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THE EVOLUTION OF DIFFERENTIAL SCANNING CALORIMETRY: A REVIEW

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ABSTRACT

The evolution of the popular and important techniques of differential scanning calorimetry (DSC) has now progressed through two decades of development and application. DSC has brought to the scientific community many time-saving analytical procedures as well as the ability to accurately assign many thermophysical properties of materials.

The development of the technology associated with the construction and manufacturing of DSC sample holders and microfurnaces has been a continuous one. However, the ever-increasing degree of computerization of the DSC technique has led to improved hardware performance and awesome data storage, manipulation, and reduction capabilities.

This paper will review the development of the differential scanning calorimetric technique from the early 1960's to its present state.

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Thermal analysis in general and Differential Scanning Calorimetry in particular, is one of the fastest growing analytical techniques. Applications are found in virtually every industry. DSC is used for basic research and quality assurance. This wide-spread growth and acceptance of the DSC technique is a result of the evolutionary development of both the analytical instrumentation and data handling devices. The instrumentation can perform the most demanding applications and yet are easier for laboratory personnel to use.

The development of DSC is particularly impressive. Since there has been considerable confusion in the literature, it should be noted that DSC, as referred to here, is of the thermal null, direct differential power messuring type. The power compensation DSC was introduced by the Perkin-Elmer Corporation in 1963. The Perkin-Elmer DSC-1 enjoyed immediate success in studies previously possible only by classical calorimetry, such as the determination of specific heat, as well as for quantitative studies in established DTA applications. In addition, because of the low thermal mass (approximately 1 gram) of the dual furnaces used in the Perkin-Elmer design, the sample temperature could be rapidly changed to higher or lower levels or maintained in precise isothermal control of better than a few hundredths of a degree. Such control and flexibility in the manipulation of the sample temperature made possible applications unique to the power compensation design. One such application which remains unique to the power compensation DSC is the study of the isothermal crystallization of polymers.

A distingushing feature of a power compensation DSC is the presence of two independent temperature controlling circuits, as shown in Figure 1. The "average power" circuit controls the preselected temperature program rate while the "differential power" circuit adjusts the power balance in order to compensate for temperature differences that arise between the sample and

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reference furnace chambers due to thermal activity of the sample material. Moreover, the power compensation design consists of an independent sample furnace and reference furnace. This dual furnace design allows for the differential power compensation between sample and reference chambers. By contrast, heat-flux type DSC's consist only of an average power circuit and a single, large mass furnace.

For all its virtues, the early power compensation DSC did have its design limitations. Furnace construction was complex, consisting of 15 individual components including a stainless steel body and support, a platinum resistance temperature sensor, a michrome heating element, several thin layers of mica for electrical insulation, and layers of gold foil for thermal diffusion. All of these components were mechanically crimped together in a very tight sandwich. For chemical, physical and mechanical reasons, this configuration limited the useful upper temperature range to 500°C.

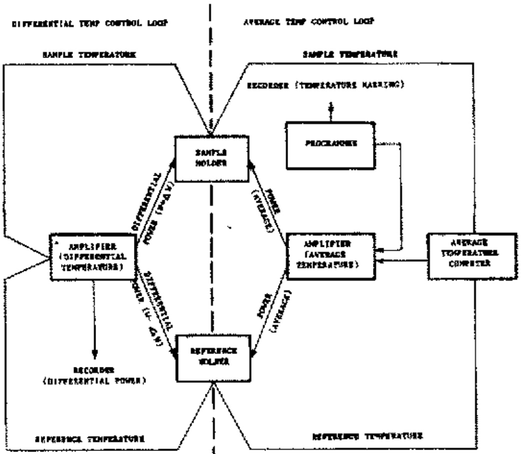

Figure 1. Block diagram, Perkin-Elmer differential scanning calorimeter

In 1972, the construction of the dual furnace cells was extensively redesigned to consist of only 3 different materials; a platinum-iridium alloy for the body and support, pure platinum wire for both heater and sensor elements and pure alpha-alumina for electrical insulation. These components are joined together by electron beam welding, which provides a strong joint without adding extraneous material. This design provided improved performance while extending the upper temperature range to 725°C. In addition, the furnace cells are mounted in a massive aluminum heat sink which markedly improved cooling performance. The DSC sample holder design will cool from room temperature to -273°C in less than two minutes when using liquid nitrogen coolant.

