

Pressure/Volume/Temperature (PVT) Behaviour of Polymers During Ultrafast Cooling

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ABSTRACT

A critical parameter in the injection moulding process is the volume shrinkage of the moulding and how it is affected by pressure. The Pressure/Volume/Temperature (PVT) relationship for a material during processing, when known, will raise the efficiency of the operation, minimise cycle times and produce a component to tighter tolerances. This report gives a description and operation of the NPL modified SWO direct measurement machine used to measure the PVT behaviour of amorphous and semi-crystalline polymers during rapid cooling. A method to obtain, for the first time, ultrafast cooling rates similar to conditions in industrial injection moulding is shown with detailed results. The repeatability and sample variability of the results under computer control are good (coefficient of variation better than 0.5%). A procedure to obtain the contribution of crystallisation to the overall shrinkage is given. The effect of sample height and diameter is investigated. A correlation of the PVT results with other techniques is given. This work is unique in demonstrating the importance of obtaining PVT data representative of commercial injection moulding as opposed to data gathered hitherto under equilibrium conditions.

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1. INTRODUCTION

There is an increasing demand for Pressure/Volume/Temperature (PVT) data in the plastic injection moulding industry in order to reduce warpage, quantify shrinkage and accurately predict moulded component dimensions at the design stage. This predictive capability, with the use of finite element analysis (F.E.A.), should allow tighter tolerances to be achieved with greater confidence and will ultimately reduce rejects and shorten cycle times. However, accurate data needs to be determined at a cooling rate commensurate with current injection moulding, in excess of 200 °C/minute. As this type of data becomes available it will enable companies to improve the predictions of F.E.A software, particularly where rapid processing is important or where tight tolerances need to be met. Due to the current design of PVT measuring instruments only data at or near equilibrium conditions has been available. The aim of this work is to determine accurately PVT data at ultrafast cooling rates on semi-crystalline, amorphous and thermoset materials by either modifying an existing technique or engineering a purpose built instrument. After a survey of the PVT instrument market the company SWO was chosen as a partner to provide a PVT instrument capable of cooling at 200 °C/minute with the desired accuracy, ease of use and adaptability (see appendix 1 for a detailed specification).

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2. THE SWO/NPL PVT100 MACHINE

Unlike the Zoller technique (1-10) in which the sample is housed in a bellows and uses mercury as a confining fluid, the SWO/NPL system is a direct measurement machine (see Photograph 1). Other references to PVT measurements and to high cooling rates are shown in References 11-26.

The sample is contained in a pressure cell (see Photograph 2) which is heated and then cooled to produce a solid cylinder of material which is void free. Pressure is applied hydraulically to a piston at the top of the cell with either a PTFE disc seal (for temperatures up to 250 °C) or a self energising Vespel system for higher temperatures (up to 420 °C). An identical piston and sealing system is located at the bottom of the cell. The standard cell (7.8 mm diameter) will allow pressures from 20 to 250 MPa (200-2500 bar) to be exerted with an optional pressure measurement to 1600 bar from the lower piston. Two other cells were manufactured to NPL specifications (6.0 mm and 14.0 mm diameter) to study the effect of temperature gradients in the sample set up on cooling from the melt.

The machine operates from 25 °C to 420 °C, as the software does not allow sub-ambient testing at present. Temperature sensors are positioned axially in the top, middle and bottom of the cell wall to monitor the imposed cooling and in the sample itself in the radial centre at a depth of 4 mm. The cell diameter (which is uniform) is accurately known and by knowing the displacement of the piston, using an electronic linear gauge, the volume of the sample is measured. From accurately weighing the sample between the seals at the end of the experiment and entering this value into the computer the specific volume is calculated.

A schematic diagram of the instrument is shown (Diagram 1). As the cell is supported on a floating spring arrangement, the test sample is subjected to an almost hydrostatic pressure regime - only the wall friction leads to a non hydrostatic state in the metal sample interface. Corrections are made for the expansion and contraction of the system (including PTFE/Vespel seals).

The use of the two non-standard test cells, i.e. 6.0 mm and 14.0 mm has implications on the hydraulic and sample pressures developed, as the system was designed using a standard test cell. For the smaller 6.0 mm test cell the piston diameter will only withstand buckling forces equivalent to a maximum pressure on the sample of 1200 bar. Also the lowest pressure delivered by the hydraulic system for the smaller diameter cell is 300 bar. For the larger 14.0 mm test cell, because of the larger surface area, the maximum pressure on the sample is limited to 700 bar, but it can operate down to 50 bar.

The experiment is completely computer controlled in both heating and cooling cycles. The specific volume is calculated and continuously recorded using the original weight of the sample and the volume calculated from the position of the displacement transducer and the cross sectional area of the cell. In the heating mode the sample temperature is raised in isothermal steps during which a pressure sweep is performed. For the cooling mode the sample is melted, consolidated and cooled at the prescribed linear rate under isobaric conditions closely simulating an injection moulding process. This cycle may be repeated up to nine times at different pressures in one experiment.

The instrument will cool automatically at a linear rate from the set temperature down to around 70 °C at cooling rates up to 50 °C per minute, (using pressurised coolant air at 0.4 bar) as measured by the middle thermocouple sited in the barrel wall. For this investigation, to match the injection moulding process, the aim was to achieve cooling rates in excess of 200 °C per minute. Though some improvement in cooling rate could be achieved by raising air pressure this was marginal and was limited by the line pressure and piping. NPL have modified the system such that the air is diverted into a copper coil immersed in liquid nitrogen and the exhaust silencer removed. With this adaptation cooling rates in excess of 200 °C per minute have been routinely achieved in the standard cell. A modification to the software has been made so that the temperature controller is inoperative when ultrafast cooling is required.

3. MATERIALS

As agreed by the Industrial Advisory Group the materials tested were as follows :-

High density polyethylene BP Chemicals Rigidex HD5740UA, NPL code HCA 000.

Polystyrene Huntsman Chemical CO Ltd. Huntsman Polystyrene 303, NPL code HAU 000.

Polyphenylene Sulphide Hoechst (Ticona) Fortron 0214 P1, NPL code HCC 000.

