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A NOVEL DATA ACQUISITION, RETENTION AND EXAMINATION SYSTEM (DARES) FOR DIFFERENTIAL SCANNING CALORIMETRY

R.H.M. HATLEY and F. FRANKS

Pafra Ltd., Biopreservation Division, 150 Cambridge Science Park, Cambridge, CB4 4GG (Gt. Britain)

M. GREEN

Mike Green Consultancy, 149–151 St. Neots Road, Harwick, Cambridge, C133 7QJ (Gt. Britain)

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ABSTRACT

A low cost data-handling system for DSC is described. The system is more flexible than dedicated systems, while avoiding the problem common to many other custom systems of being unduly complex to use. The software uses a mouse-controlled menu system, so that operators need little knowledge of computer systems. The main feature of the system is that it has been designed for exploratory research into unknown systems. Hence, the software provides tools to assist the analyst in interpreting the data, but does not 'correct' data as is commonly the case with dedicated systems. The open structure of the software program enables it, with a suitable interface, to be connected to other research instrumentation.

INTRODUCTION

Differential scanning calorimetry (DSC) is a widely used technique for obtaining thermodynamic and kinetic information about materials as diverse as metals and proteins [1]. Within its limits, the Perkin–Elmer DSC-2 calorimeter is capable of producing reliable and accurate results, but its chart recorder output considerably restricts the potential of the instrument. There is always a trade-off between resolution and bandwidth. The bandwidth is selected by a range switch which, when set at maximum sensitivity and accurately zeroed to observe minor thermal events, makes it impossible to record any associated larger effects, or even unrelated effects of similar magnitude. Conversely, when set up to record a major transition, the sensitivity is too low for low amplitude processes to be detected. As a consequence, where two or more events of different amplitude are to be measured on one sample, multiple scans have to be run; this is time-consum-

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ing, and can also introduce errors owing to inter-run variation, which can originate from instrumental instability or from physical and/or chemical changes within the sample during the first heat/cool cycle.

More advanced calorimeters have dedicated computers which collect data and analyse the results. Such systems work well in routine tests but can be unduly restrictive in research applications, where a more flexible approach is needed for data analysis. The sales literature accompanying such instruments often describes features such as automatic smoothing routines and automatic baseline levelling. In fact, one publication on automation [2] states that the associated computer can provide "... the ability to produce a report without the operator even lifting a pen". For a well-defined quality control routine, this is adequate, but in calorimetric research applications such features can create a barrier between the researcher and the data. Automatic smoothing by computer may obscure genuine microscopic changes superimposed on larger transitions, and automatic levelling may mistakenly correct sloping traces that correspond to real specific heat changes. The consequence is that the user, presented with such 'corrected' data, may be unable to arrive at correct interpretations because important events have been obscured, or even removed. It should be the purpose of a computer to aid decision-making by an operator but not to attempt an analysis without reference to the operator [3]. A system should therefore present the user with the raw experimental data, but supply data-handling tools that enable him to select the best approach by which to analyse the results.

A further problem with some commercially available computerized data-handling systems concerns inherent software programming errors which can, under certain circumstances, give rise to ambiguous or misleading output. For example, the data collection system supplied with the Perkin–Elmer DSC-7 has no provision for the display of negative heat flows, such as would be associated with cooling a sample through a rubber/glass transition. Even experienced users have been confused by this fault, particularly in the presentation of their cooling scans, and this has led to the publication of data in a manner that cannot easily be understood by readers who are not fully conversant with the idiosyncracies of the particular instrument used [4].

Our own researches into improved freeze-drying techniques rely heavily on the detection and identification of both macro- and microscopic thermal transitions, and the correct interpretation of thermodynamic and kinetic data from DSC measurements. The DSC-2 produces excellent data but, as outlined above, data collection and analysis are impeded by the conventional chart recorder system. We therefore decided that an improved technique was needed; the attachment of a computer-based system was an obvious solution. The inflexibility and unsuitability for research applications of commercially available systems necessitated the design of a custom-made system. The principal requirements of the system were that it should be easy to use, should collect and store data in their original form, and should provide the user with tools with which to accurately interpret, analyse and display such data.