This sample holder was first used in the Perkin-Elmer DSC-2, a top of the line instrument introduced in 1972. The DSC-2 featured unprecedented heating and cooling rates of more than 300°C per minute, near perfect baseline repeatability, sensitivity to 0.01 millicalorie per second, temperature accuracy to 0.1 C and calorimetric accuracy to 0.5 percent. As such, it remained the premier instrument in the marketplace until it was replaced by the DSC 7 in 1984.

Clearly, the next area requiring improvement was in data handling. Early DSC's used an analog recorder as the output device. Initial attempts of improving data handling used punched paper devices and desk-top calculator systems. These systems left much to be desired. The first major advance in data handling was the introduction of the Thermal Analysis Data Station (TADS) by Perkin-Elmer in 1980. (Figure 2) The TADS is a modular microcomputer consisting of a Central Processing Unit (CPU), Video Display Unit (VDU) and Alphanumeric keyboard. The CPU contains 64K of memory with an additional 32K available for graphics and user interactive command entry. Also included are two 5-1/4 inch double-sided floppy disk drives each having greater than 165,000 bytes of memory. One drive may be used for program storage and the other for data collection. Data is permanently stored on the floppy disk.

The VDU is a 12 inch monitor. The detachable keyboard contains the full ASCII characters as well as a separate numeric keypad for entering numeric data and a cursor keypad for interactive cursor routines. All programs make extensive use of the 48 user-programmable function keys for single keystroke entry of many program commands. While the TADS is fully programmable by the user in BASIC, the system is supported by an extensive standard software library (Table 1). The standard library contains programs to select operational parameters for the analysis, optimize the DSC curve, perform standard calculations and visually compare two thermal curves. In addition, to meet the growing areas of applications, a series of specific advanced calculation programs have been developed. Programs are available for the determination of the kinetic parameters, advanced peak analysis of complex heating and cooling curves, determination of the absolute purity of crystalline compounds, analysis of isothermal data, and the determination of specific heat. The TADS truly advanced thermal analysis into the computer age. The TADS can be used with either the DSC-4 or DSC-2.

TADS, DSC standard software library

MODIFY PARAMETERS	Displays and allows modification of the current program parameters
CONDITIONS	Displays and allows modification of the current set-up conditions
ZERO	Displays the current analyzer zero position
READY	Sets up the Graphics Plotter 2 for plotting during data acquisition
START	Begins data acquisition and storage
STOP	Allows for manual termination of data acquisition and storage
QUICK COOL	Terminates data acquisition and automatically cools the analyzer to the starting temperature
OVERRIDE T	Overrides the upper temperature limit during data acquisition
GO TO ANALYSIS	Activates the library of programs for analyzing data
GO TO SET UP	Activates the library of programs for setting up, acquiring and storing data
CONTENT	Displays the files currently stored on the data disk on the CRT
PLOT CONTENT	Generates a hard-copy printout of the files currently stored on the data disk
RECALL	Recalls and displays previously run data on the CRT
SAVE	Saves a data file on the data disk
DELETE	Deletes a data file from the data disk
RESCALE T	Rescales the temperature or time axis to user defined limits
SLOPE	Changes the slope of the curve displayed on the CRT
Y SHIFT	Shifts the curve on the CRT along the Y axis
RESCALE Y	Rescales the Y axis display on the CRT
NORMALIZE	Normalizes a curve with respect to its sample weight for easy comparison of different data sets
RECALL 2nd CURVE	Recalls a second curve to the screen for comparison with the first curve
COMPARE	Shades in the differences between two curves for simple visual comparison
SUBTRACT	Subtracts a second curve from a first curve and displays the difference
RESTORE ORIGINAL	Restores a curve to the screen as it was originally stored on the disk
T/G	Analyzes the onset, midpoint, and change in specific heat of a glass transition
DERIVATIVE	Calculates and displays the first derivative of any curve
PEAK	Analyzes peak area (ΔH), peak limits, onset temperature, and peak maximum of any peak
PLOT SCREEN	Generates a hard-copy printout of any screen display on the Graphics Plotter 2
PLOT CALC	Generates a hard-copy printout of any calculation currently displayed on the screen
OPTIONS	Displays a menu on the CRT of the currently active function key with a short description of each key
RESULTS	Displays the results of any calculations performed and permits a hard-copy printout of these results