4. EXPERIMENTAL TEST PROCEDURE

4. ZEROING DISPLACEMENT TRANSDUCER AND TEST PROCEDURE

At the start of each test the zero position for the piston must be established. For testing at temperatures below 250 °C, PTFE seals may be used. To zero the displacement transducer the lower piston is screwed into the machine and two PTFE seals inserted into the cell. The linear adjustment procedure is activated from the software and the zero position is established after the piston has entered the cell and 1600 bar applied.

The piston and seals are then removed and the lower piston and lower seal replaced so that a weighed amount of sample can be added to the cell to give a consolidated height of 15 mm. A sample height of 15 mm ensures the thermocouples are situated symmetrically around the sample. The upper seal is added to the cell and the upper piston screwed into the hydraulic assembly and the test regime commenced.

All of the experiments in this report are carried out in the isobaric mode.

After setting up the test conditions the experiment is started which follows the isobaric cooling procedure shown in Figure 1 for a single cycle. The sample is ejected after the experiment by removing the lower piston and driving the upper piston through the cell. The sample is weighed to the accuracy of $\pm 0.0001\text{g}$ and the weight is entered into the computer to derive an accurate specific volume measurement.

4.2 UNCERTAINTIES

4.2.1 Temperature

Measurement accuracy $\pm 0.3\text{ }^{\circ}\text{C}$ for the controlling thermocouple.

4.2.2 Specific volume

The measuring accuracy for the cell radius	= $\pm 0.0001\text{cm.}$
displacement transducer	= $\pm 0.0001\text{cm.}$
weight	= $\pm 0.0001\text{g.}$
Fractional uncertainty for displacement	8×10^{-4}
Fractional uncertainty for 5 mm height sample	2×10^{-4} .
Fractional uncertainty for 15 mm height sample	7×10^{-5} .
Fractional uncertainty for 25 mm height sample	4×10^{-5} .
Fractional uncertainty for 5 mm weight of sample	1.5×10^{-4} .
Fractional uncertainty for 15 mm weight of sample	4.4×10^{-4} .
Fractional uncertainty for 25 mm weight of sample	8.8×10^{-5} .

The combined uncertainty for each sample height is then

5 mm	= $\pm 1.2 \times 10^{-3} \text{ cm}^3/\text{g}$.
15 mm	= $\pm 1.2 \times 10^{-3} \text{ cm}^3/\text{g}$.
25 mm	= $\pm 1.1 \times 10^{-3} \text{ cm}^3/\text{g}$.

4.2.3 Pressure

$\pm 1\%$ of the actual pressure reading.

4.2.4 Calibration

Calibrated to ISO 9000 and certified for displacement length, cell diameter, temperature (thermocouples), and pressure by SWO. Cell diameter and temperature within the cell at the midpoint checked by NPL using UKAS calibration service.

5. EXPERIMENTAL RESULTS AND DISCUSSION

5.1 COOLING POTENTIAL AND RATE

Figure 2 shows the linearity of the cooling curves for the machine cooled with ambient forced air and with liquid nitrogen cooled air. Figure 2 also shows, surprisingly, that the cooling rate for the liquid nitrogen cooled air experiment is linear (lowest line). When the sample is cooled automatically at relatively high cooling rates, above 25 °C/minute, opening the air control valve produces a small ripple in the cooling curve as shown in Figure 3 which will be referred to in the next section. The temperature response for the polymer, as measured by a thermocouple imbedded in the radial centre of the sample under the piston, is shown in Figure 4 with the imposed cooling from the cell wall at two locations. After a short delay in the response from the electronic system, the cell wall cools rapidly and linearly but the temperature at the radial centre of the sample lags behind due to the poor conductivity of the polymer. It is observed that even after the test has finished, when the temperature programme has reached 25 °C, the temperature at the radial centre of the sample is still above 100 °C and is only just crystalline. This would also be the case for injection moulded components where there are thick sections.

Cooling rate tests were performed on the other PVT cells and because of the difference in thermal mass and cooling coil dimensions the cooling rates were found to be different but still a linear function with time. Typically the larger test cell (14.0 mm) gave a cooling rate of 135 °C/minute while the smaller test cell (6.0 mm) cooled at 150 °C/minute.

5.2 REPEATABILITY AND SAMPLE VARIANCE OF RESULTS

To assess the repeatability of the PVT results an experiment was carried out where a sample was isobarically cooled automatically (i.e. computer controlled) at 35 °C /minute under 800 bar nine times. At this relatively fast cooling rate a slight ripple effect in the cooling curve is

produced when the air valve is opened and is reflected in the specific volume/temperature plot Figure 5, thus affecting the closeness of the results. This relatively fast cooling rate was selected as this would likely give rise to the “worst case” as regards repeatability. Five separate tests were carried out, under the same conditions and again cooled at 35 °C/minute. The results for sample variation is shown in Figure 6. The results in Table 1 show a good level of repeatability (coefficient of variation less than 0.25%) and a small variation (less than 0.5%) between samples.

5.3 EFFECT OF COOLING RATE ON SPECIFIC VOLUME FOR AMORPHOUS AND SEMI-CRYSTALLINE POLYMERS

Figures 7, 8, and 9 show the effect of cooling rate on the shrinkage of amorphous and semi-crystalline polymers from the melt state; the temperature being measured and controlled axially in the cell wall in the middle thermocouple position. The overall shrinkage for amorphous polystyrene at slow cooling rates is relatively small as the material passes through the glass transition to the glassy state. On ultrafast cooling the shrinkage is considerably less, so that the final glassy state has a higher specific volume and as a result would exhibit different material properties.

The polyethylene PVT curves in Figure 8 show how the crystallisation region, which is sharp at 5 °C/minute, apparently becomes more diffuse as the cooling rate increases. It can also be observed that the final crystallinity of the polymer will be less at faster cooling rates and that crystallisation considerably raises the overall shrinkage compared to an amorphous polymer.

The latter comments also apply to the polyphenylene sulphide PVT data (Figure 9) where the crystallisation can be seen to occur at a much higher temperature and the overall shrinkage is less than polyethylene.

