E.M. Barrall (II), in R.S. Porter and J.F. Johnson (Eds.), Analytical Calorimetry, Vol. 4, Plenum Press, New York and London, 1976, p. 1.
7 J.G. Dunn, B.T. Sturman and W. Van Bronswijk, Thermochim. Acta, 37 (1980) 337.
8 Y.S. Touloukian and T. Makita (Eds.), Thermophysical Properties of Matter, Vol. 6, Specific Heat, Nonmetallic Liquids and Gases, IFI/Plenum, New York and Washington, 1970.
9 Perkin-Elmer DSC-2 Instruction Manual, Perkin-Elmer Corporation, Norwalk, Connecticut, 1978, pp. 3–12.