Table 1

Most recently, the technique of DSC has been elevated to an even high pinnacle with the introduction of the DSC 7 in March, 1984. (Figure 3) The heart of the DSC 7 is the PE 7500 Professional Computer, a modular, high performance microcomputer. This computer features 32-bit performance for fast, accurate computing and data handling. Memory capacity is 1.64 Mbytes of Random Access Memory (RAM) and 32K of Read-Only Memory (ROM). Program and data storage consists of two double-density, double-sided floppy disk drives and a choice of either a 10 or 15 Mbyte hard disk for massive program and data storage. The PE 7500 has a full ASCII detachable typewriter keyboard enhanced through the addition of 32 user-definable function keys (shiftable to 64). Communication to and from the computer is provided by four integral RS-232C communications ports. Software-selectable communications permit the ports to be configured for baud rate, stop and data bits, and parity. An industry standard IEEE-488 interface is available as an option.

The PE 7500 can also be programmed in BASIC or FORTRAN, making the computer ideally suited for data acquisition from other laboratory instruments or as a general-purpose computer. General-purpose software programs for word processing, spreadsheets, and database management are also available.

All of the software for use with the DSC 7 utilizes a "soft key" approach. Soft keys, a recent development in the computer industry, are keys whose actions are constantly updated as the state of the system is changed. The PE 7500 uses 8 soft keys, which are located just at the base of the CRT screen. The function of each soft key at any time is identified by a color-coded menu of easy-to-understand prompts located directly above each key on the color CRT. When a soft key is selected, this menu is automatically updated, changing the action of each soft key to define the current state of the system.

For maximum productivity, the operating system used with the PE 7500 computer permits the system to be operated in a multitasking mode. This means that multiple instruments or tasks can be operated simultaneously and completely independent of each other. For example, an operator can run two DSC 7's simultaneously and completely independent of each other and at the same time plot out data; or a run can be in progress on one analyzer while results and calculations are performed on the data collected from another analyzer. Changing from one task to another requires only a single keystroke.

Power compensation DSC instrumentation has been advanced considerably during the past 20 years. However, just as impressive has been the advance in the development of its applications. It has been this growth in the use of DSC instrumentation and the need for sophisticated analyses that has driven the development of the instrumentation.

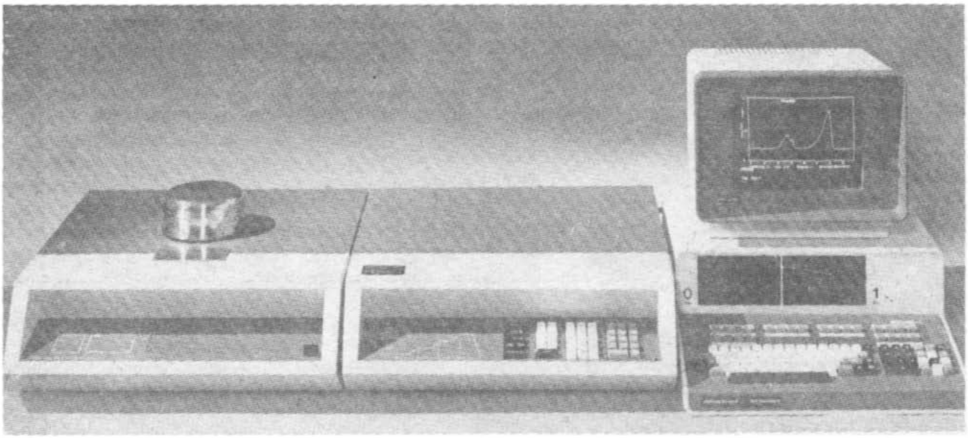

Figure 2. Perkin-Elmer DSC-4 Differential Scanning Calorimeter and Thermal Analysis Data Station