5.4 EFFECT OF PRESSURE ON SPECIFIC VOLUME AND CRYSTALLISATION OF POLYETHYLENE UNDER SLOW ISOBARIC COOLING

It is shown that increasing the pressure on isobaric cooling at 5 °C/minute for high density polyethylene progressively reduces the specific volume and raises the temperature at which the polymer crystallises (Figure 10). For this experiment the temperature was measured axially in the cell wall in the middle position. This experiment can also be performed with a temperature sensor in the centre of the polymer itself which gives a sharper and narrower crystallisation region (Figure 11). Because of the presence of the thermocouple in the piston and the resulting lower strength of the piston only pressures up to 1600 bar may be obtained in this mode. The pressure of 1600 bar has shifted the onset of crystallisation by 36 °C compared with 200 bar. The specific volume has been reduced by up to 12 %.

When the temperature of the polymer is monitored as a function of time, while cooling at 5 °C/minute it was found that for each isobaric test an isothermal region occurred at the crystallisation region. Two isobaric cooling curves are shown in Figure 12 as examples. The crystallisation temperature for each isobar is plotted against pressure in Figure 13 giving a linear relationship with a slope of 40 bar per °C shift in crystallisation temperature.

5.5 THE EFFECT OF PRESSURE ON SPECIFIC VOLUME UNDER ULTRAFAST COOLING CONDITIONS FOR HIGH DENSITY POLYETHYLENE

As mentioned previously (5.3) when polyethylene is “ultrafast” cooled the specific volume temperature curve is more diffuse and the curve straightened as the polymer progressively crystallises from the cell wall to the centre. This feature is clearly shown in Figure 14 along with the effect of increasing pressure reducing the specific volume (i.e. increasing density). The temperature axis is derived from a thermocouple axially positioned in the cell wall. If the temperature of the polymer is taken in the radial centre, a sharper response to the onset and end of crystallisation is apparent, both occurring at higher temperatures (see Figure 15). The cooling rates for these curves for different pressures are shown in Table 2.

5.6 CONTRIBUTION OF CRYSTALLISATION TO THE OVERALL SHRINKAGE OF POLYETHYLENE

There are two main causes of volume reduction (or shrinkage) as a material cools through a phase transition such as crystallisation. Firstly the density of the crystalline phase is greater than in the molten phase, since the polymer chains are able to pack together more efficiently. Thus a volume reduction is expected on crystallisation. The second cause of shrinkage is the normal reduction in volume on cooling. This effect is characterised by a thermal expansion coefficient (which of course becomes a thermal contraction during cooling).

During rapid cooling, where there may be large temperature gradients in the sample, there are thus two potential contributions to the PVT behaviour during crystallisation (or any other molecular kinetic process involving a step change in density). The challenge is to separate the contribution due to crystallisation alone. A relatively simple procedure for doing this has been developed and is described below.

Typical PVT behaviour of a semi-crystalline polymer is shown in Figure 11. At high temperature, prior to the onset on crystallisation, the reduction in volume is approximately linear. The slope of this line is the thermal contraction coefficient of the polymer melt (which is equal to -1 times the thermal expansion coefficient). After crystallisation has finished the contraction is again approximately linear, this time described by the thermal contraction coefficient of the solid polymer.

During crystallisation it is assumed that the *molten* material will continue to contract at the same rate as it did prior to the onset of crystallisation and that the *solid* material will contract at the same rate as the material contracts after crystallisation has finished. Thus as long as the volume fractions of molten and solid material are known, the effect of the normal reduction in volume with temperature can be extrapolated from the PVT behaviour just before and just after crystallisation.

It is possible to calculate the approximate volume fraction (Φ_{liquid}) of melt in a sample at any temperature (T), simply from the proportion of reduction in volume since the start of crystallisation. The volume fraction of solid material is 1 minus the volume fraction of the melt.

Thus the total volume change can be expressed as three terms:

$$\Delta V_{Total} = \Delta V_{Solid} + \Delta V_{Liquid} + \Delta V_C$$

$$\Delta V_{Total} = V_{Total} - V_Y = (T_R - T) \left(\frac{\delta V}{\delta T} \right)_{solid} \Phi_{solid} + (T_R - T) \left(\frac{\delta V}{\delta T} \right)_{liquid} \Phi_{liquid} + \Delta V_C$$

Where V_{Total} = specific volume at temperature T (measured in the centre of the polymer in this case).

T_R = reference temperature, where slope changes abruptly (i.e. when crystallisation starts).

$\left(\frac{\delta V}{\delta T} \right)_{Liquid\ or\ Solid}$ = slope of volume vs. temperature curve before and after crystallisation.

$\Phi_{Liquid\ or\ Solid}$ = volume fraction, i.e. $\left(\frac{V_T - V_Y}{V_R - V_Y} \right)_{Liquid}$ and $\left(\frac{V_R - V_T}{V_R - V_Y} \right)_{Solid}$ respectively.

Where V_R = reference volume (Liquid) corresponding to T_R , the start of crystallisation.

V_Y = reference volume (Solid) corresponding to T_Y , i.e. return to linear shrinkage after crystallisation.

ΔV_C = volume change due only to crystallisation (only valid between V_R and V_Y or T_R and T_Y).

The only unknown in the above equation is the contribution to the volume reduction arising from crystallisation alone (ΔV_C). Thus it is possible to separate the contribution just due to crystallisation, as required. Figure 16 illustrates the procedure schematically.

To show the results of this procedure, it has been applied to high density polyethylene cooled at 218 °C/min under a pressure of 160 bar and at 5 °C/min, under a pressure of 200 bar. The PVT curves for these two cooling rates are shown in Figures 15 and 11. In the 5 °C/min/200 bar case reference points for the start and end of crystallisation were chosen to be 128 °C and 92 °C. In the high pressure high cooling rate case the start and end of crystallisation were taken to be 207 °C and 142 °C. Figure 17 shows the contribution to the total change in volume arising from the three terms in the above equation, i.e. from crystallisation alone, from shrinkage of the melt and from shrinkage of the solid. By far the most dominant term is the contribution from crystallisation alone. The same result is obtained in the second example (Figure 18).

