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A novel approach to precision controlled cooling of a Differential Scanning Calorimeter.

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Abstract

A system is described which introduces a cooling system based on a proportional liquid nitrogen control valve. This is driven directly from the 3 term P.I.D. output of the DSC controller which in turn is controlled directly from the Polymer Laboratories Limited software system.

The proportioning valve adjusts the amount of liquid nitrogen required by the DSC as determined by the P.I.D. control algorithm. By varying the nitrogen flow according to demand, absolute repeatability is ensured from run to run and a considerable saving in liquid nitrogen is achieved. Thus the DSC performs identically in heating or cooling mode.

1. INTRODUCTION

Traditional methods of precision controlled cooling use liquified gas as a refrigerant to provide a constant cooling effect. This is then offset by a variable heating effect controlled by a feedback control loop. The net heat transfer to or from the system is therefore actually controlled by varying the heating effect only.

The design discussed here controls both heating and cooling. This is done in a push-pull manner. When the feedback controller requests more heat, the cooling effect is reduced and vice-versa. The result is tighter control, more efficient usage of coolant and greatly improved ease of use.

2. METHODOLOGY

The system to be controlled is fitted with both a heater and a cooling jacket, Figure 1. A sensor measures the temperature of the system and relays this information back to a master temperature controller operating in a negative feedback mode. The master controller generates a power demand signal using a P.I.D. or a similar control method.

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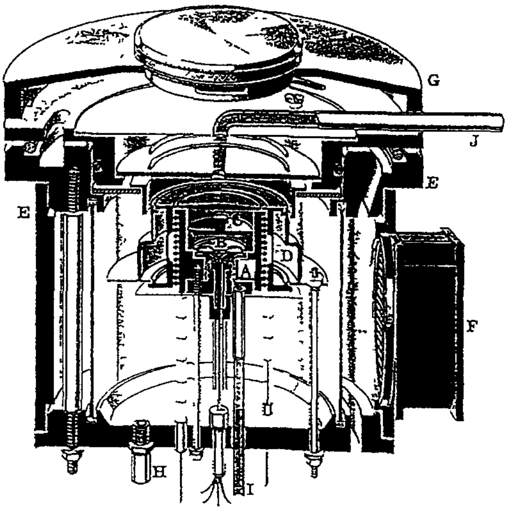


A SILVER CELL
B HEAT FLUX PLATE
C CELL LID
D COOLING CHAMBER
E OUTER CASING
F FAN
G OUTER COVER
H BLANKET PURGE
I PURGE GAS INLET
J PURGE GAS OUTLET

FIGURE 1

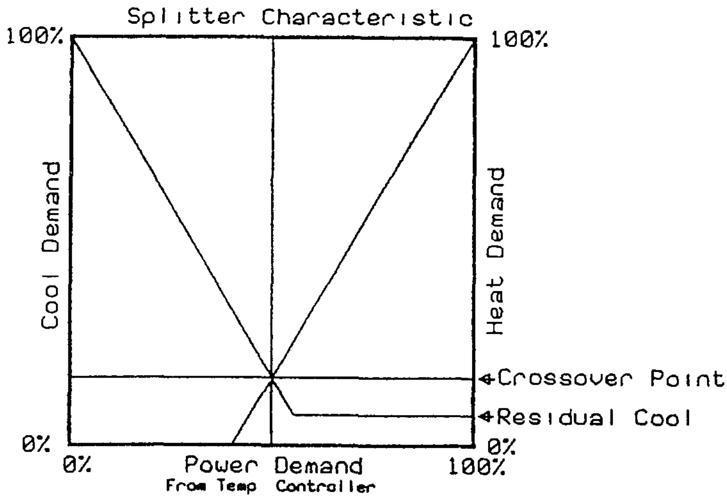


FIGURE 2

In this design, the power demand signal is divided electronically into a heating and a cooling band, Figure 2.

Heating is controlled by varying the power into the heater, typically by varying the current through an electrical heating element.

