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AUTOMATION OF THE PERKIN-ELMER DSC 2*

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ABSTRACT

With help of the interface system TRIFACE[1] we are able to control the DSC 2, to read its displayed temperature, and to measure the heat flow without any hardware modification. Our software allows simultaneous measurements of all quantities as well as efficient and versatile data analysis and representation. With a high accuracy digital multimeter the reproducibility and the resolution of the DSC measurements have been improved.

INDRODUCTION

Normally, the DSC 2 is either controlled manually or with an old Tektronix[2] computer. There are two problems with these methods : First, it is necessary to continually supervise the machine to carry out the measurements. Secondly, extensive data analysis and graphic representations are not possible. To avoid these disadvantages we have developed an interface system to control the DSC with any computer including a RS 232 interface - an interface which is spread widely. The control and analysis software has been written for an ATARI ST computer because of its excellent graphic possibilities and its low costs.

AUTOMATION PRINCIPLE

To measure specific heat capacity or heat of transition with help of a scanning calorimeter, heat flow, temperature, and time must be measured. The heat flow measurement was carried out using a 6 1/2 - digit multimeter (Fullscale 0.2 or 2 V) by measuring the recorder output signal of the DSC 2. The interface system TRIFACE communicates via IEEE-Bus with this digital multimeter. The DSC module of the interface system copies the BCD-coded temperature display from the DSC 2 (outlying connector) into the interface which transfers a decimal-coded temperature reading into the computer. Realtime is obtained using the computer clock. All three quantities are measured simultaneously because all measurements are triggered at the same moment.

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The DSC module already controls electronically the heat button as well as the hol and cool buttons. But until now, the switches controlling range, rate and outer tempe rature limits had to be adjusted manually. In the future, these relevant switches shoul be replaced by a relay module and should be controlled by the computer. Furthermore the potentiometers which determine the signal offset voltage (Zero) and the slope o the baseline (Slope) should be replaced by DA-converter modules. Both the relay module as well as the DA-converter module can be obtained with the interface system

To describe an actual measurement, I will start with the first measurement step Here, the program records the isothermal behaviour at the starting temperature. The following heating or cooling sequence ends when the final temperature is reached. Then the program records the relaxation towards the thermal equilibrium as well as the equilibrium isothermal behaviour. All measured data are plotted directly on the screen The measurements can be interrupted at any time. At the end the isothermal background of the measurement is subtracted. The isothermal background correction is calculated using two linear fits of the starting and the final isothermal behaviour. These fits deliver the isothermal voltages of the starting and final times. Investigations have shown that this procedure leads to the best results. To save on storage capacity, the data are averaged to such an extent that every 0.1 degree one value is stored. This resolution is identical with the resolution of the temperature display. Characteristic data about sample material, sample pans, the DSC settings, as well as date and time of measurement are stored within the same file. In contrast to other software available for the DSC 2, the user can at any time read the original data directly for further analysis.

Up to ten measurements can be made and stored automatically in one cycle in such a way that absolutely no manual intervention has to be performed during the whole procedure. Presently, the system does not automatically select heating and cooling rates On the other hand the program can set a waiting time between 0 and 9999 minutes in addition to the normal equilibration time and the accumulation time of the isothermal behaviour. Therefore, one can heat or cool e.g. a glassforming polymer sample towards a fixed temperature, in order to anneal it for different time period. In this way, up to ten scans can be made even during the night or on a weekend to study the influence of different annealing times on the glass transition.

SOFTWARE[1]

The control and analysis program has been written with help of the GFA–BASIC[2] developement software. It includes two pull-down menus, one for measurement and one for analysis, and is supported by GEM. The program starts to ask for date and time and with the request to turn on all necessary instruments. Then the program sets

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all instruments into the right operating conditions and the measurement menu appears indicating that the computer asks for the user's intervention.

Measurement Menu

One selectable menu title named "floppy" can be used to make directories, delete files and carry out other disc handling tasks. Another menu title, named "DSC- direct", includes the menu entries "heat", "hold" and "cool". With these subroutines you can heat or cool to any temperatures within the outer temperature limits.