This result is not surprising as the step change in specific volume can be seen to be large compared to the slopes of the curves before and after crystallisation (Figures 11 and 15). For

the case of polyethylene an important conclusion can be drawn; the contribution to shrinkage from intrinsic crystallisation is much more important than any other contribution.

5.7 EFFECT OF SAMPLE HEIGHT ON THE PVT RESULTS

5.7.1 Standard Test cell (7.8 mm)

The effect of varying the sample height from 5 mm to 25 mm is explored in Figures 19-20 for polyethylene and Figures 21-22 for polystyrene. The greatest difference in the PVT data is shown by the ultrafast cooling experiments probably due to the slight differences in the cooling rate, though these are quite small. It is concluded that the sample height itself within the height limits tested has little effect on the PVT curves. Also the variation in the heat given out on crystallisation for different sample masses had no effect on the PVT curves.

5.7.2 6.0 mm Test cell

For testing large samples (i.e. 25 mm high), considerably greater than the standard 15 mm height, too much of the relatively weak piston would protrude out of the cell barrel, such that piston introduction and operation might cause dangerous buckling. It is for this reason that only a small sample (5 mm) was tested and compared to the standard 15 mm height. Figures 23-24 and 25-26 show the effect of sample height on the PVT results for polyethylene and polystyrene respectively. While the polyethylene data are similar at 5 °C/minute the polystyrene sample gave slightly lower specific volume values for both the slow and ultrafast cooling experiments even though volume corrections were made to the results as the test cell bore diameter was found to be slightly larger (6.04 mm) than the stated 6.0 mm. This difference is probably due to the brittle nature of polystyrene where there was some weight loss on removing the seals.

5.7.3 14.0 mm Test cell

PVT data for polyethylene and polystyrene are given in Figures 27-28 and 29-30 respectively using the 14.0 mm test cell. There is little difference in using the larger 25 mm sample in this test cell for either polyethylene or polystyrene. This is despite the presence of cavitation or bubbles found in the polystyrene sample after testing in the ultrafast cooled mode, which would be expected to raise the measured specific volume. This phenomenon was an outcome of ultrafast cooling which even occurred from a void free slow cooled sample introduced into the test cell and then subsequently cooled rapidly from the melt. A similar phenomena is known to occur during injection moulding of thick sections of polystyrene.

5.8 EFFECT OF THE TEST CELL DIAMETER ON THE PVT RESULTS

As a sample is cooled from the melt the material cools from the cell wall with a temperature gradient dependent on the thermal diffusivity of the material. For semi-crystalline polymers a further complication occurs in the crystallisation region when heat is given out. So at any one

time during the cooling process the measured specific volume is a sum of the local specific volumes which is a function of the material state, its temperature and amount of that material in that state.

As the test cell increases in diameter the sample temperature difference from the edge to the centre increases and is further from an equilibrium temperature condition even at slow cooling rates (5 °C/minute). This has the effect of extending the crystallisation region over a wider temperature range as measured by a thermocouple at a single position in the cell wall as shown in Figure 31.

The amount of molten material in a cell above the crystallisation temperature increases with diameter for a given temperature at the cell wall. The specific volume of the melt is more than the solid state, therefore, on rapid cooling, a large diameter cell at the same temperature at the barrel wall as a small cell would record a higher specific volume. This is shown graphically in Figure 32 (15 mm sample) for polyethylene. Figure 33, for a 5 mm sample of polyethylene, again illustrates the above point.

Samples of polystyrene tested under the same conditions as polyethylene, i.e. sample size, cooling rate and isobaric pressure are shown in Figures 34-37. These curves are quite similar (the overall shrinkage for polystyrene is small) except Figure 35 for the ultrafast cooling of polystyrene (a comparison of the 6.0 mm with the 14.0 mm test cell) where the temperature gradient has an effect on the measured specific volume curves.

5.9 CORRELATION OF THE SWO/NPL PVT DATA WITH AN INDEPENDENT ORGANISATION (RAPRA) AND DSC MEASUREMENTS

The PVT results performed at Rapra from a confining mercury fluid test using the Zoller type bellows technique for a high density polyethylene grade are given in Figure 38. The sample is melted and cooled to a set constant temperature when pressure is applied to obtain the specific volume under equilibrium conditions. The temperature is then lowered and measurements again recorded when a steady state is achieved. The same high density polyethylene was tested in the SWO/NPL machine cooled at 0.1°C/minute for 1000 and 2000 bar, and as can be seen there is a small vertical shift, of about 3%, in the curves probably due to a slight calibration error.

The SWO/NPL data also appear to show a sharper change in specific volume on crystallisation. This may be due to insufficient data points in this region of the Rapra data or to insufficient time allowed between collecting data points for equilibrium to be obtained.

The report on “Preliminary PVT and DSC Measurements Comparing Data for Polyethylene and Polyacetal” (16) concludes good agreement was found between the DSC and PVT results for equilibrium conditions but differed at high cooling rates. As mentioned earlier temperature gradients developed for large samples at ultrafast cooling rates would undoubtedly contribute to this difference. The effect of high pressure is a further complication to any true comparison as not only will the specific volume be reduced by pressure but the crystallisation temperature will be raised. More work needs to be undertaken to establish the effect of temperature gradients, high pressure and ultrafast cooling on shrinkage in order to compare PVT data with that extrapolated by DSC by some workers. A correlation has been made by C-Mold (27) but

needs to be verified by comparing PVT and “high pressure DSC” over the pressure range where the techniques overlap.

6. CONCLUSIONS

- The NPL/SWO PVT100 machine is capable of giving accurate, repeatable PVT data with a small variation between different samples.
- The PVT100 machine with the adaptation of liquid nitrogen cooled forced air produces linear cooling rates in excess of 200 °C/minute.
- The PVT data of polyethylene and polystyrene measured at ultrafast cooling rates were found to be significantly different from slow cooling data.
- Large differences in temperature, up to 75 °C, between the imposed cooling at the cell wall (axially) and the melt in the interior (radial centre) were found during ultrafast cooling.
- The effect of pressure on the specific volume of amorphous and semi-crystalline polymers was shown to be significant (up to 36 °C difference in the onset of crystallisation and up to 12% reduction in specific volume).
- The relationship between increasing pressure and the consequent increase in crystallisation temperature was found to be linear with a slope of 40 bar per °C shift in crystallisation temperature.