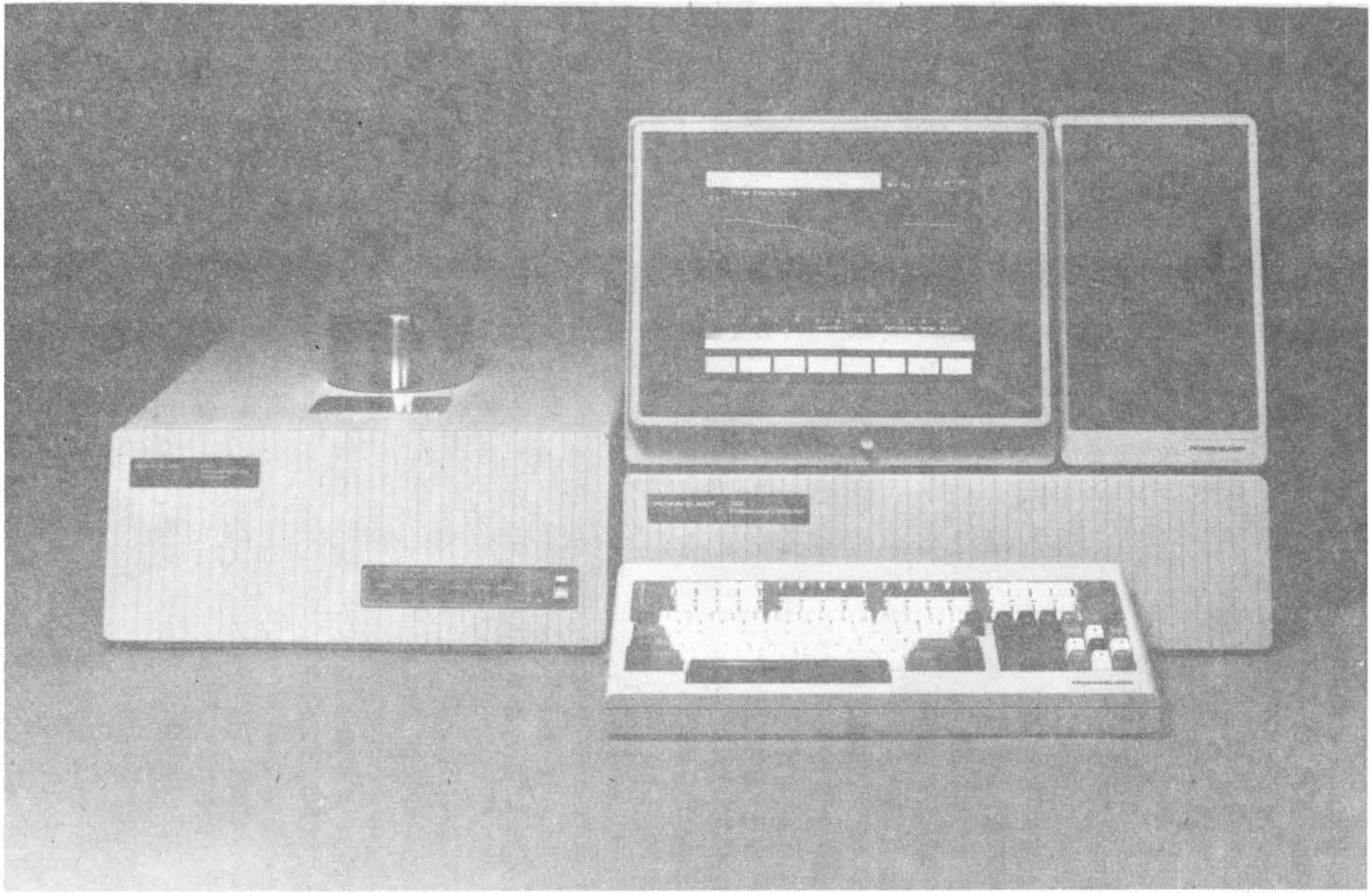

Figure 3. Perkin-Elmer DSC 7 Differential Scanning Calorimeter and 7500 Professional Computer