Cooling is controlled as follows:

The cooling effect used is the vaporisation of a liquid which has its boiling point below the temperature of interest. The coolant is stored in a pressurised reservoir and syphoned directly into the cooling jacket. At this point boiling occurs absorbing heat from the jacket. The egress of vapour is controlled at the jacket outlet. This generates a back pressure which in turn controls the ingress of coolant to the jacket. The coolant vapour egress is controlled by a fast response, variable gas control valve fitted with a flow sensor and local electronic controller This forms a gas flow controller which adjusts the gas flow in response to the power demand from the master temperature controller

It is worth noting that if the temperature of the jacket is very much above the boiling point of the liquid, the liquid will boil in the feed pipe In this mode, it is the vapour, which is at the coolants boiling point, which is responsible for the cooling effect.

The technique not only works well for either effect, heating or cooling, but by its very nature gives a very smooth transition between the two modes.

The coolant vapour controller is designed to pass a small flow of gas even whilst the system is in the heating mode. This ensures that the refrigerant feed pipework is itself kept cold Failure to do so allows the feed pipework to warm up during the heating phases. This results in a delay in delivery of the coolant when it's required. This in turn can cause instability in the control loop.

A key feature of the method is the provision of a "crossover" band, which smoothes the transition between heating to cooling by allowing moderate heating and cooling to be applied at the changeover point

EXAMPLE INSTALLATION

This describes a typical application of the cryogenic control system with the Polymer Laboratories Limited Differential Scanning Calorimeter equipment (PL-DSC).

The PL-DSC measurement cell, Figure 1, comprises a sensor in a controlled thermal environment The sensor takes the form of a thin metal plate, the heat flux plate, coupled to a thermocouple system. It measures very small energy changes in samples under test by detecting anomolies in temperature as the thermal environment is changed in a very precise and controlled manner.

The thermal environment is maintained by a heater wound on a silver block and surrounded by a cooling jacket. For accurate measurement, tight control of the thermal environment is crucial The temperature range is from -160°C to +770°C.

A schematic of a typical configuration is shown in Figure 3

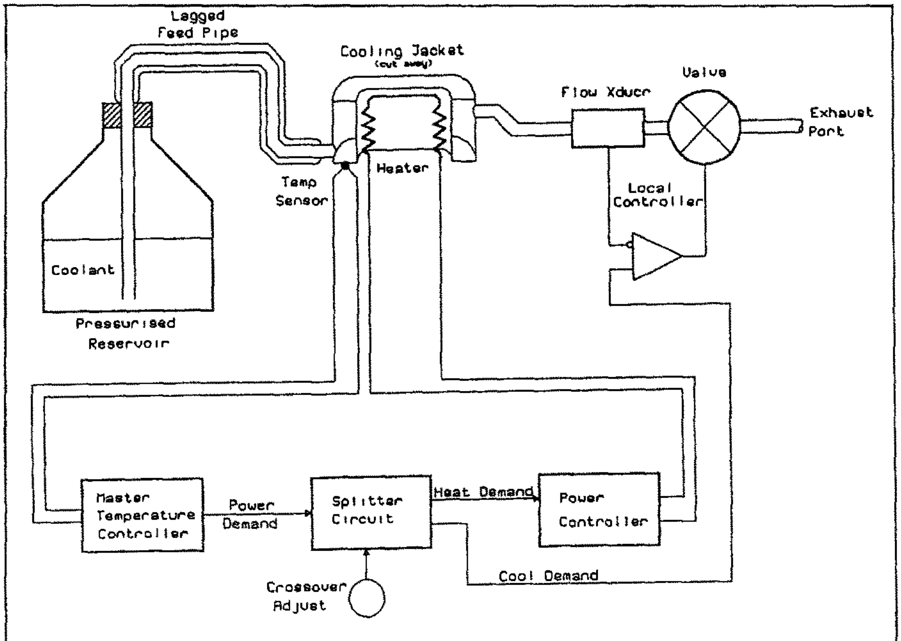
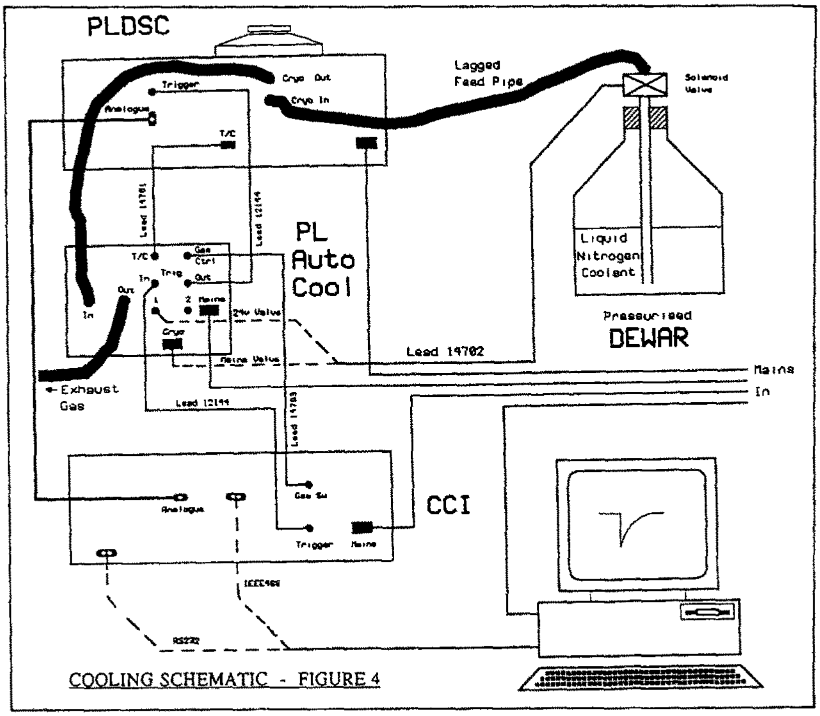