A procedure to calculate the approximate contribution to the change in specific volume due to crystallisation alone on cooling from the melt was proposed. For polyethylene the contribution from crystallisation was found to dominate.

- The effect of sample height was found to be minimal but the diameter of the test sample beyond 7.8 mm produced significant temperature gradients in the sample and affected the shape of the specific volume temperature curves.
- Agreement, to within a few percent, between the PVT data and another technique (DSC) was obtained at equilibrium cooling rates.
- Further work is required to improve the technique to measure to lower temperatures, to thinner sample sections and to control the rate of cooling.

7. REFERENCES

- Fakhreddine, Y.A. and Zoller, P. Proc. 'ANTEC 91' Conf. p 1642, 1991
2. He, J. and Zoller, P. Proc. 'ANTEC 91' Conf. P 1723, 1991
3. Zoller, P. Polymer Handbook, 3rd Ed. Wiley, 1989.
4. Zoller, P. Encyl. Mat. Sci. & Eng., Vol 6, p 3771, Pergamon Press, 1986.
5. He, J., Fakhreddine, Y.A. and Zoller, P. J. Appl. Poly. Sci., Vol.45, p 745, 1992.
6. Zoller, P., Starkweather, H.W. Jr. And Jones, G.A. J. Poly. Sci., Pt. B, Vol.24, No.7. p 1451, 1986.
7. Starkweather, H.D., Jones, G.A. and Zoller, P. J. Poly. Sci., Poly. Phys., Vol.26, No.2, p 25, 1988.
8. Zoller, P.J. Poly. Sci., Vol.16, p 1261, 1978.
9. Zoller, P., Kehl, T.A., Starkweather, H.W. and Jones, G.A. J. Poly. Sci., Poly. Phys., Vol.27, No.5, p 993, 1989.
10. Fakhreddine, Y.A. and Zoller, P. J. Poly. Sci., Part B, Vol.29, p 1141, 1991
1. Menges, G. and Thienel, P. Kunststoffe, Vol.65, No.10, p 696, 1975.
12. Menges, G. and Thienel, P. Polym. Eng. Sci., Vol.17, No.10, p 758, Oct 1977.
13. Michaeli, W. and Tietz, W. Proc. Conf. ANTEC 93, Vol.2, p 2209, 1993
14. Michaeli, W. and Tietz, W. Polimeri, Vol.14, No.6, p 305, 1993.
15. Weigmann, T. and Oehmke, F. Proc. Conf. ANTEC 91, p 1646, 1991
16. Internal Report of Preliminary PVT and DSC Measurements Comparing Data for Polyethylene and Polyacetal by C.R.G.Allen and C.S.Brown NPL Report CMMT (C) 33 October 1997.
17. Oehmke, F. and Wiegmann, T. Proc. Conf. ANTEC 94, Vol.2, p 2247, 1994.
18. Oehmke, F and Wiegmann, T. Poliplasti Plast. Rinf., Vol.40, Part 415, p 60, June 1992.
19. Wiegmann, T and Oehmke, F. Kunststoffe, Vol.80, No.11, p 1255, 1990.
20. Schafer, V I. Kunststoffberater, Vol.33, Part 9, p 57, September 1988.

21. Bhatt, S M and McCarthy, S P. Proc. Conf. ANTEC 94, Vol.2, p 1831, 1994.
22. Kooppelmann, J and Fleischmann, E. Kunststoffe, Vol.78, Part 4, p 312, April 1988.
23. Fleischmann, E and Koppelmann, E. J. Appl. Polym. Sci., Vol.41, p 1115, 1990.
24. Nguyen, K T, Nelson, B I and Diraddo R W. Proc. Conf. ANTEC 93, p 2203, 1993.
25. Kenndaten fur die Verarbeitung Thermoplastischer Kunststoffe, Teil 1, Thermodynamik, Carl Hanser Munchen Wein, 1979.
26. Fakhreddine, Y A and Zoller, P. Proc. Conf. ANTEC 92, p 711, 1992.
27. Medina, P. C-Mold Press Release, Feb 23 1998.

8. ACKNOWLEDGEMENTS

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Table 1

Repeatability and sample variability results for high density polyethylene

	Isobar	Coefficient of Variation (%)	Standard Deviation (cm ³ /g)
Repeatability ^{*1}	800	0.045-0.227	0.001-.003
Sample Variability ^{*2}	1600	0.137-0.451	0.002-0.005