GENERAL OVERVIEW

The DARES system is based on the Amstrad 1512DD, an IBM-compatible PC. With a mouse-operated cursor, the user is able to select the required functions directly from on-screen menus. The computer is programmed to collect, record, store, display and print information from the calorimeter at the maximum possible instrumental precision and accuracy, and provide the operator with a range of tools for viewing, analysing and printing the data.

The use of a general purpose computer has a number of advantages over dedicated systems. The computers are produced in much larger volumes, and economies of scale therefore ensure a favourable price performance; a much wider range of equipment and software tools is available; and, additionally, the software can be written as an open system, which can be made to grow and adapt to changing needs. Further, collected data can be analysed on other computers away from the instrument. Hence, the DSC can be used more productively for its primary purpose of data collection.

DATA COLLECTION

Other custom data collection systems reported in the literature (e.g. ref. 5) usually ask the user to input complicated set-up procedures involving acquisition rate, acquisition channel(s), starting temperature, finishing temperature and scanning rate. This not only makes the system unnecessarily complicated, but also precludes the possibility of further flexibility once the conditions have been determined and the run commenced. With the DARES system, as described below, the user simply presses a key to start recording data and again to stop. Hence, the only constraints on data collection are those inherent in the DSC itself, and full flexibility of runs can be maintained.

CALORIMETER INTERFACE

The output from the DSC-2 to a plotter is fed through a gain switch network which reduces the signal level to a maximum of 10 mV. This renders the output relatively sensitive to electrical noise, e.g. the power surge when a laboratory refrigerator motor cuts in.

Much of this noise can be eliminated by taking a signal from the input side of the range switch, the signal here being of the order of volts. An additional benefit is that errors introduced into the data by the switch network itself are avoided. The exclusion of the switch itself is not important; since the computer collects data at maximum sensitivity at all times, the switch becomes redundant.

The signal is fed into the computer by means of an analog-to-digital converter (ADC). As speed is not important, it is possible to use a relatively low cost integrating ADC. The system here described uses a 12-bit ADC with a 30 Hz sampling rate.

In order to provide high sensitivity at the bottom end of the signal range, a switched gain pre-amplifier (1/10/100/1000) is used. To maintain ease of operation this is controlled by the computer, which dynamically adjusts the gain as the input signal varies. The choice of amplifier is of the utmost importance, as any variation in gain will produce discontinuities in the data.

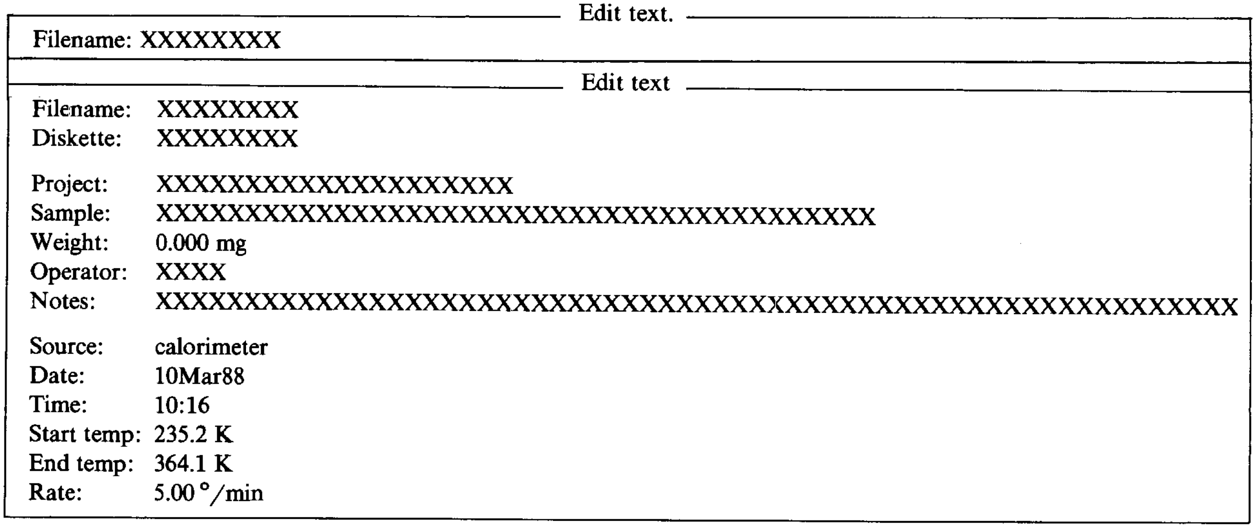
The thermal absorption/emission data must be stored as a function of temperature. The DSC-2 provides a 4-digit BCD output, and this is read with the aid of a standard digital interface.