FIGURE 3



COOLING SCHEMATIC - FIGURE 4

The PL-DSC is designed for use with liquid nitrogen as the coolant. The master temperature controller used would be typically the PL-Computer Controlled Interface (PL-CCI), a custom built P.I.D. temperature programmer/ controller and data logger. It would work, however, with any generic P.I.D. temperature controller.

The liquid nitrogen is supplied from a dewar pressurised at 10 p.s.i. directly into the PL-DSC Cryogenic Import port, Figure 4.

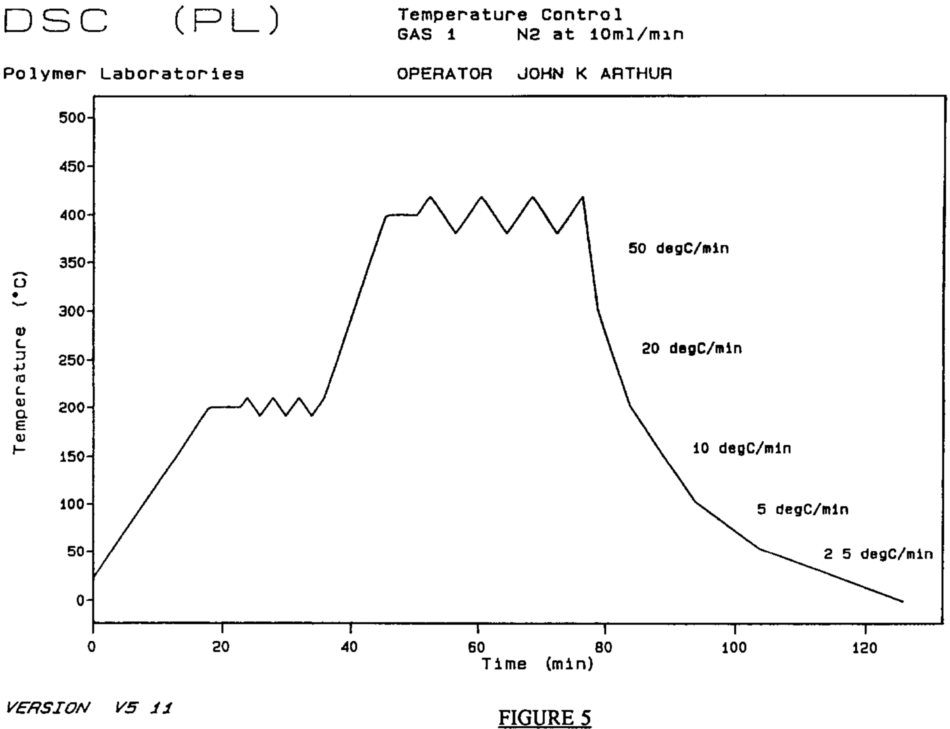


FIGURE 5

Figure 5 Empty pans were placed in the sample and reference positions. A complex heating and cooling profile was set up in the method and an output of real sample position cell temperature against time is presented. Points to note on heat up is no overshoot whatsoever at segment changeover points and knife edge precision of changeover from one segment to the next even on cooldown. The different rates covering much of the specified range are shown.