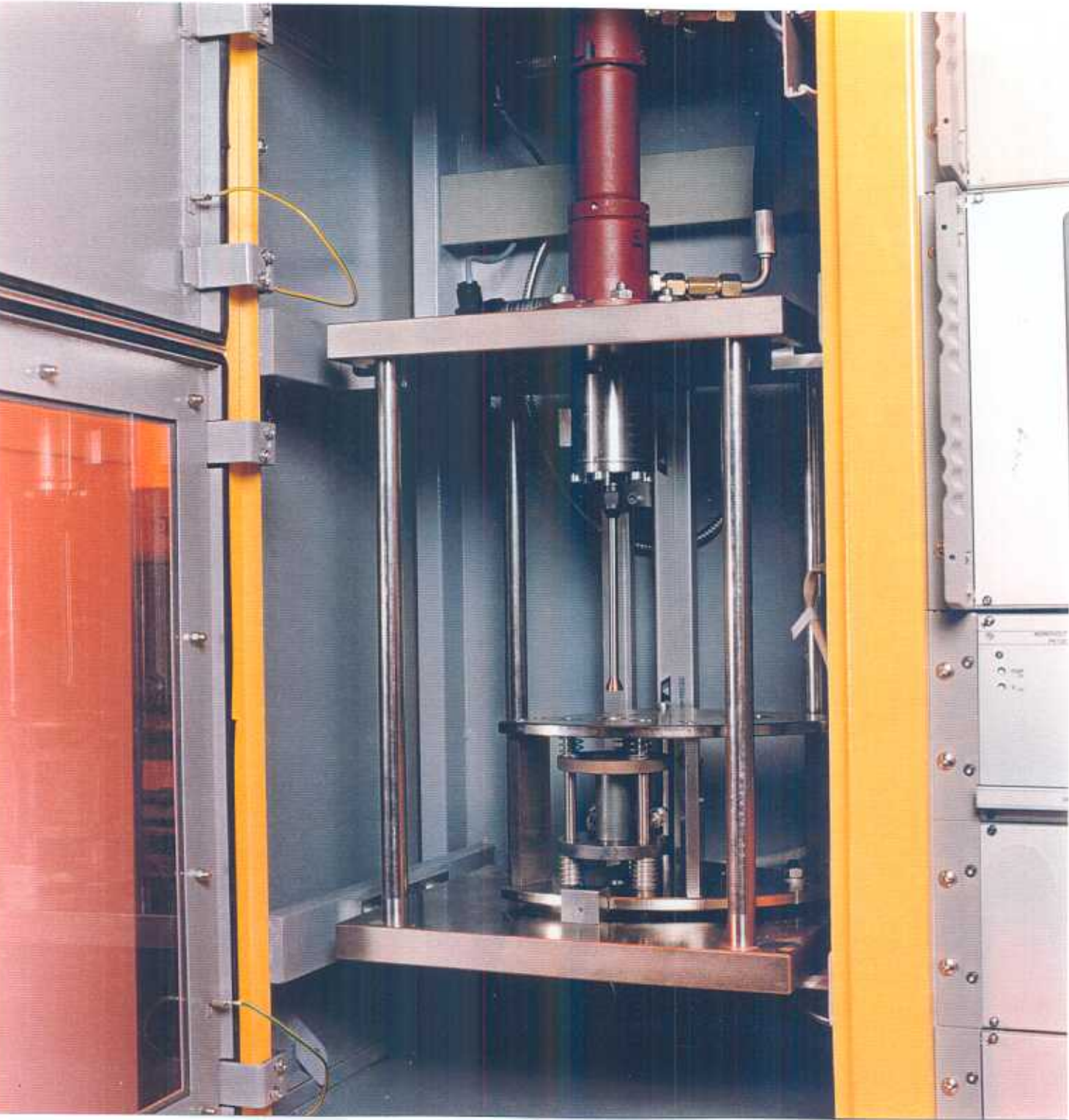
^{*1} Variation in results measured on the same sample under the same conditions, in the same instrument by the same operator.

^{*2} Variation in results measure on different samples under the same conditions, in the same instrument by the same operator.

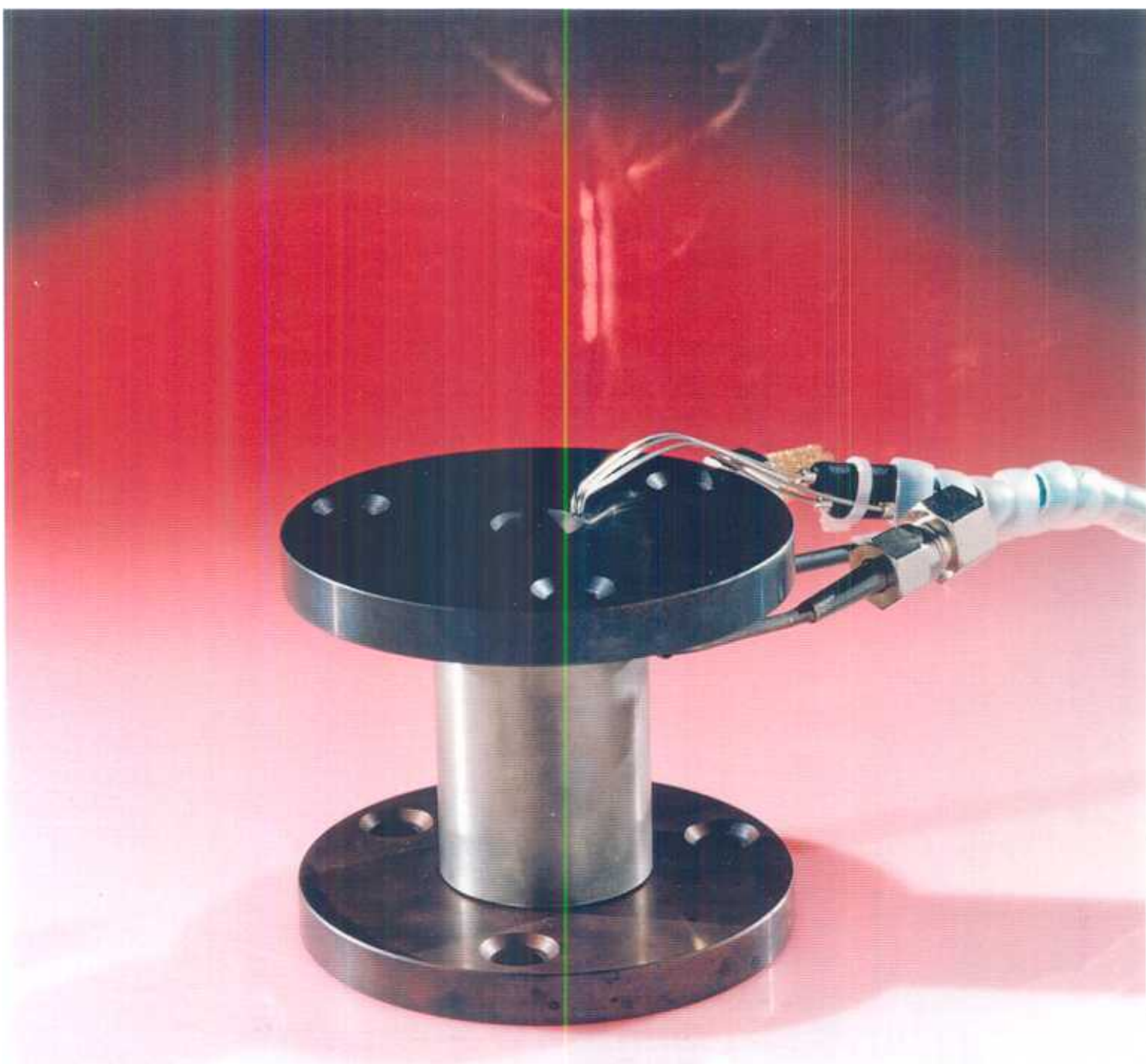
Table 2

Cooling rates for high density polyethylene, ultrafast cooled, standard 7.8 mm test cell (derived from experiment Figure 15)