As mentioned earlier, the ADC is capable of producing 30 readings per second. As it is necessary to record the reading only every tenth of a degree, the computer can average a number of readings whilst the calorimeter registers a particular temperature. This greatly improves the sensitivity for slow transitions while not adversely affecting the accuracy of recording of more rapid events that take place over small temperature intervals. Additionally, the heating/cooling rates are calculated directly from the temperature input, using the computer clock. Thus, a direct relative reading of the specific heat C is provided on the ordinate axis when the data are displayed. With the calorimeter/chart recorder system, as supplied, the accuracy of this scale is only $\pm 5\%$. For meaningful relative C determinations, repeated calibrations have to be made against a standard sample.

USER INTERFACE

DARES is mouse-operated and functions are selected by moving the screen cursor to the required position in the function menu and depressing the mouse key. On selection of "input", the data being fed from the calorimeter via the interface to the computer are monitored and echoed on a screen display. At any time, pressing a key will switch the computer from the monitoring mode to a recording mode, and a further press of a key will end recording. Once the calorimeter has been shown to operate faultlessly over the required temperature range, this selective recording permits the user to record only the data of interest, rather than having to check every run against the starting and finishing isothermals.

Having recorded the data, the computer displays a menu allowing the user to input information about the trace (see Fig. 1). This is attached to the trace



```
                               Edit text.
Filename: XXXXXXXX
                               Edit text
Filename:   XXXXXXXX
Diskette:   XXXXXXXX

Project:    XXXXXXXXXXXXXXXXXXXX
Sample:     XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
Weight:     0.000 mg
Operator:   XXXX
Notes:      XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

Source:     calorimeter
Date:       10Mar88
Time:       10:16
Start temp: 235.2 K
End temp:   364.1 K
Rate:       5.00 °/min
```

Fig. 1. An example of a "notes" screen. The upper window displays the field to be edited. The lower window contains the user variable and fixed data information. This information is used in all subsequent operations (e.g. area calculations), and input error is thus eliminated.

when it is stored on disk, and printed out whenever a hard copy is made. Next, the computer displays the data at maximum sensitivity and the operator may, if desired, store the results on diskette or use the tools provided (see next section) to help analyse the data. Any changes made to the data before writing to disk will also be recorded alongside the data, and if the trace is called up in future, the drawing will show these features. However, changes to the display do not alter the recorded data points themselves ; these are still in the raw form, as received from the calorimeter. Hence, if the raw data are subsequently required (e.g. for analysis of, or comparison with a different event) they can still be viewed by simply cancelling the display functions.

ANALYSIS TOOLS

The package provides a number of tools for the analysis of traces, both individually and in conjunction with other traces. Although it is beyond the scope of this report to explain all the tools in detail (they are summarized in Table 1), some are described below, in order to provide an insight into the versatility of the system.

The computer can zoom in on any section of the trace and enlarge it as required. As data are always stored to maximum precision, it is possible to observe both minor and major thermal effects from a single scan. Hence, the operator needs to spend less time collecting data and has more time for their analysis. The benefit becomes clear from the example study of the effects of freezing on a sucrose solution, the aim of which was to obtain information on its freeze-drying characteristics. The macro trace, shown in Fig. 2, can be used in conjunction with the area measurement facility to calculate the amount of unfrozen water when the solution has been maximally freeze-con-

TABLE 1

Major features available within the program; selection is from menus with the aid of a mouse