The feed pipework is kept as short as possible, preferably less than 0.5 metre and must be extremely well insulated over its entire length

It is normal for the system to be supplied with a convoluted vacuum jacketed supply tube.

The Cryogenic Output from the PL-DSC is connected to the Cryogenic Input of the coolant controller The length of this pipe is not critical and it need not be insulated. In fact it is essential that liquid nitrogen does not enter the cooling control valve. Unlagged output piping will therefore be of great help. About one metre is normally suitable.

The Cryogenic Output from the coolant controller may be ducted away as required but care should be taken not to restrict the flow significantly A loosely coupled duct is recommended if possible, or large bore tubing.

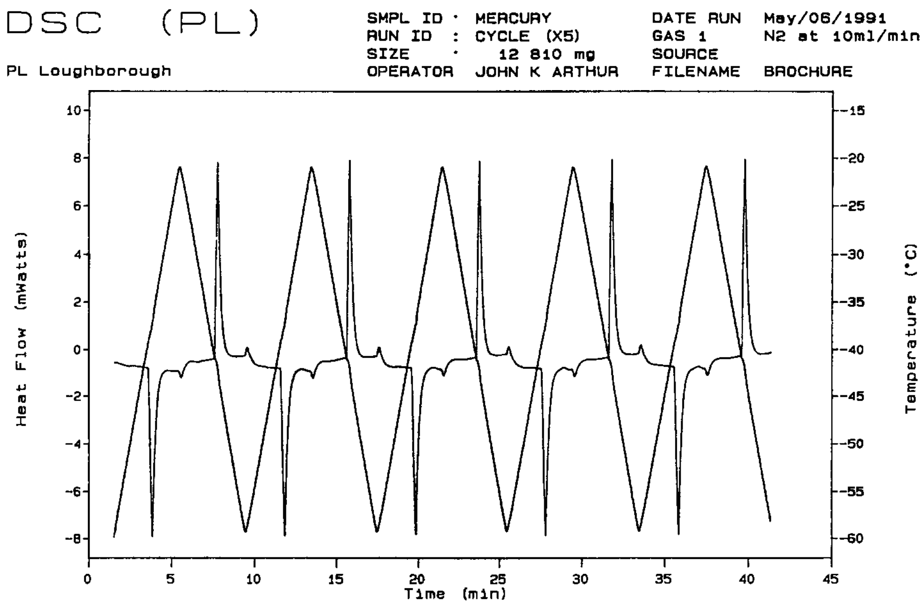


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FIGURE 6

Figure 6 This illustrates a cycle run on a sample of mercury encapsulated in a crucible. The crucible is heated and cooled at the same rate, 10°C/minute for five successive cycles. These are shown as a temperature against time plot and heat flow aginst time plot. Again the knife edge changeover is clearly evident.

The Control Valve and internal pipework are fitted with a small heater to reduce condensation and frosting. Also this ensures that liquid nitrogen does not enter the control valve. During protracted sub-ambient runs some internal condensation may still occur, however, drainage holes are provided to allow moisture to escape. Care should be taken to locate the unit where any such drainage can do no harm.

APPLICATION AND BENEFITS

A series of experiments are shown which illustrate the benefit and precision of the control system that has been discussed in this paper.