The menu title "measurement" includes four menu entries. The entry "isotherm " gives you the advantage to watch the isothermal behaviour of the sample. In this way you can check whether the calorimeter is in equilibrium or not when you want to start a measurement. Furthermore, you can observe isothermal long term relaxations and store the accompanying data. The entries "empty", "reference" and "sample" lead to the subroutine which measures either empty pans, or a reference material (sapphire, indium, etc.), or any other sample material. The results of these measurements are stored in three different folders to make it easier for you to find a certain file in the future. In all three cases a dialog box first appears. Then you have to enter the name and mass of the sample, the temperature interval, the mass and the type of the pan, the DSC- settings etc. Incorrect inputs are ignored and all accepted inputs can be changed easily because all dialog boxes are GEM applications.

The menu title "analysis" in the measurement menu shows three entries. If the entry "c_p" is selected the user must first select a measurement with an empty pan and then the appropriate measurement of the sample. Now both data sets are substracted and a correction of the different pan masses is calculated. Then the user can decide whether the results should be multiplied by a single temperature-independent correction factor (determined e.g. by an indium measurement), or by a temperature-dependent correction factor. In the latter case a chosen measurement on a sapphire sample is read from the disc and compared with the true specific heat capacity of sapphire. This procedure leads to a temperature-dependent correction factor. The final results are displayed on screen and can be stored. If the entries "peak" or "plot" are selected, the analysis menu bar is shown on the screen.

Analysis Menu

In this menu the peak area e.g. of a melting transition can be calculated if the menu title "peak" is selected. Using the mouse and the picture of the measured peak (which is shown on screen), the user can select four temperatures $T_1 « ... « T_4$, namely two temperature values on each side of the peak at the baseline (fig.1). The program calculates two straight lines, one between T_1 and T_2 and one between T_3 and T_4. At first, these two fits lead to two heat capacity values at T_2 and T_3 , which are used to determine a linear baseline and the peak area between this baseline and the measured data. Secondly these two fits are used to calculate a steplike baseline which take into

account a steplike behaviour and a change in slope of the heat capacity after and before the transition. It is an iterative procedure which assumes that during the thermal event the sample consists of a mixture of converted and not yet converted material. The degree of conversion determines the change of the value and the slope of the baseline. This procedure is well known (refs. 1-2) in literature.

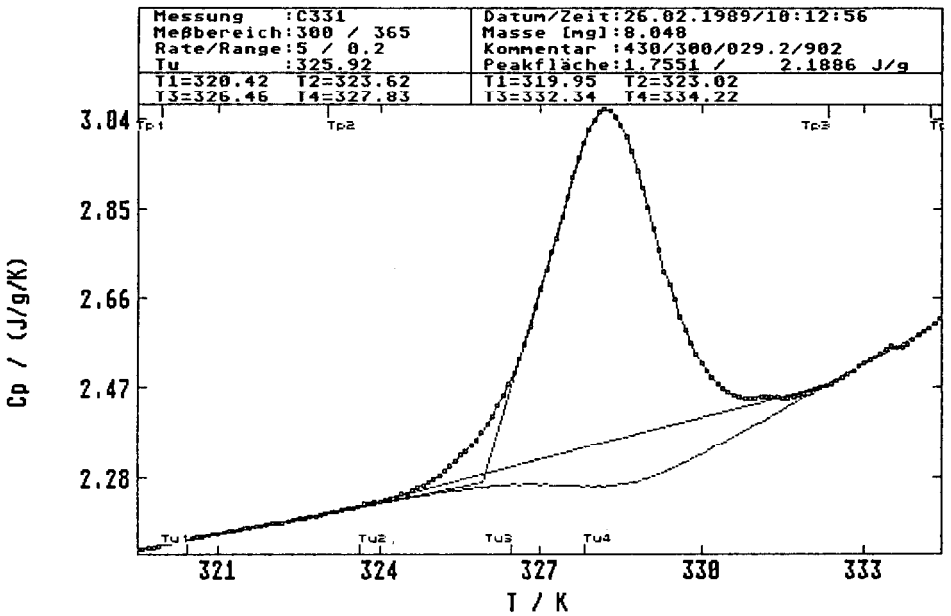

Fig. 1. Screencopy showing the baseline construction and the onset temperarure.