Visual aids	Calculations	Output facilities	Input/edit facilities
Extrapolate line Scale display Mark transition temperature Overlay traces Level trace	Area calculation Transition temperature Slope gradient Differentiate (any order) Subtract traces Average traces Divide traces	Print graph as displayed Print-out of data Output to disk as ASCII file Print index of disk contents Backup disk Delete files Write calorimeter data to disk Write edited data to disk	Take data from calorimeter Input stored file from disk Edit user variable fields

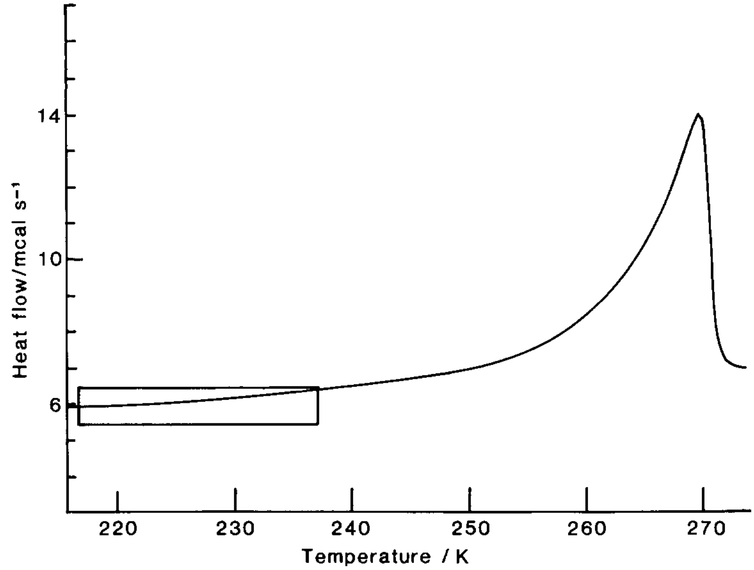


Fig. 2. The complete melting trace of a frozen sucrose solution, subjected to a typical freeze-drying process.

centrated w_g'. Zooming permits observation of the low-amplitude glass transition at the temperature of maximal freeze concentration T_g', shown in Fig. 3. The importance of these two measurements in the optimization of freeze-drying is discussed elsewhere [6].

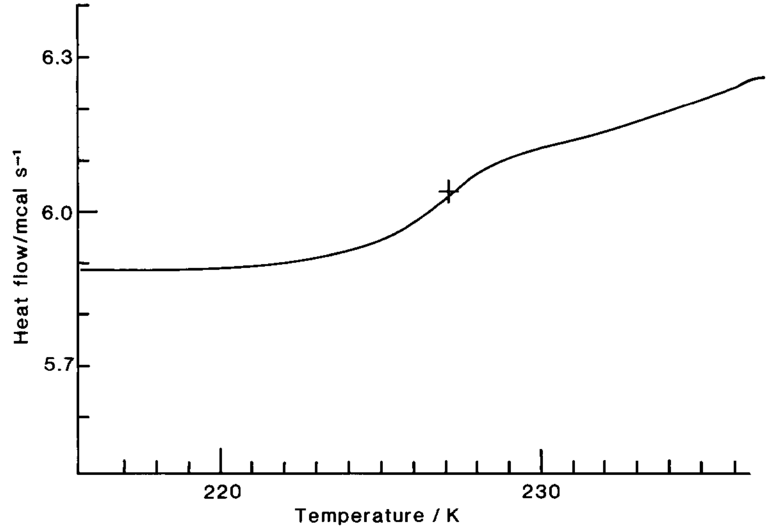


Fig. 3. An expansion of the portion within the rectangle in Fig. 2. The glass transition at 227 K can be clearly seen. This T_g' value is of critical importance in freeze drying; to obtain a consistently optimal product, primary drying must be carried out below this temperature [6].