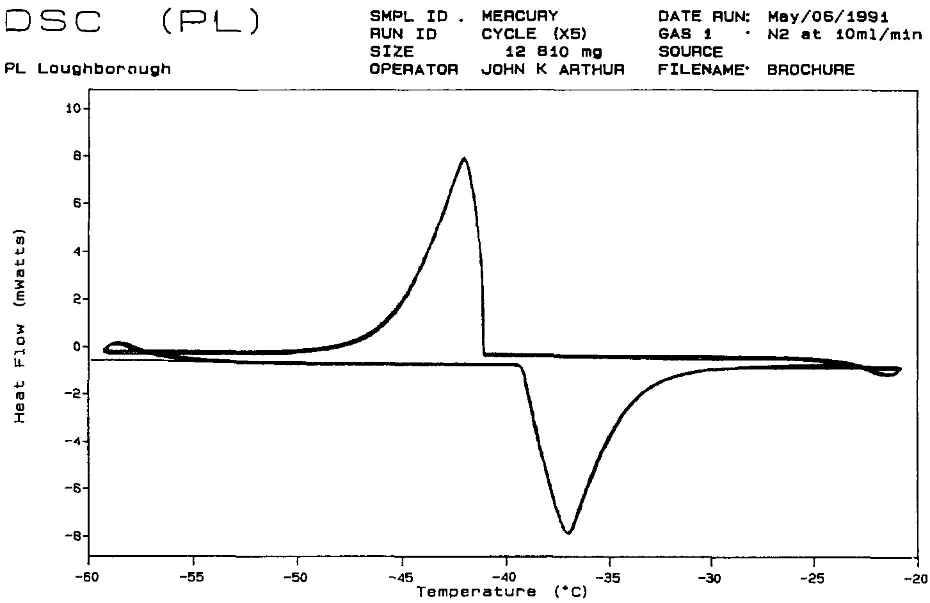

FIGURE 7

Figure 7 Shows the same data as Figure 6 but presented as a plot of heat flow against temperature. This clearly highlights the highly reproducible results possible

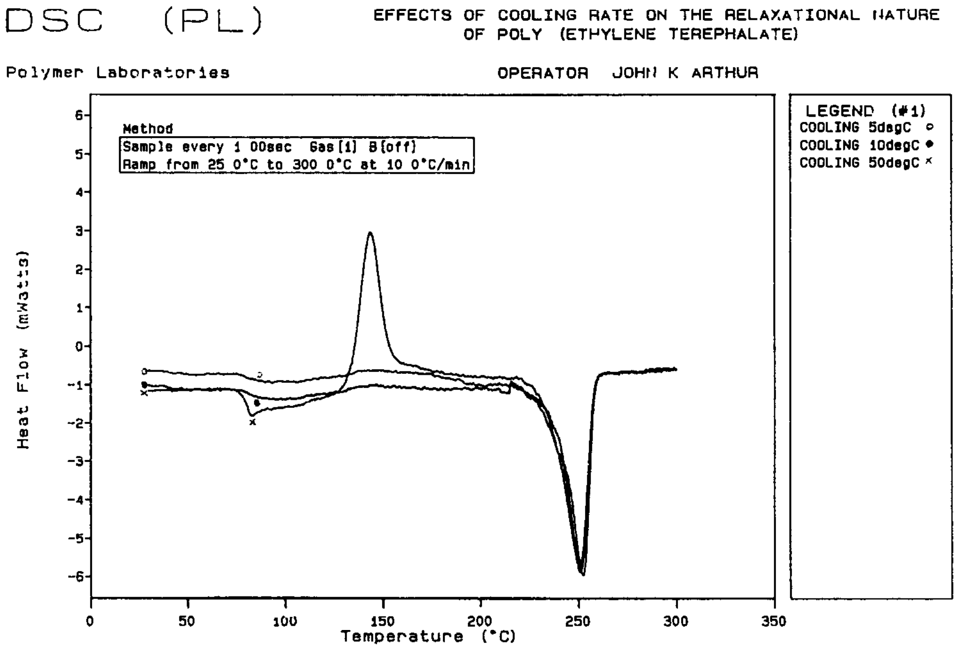

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FIGURE 8

Figure 8 A more practical illustration of differing cooling rates on the relaxational nature of polyethylene terephalate. The effect of three cooling rates is shown. At 5°C/minute a highly crystalline material is evident. 10°C/minute also shows a fairly crystalline behaviour whereas a very definite amorphous PET is formed with 50°C cooling of the sample. The Tg becomes more predominant with reduced crystallinity.

CONCLUSIONS

From this appended data it is clear that a highly controlled thermal environment is possible both in the heating and cooling mode of a thermal analyser. The system is highly flexible and although here it has been discussed essentially for use with the PL-DSC, it can be used with any P.I.D. controlled system providing that a suitable heating/cooling jacket can be provided. Savings are possible in the amount of cryogenic fluid normally required. Finally the system provides an exceptionally easy operating regime for the instrument user whilst maintaining "state of the art" thermal control.