To determine the transition temperature, the user must select the menu title "T_u". Using the mouse and the measurement curve (which is shown on the screen), four temperatures must be again selected. T_1 and T_2 are located on the pretransition baseline and T_3 and T_4 are located near the point of inflection at the flank of the peak. The program calculates two straight lines and the temperature at which they intersect. This so-called "onset temperature" and the straight lines are displayed on screen. Fig. 1 shows the two different baseline constructions and the straight lines of the onset temperature. Within the header you find the values of the two transition heats, the onset temperature as well as the the temperatures T_1...T_4, which are also marked in the picture.

To analyse small details of the measurement curve, the user can choose any part of it by selecting the menu entry "zoom". The user can choose an upper left point and a lower right point with two "mouse clicks". This part of the measurement curve is zoomed on the whole screen.

I want to finish the description of the software by noting that every picture shown on screen can be transferred onto paper with a hardcopy routine. Furthermore, screencopies can be stored on disc. With a proper text-system program you can incorporate the pictures directly into a text just as it is done here.

RESULTS

During our measurements we did not use any temperature regulator to control the temperature of the metal block surrounding the pan holders. Only cold water cooling is used. In fig. 2 some measurements on a sapphire sample are shown to demonstrate the reproducibility and the "noise". Some relevant information can be seen within the header. All measurements were done between 320 K and 460 K. The specific heat capacities of all runs are calculated with one and the same measurement of empty pans. One of the five measurements is taken as calibration measurement (zero line in fig. 2) and the true specific heat capacity of sapphire is substracted from all measurements. The reproducibility as well as the scanning "noise" were always better than +/- 20 µW. The isothermal "noise" is better than +/- 2 µW. These values are three times as good as the values that can be attained with this machine before automation.

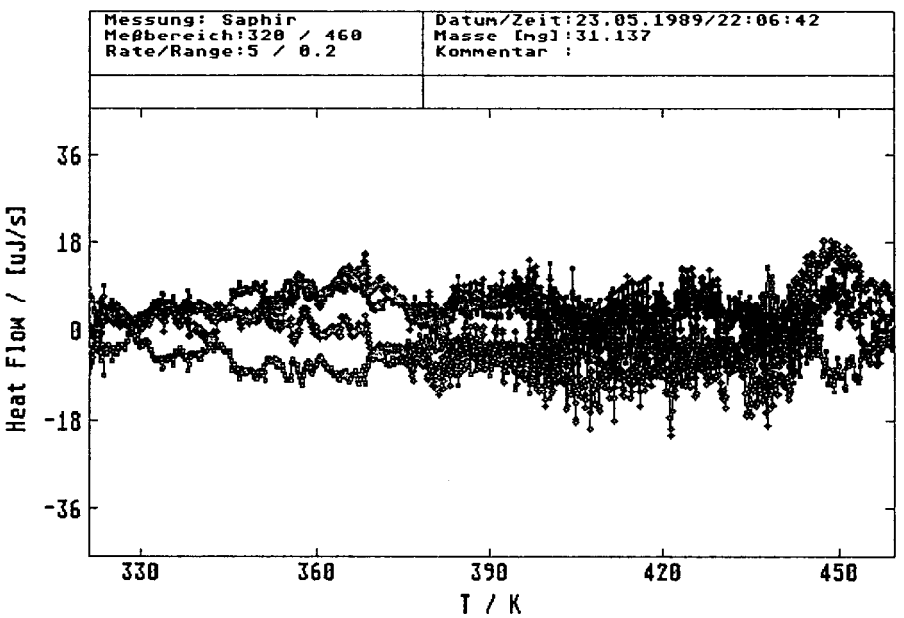

Fig. 2. Screencopy showing the reproducibility and the "noise" of five measurements done in one cycle during night. The zero line corresponds with one of the measurements.

CONCLUSION

With the described software and the developed interface one can measure specific heat capacity with an improved reproducibility and a reduced "noise". The automatic measurements require very little user supervision. After completing a measurement it takes only a few moments to calculate the specific heat capacity, heat of transition, and transition temperature. This fast speed is obtained even though the measurement of empty pans, the measurement of a reference material, and the different weights of pans are taken into account. The control and analysis program is easy to use. The DSC measurements as well as the ensuing data analysis can be handled as a routine matter by any laboratory assistant.

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