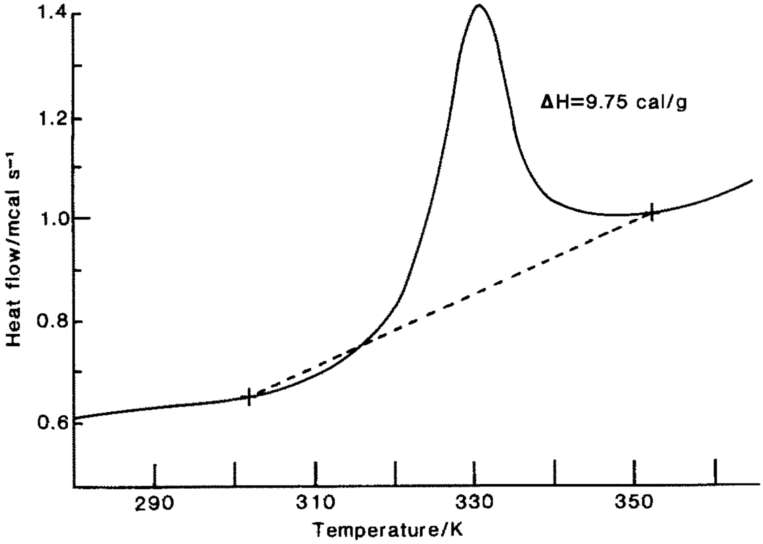


Fig. 4. Area measurement between two temperatures (the method used with most commercial systems). It is apparent that the value obtained is only approximate. In fact, a negative area is measured below 315 K.

Area calculations are under the full control of the operator. The computer calculates the area between the experimental trace and a base curve (line) drawn through five or fewer user-defined points. Most dedicated systems

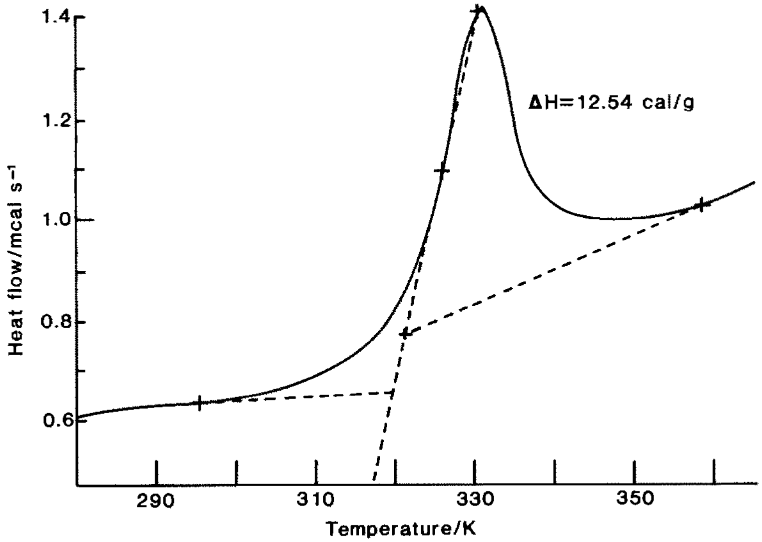


Fig. 5. DARES area measurement of the trace shown in Fig. 4, but with four user-determined points. Allowance is made for the large ΔC. Area measurement is no longer an approximation.

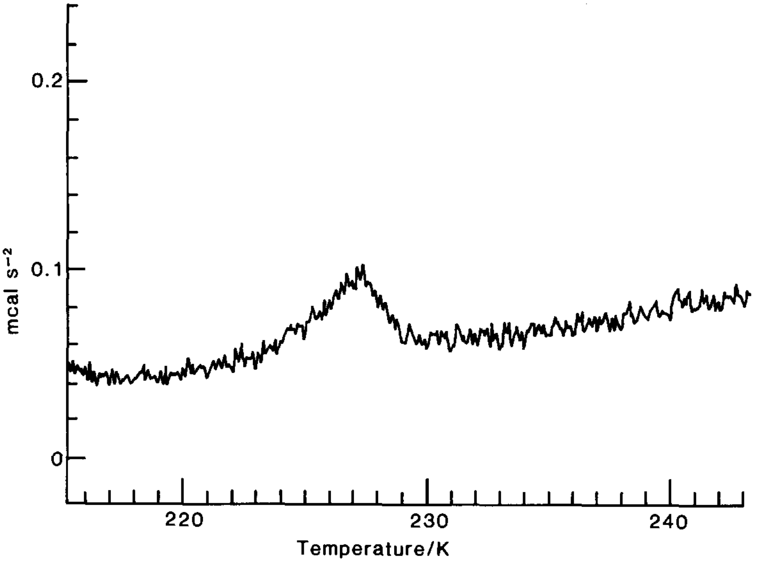


Fig. 6. A first derivative of a heating scan. The peak corresponds to a second order transition on the original trace.

only allow measurement of the area between the trace and a line defined by two points marked on the trace. Although there is no general agreement on the most accurate way of measuring enthalpy changes [7,8], it is clear that the latter method is inaccurate, particularly for enthalpy changes which are accompanied by a large ΔC (Figs. 4 and 5).

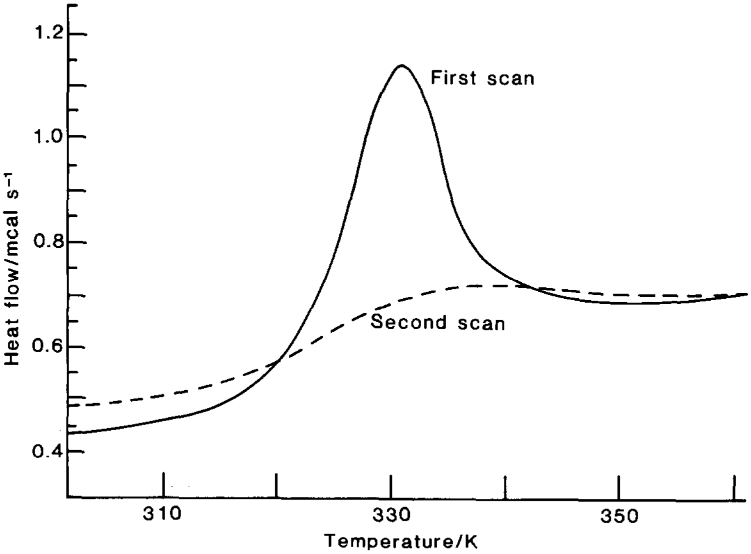


Fig. 7. The overlayed traces obtained on the first and second heating scans of a product expected to show a second order (glass) transition. The implications are discussed in the text.

Instrumentally skewed traces need not be discarded, but neither are they automatically levelled. Instead, the operator can use the level function, to level the line to any desired degree. Usually, this is done relative to some known standard, so that any baseline slope reflecting a genuine $C(T)$ effect is retained.

The first derivative is a useful indicator of the presence of minor transitions, aiding the user in the detection of minor thermal events hidden in the original trace (Fig. 6).

DARES also provides a number of functions to assist in comparisons of successive traces. These functions include the overlaying of traces on the screen, signal averaging, and subtraction and division of traces. The most effective way to observe the relationship between two traces is to display both together on the screen. Any differences (or similarities) soon become apparent. An example is given in Fig. 7, which shows the first heating scan for a freeze-dried product; overlayed is the second heating scan for the same product. From the first trace, inspected in isolation, it would appear that the primary event at 327 K is an endotherm, but when the first trace is compared to the second, it becomes immediately apparent that the thermal event was in reality a glass transition with a high degree of stress relaxation.

DATA STORAGE AND OUTPUT

While storing data in their original form goes a long way towards making the most effective use of experimental runs, the user is given much greater assistance in managing results if his annotations are stored together with the original data. To this end it is possible for the user to recall, study or rework in depth the original data, and to store notes and amendments, made at any time, alongside the original data.

The data are stored in compressed form and take up a small amount of disk space: it is possible to store 50 or more traces on one 360 K diskette. The software also contains the facility to convert such compressed data into a sequential ASCII file which, in turn, allows its importation into most standard graphical and statistical packages.

BENEFITS

There are many benefits associated with the flexible approach to data collection and analysis described in this article:

- improved sensitivity and accuracy compared to chart recorder output,
- much greater flexibility than is provided by most dedicated computer systems,
- the user requires no knowledge of computers,

— no complicated set-up procedures are needed for data collection,
— the operator is in control of the instrument throughout the experimental run.

We have reported here on the attachment of DARES to a Perkin–Elmer DSC-2. However, the versatility of the program and system enable it to be easily adapted for connection, via a suitable interface, to other types of research instrumentation.

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