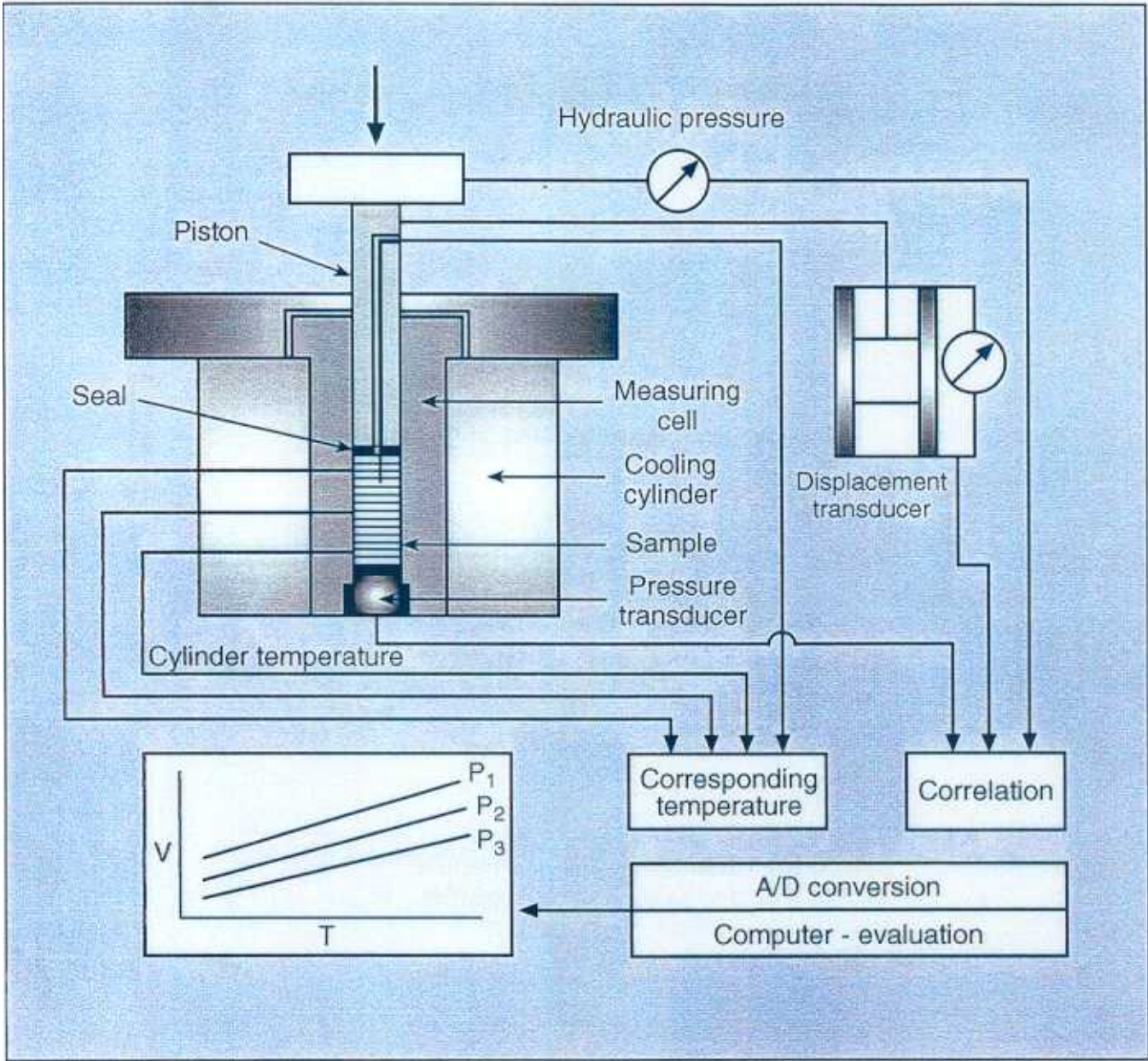
Pressure (bar)	Cooling rate at polymer radial centre (°C/minute)	Cooling rate at axial middle of the cell wall (°C/minute)
200	144	224
400	178	255
800	140	242
1200	141	237
1600	127	218



Photograph 1: SWO/NPL PVT 100 machine.



Photograph 2: 7.8 mm diameter standard PVT test cell.



Schematic diagram of PVT apparatus

Diagram 1:

Figure 1

Isobaric Cooling Test Procedure

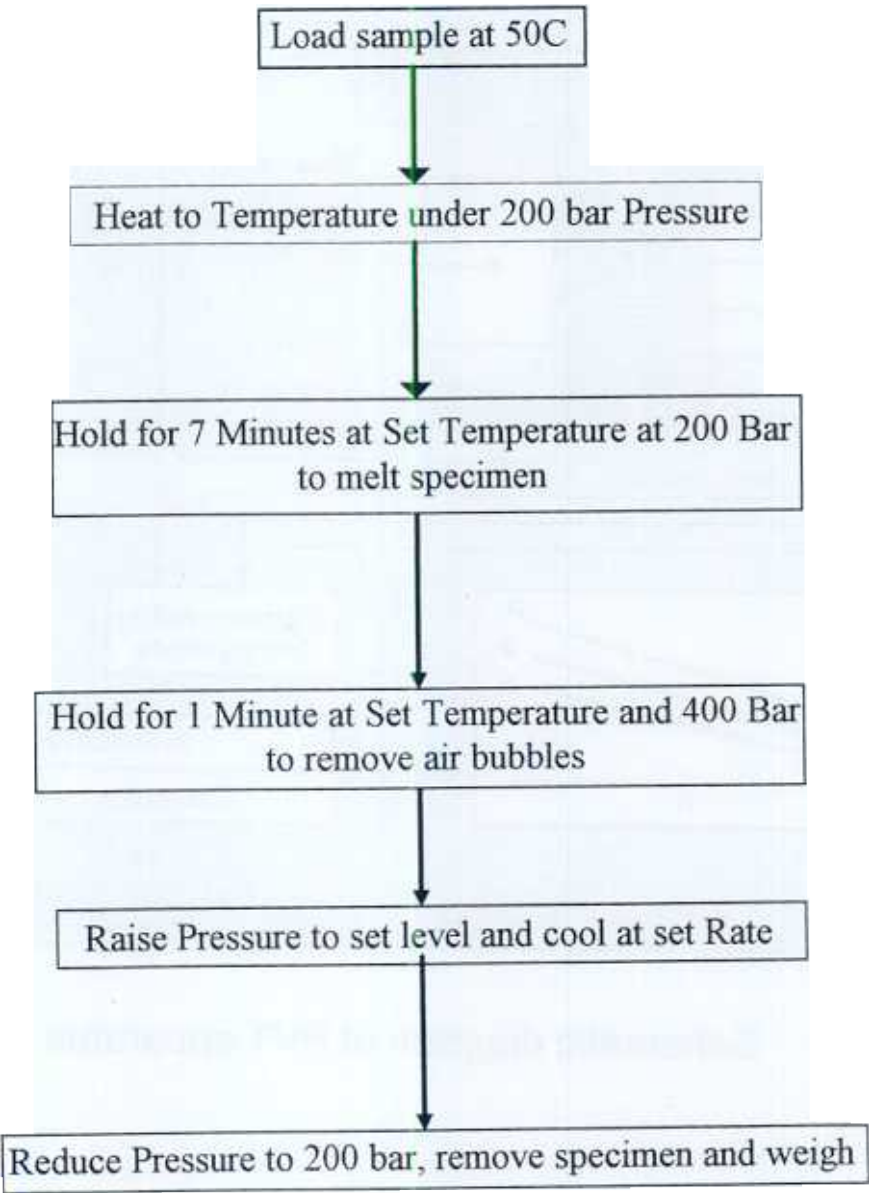


Figure 2

Effect of Set Cooling Rate and Air Pressure on the Cooling Profile
(High Density Polyethylene 800 Bar)

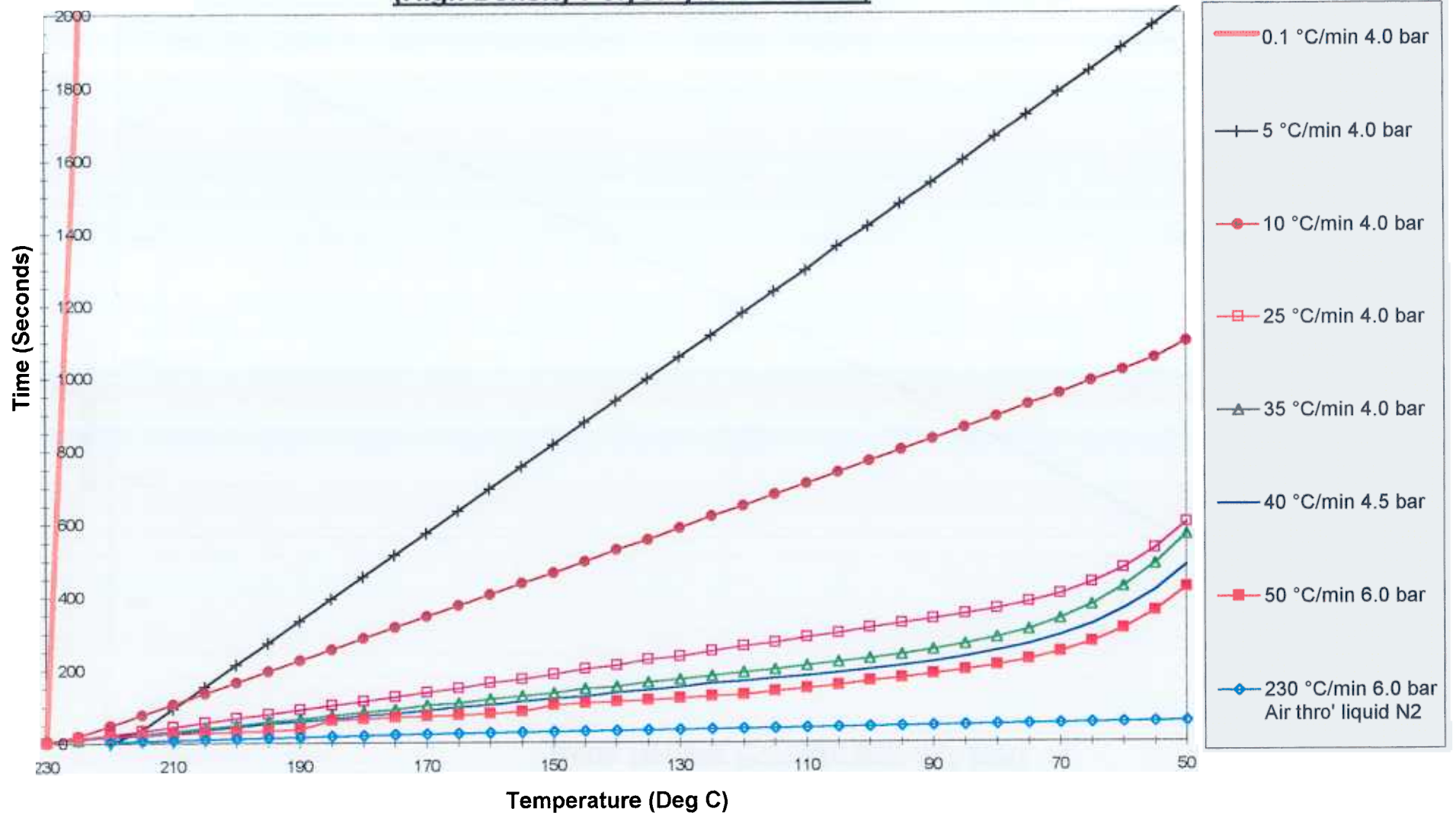


Figure 3

Cooling Profile At a Cooling Rate of 35 °C /minute
(High Density Polyethylene 800 Bar)

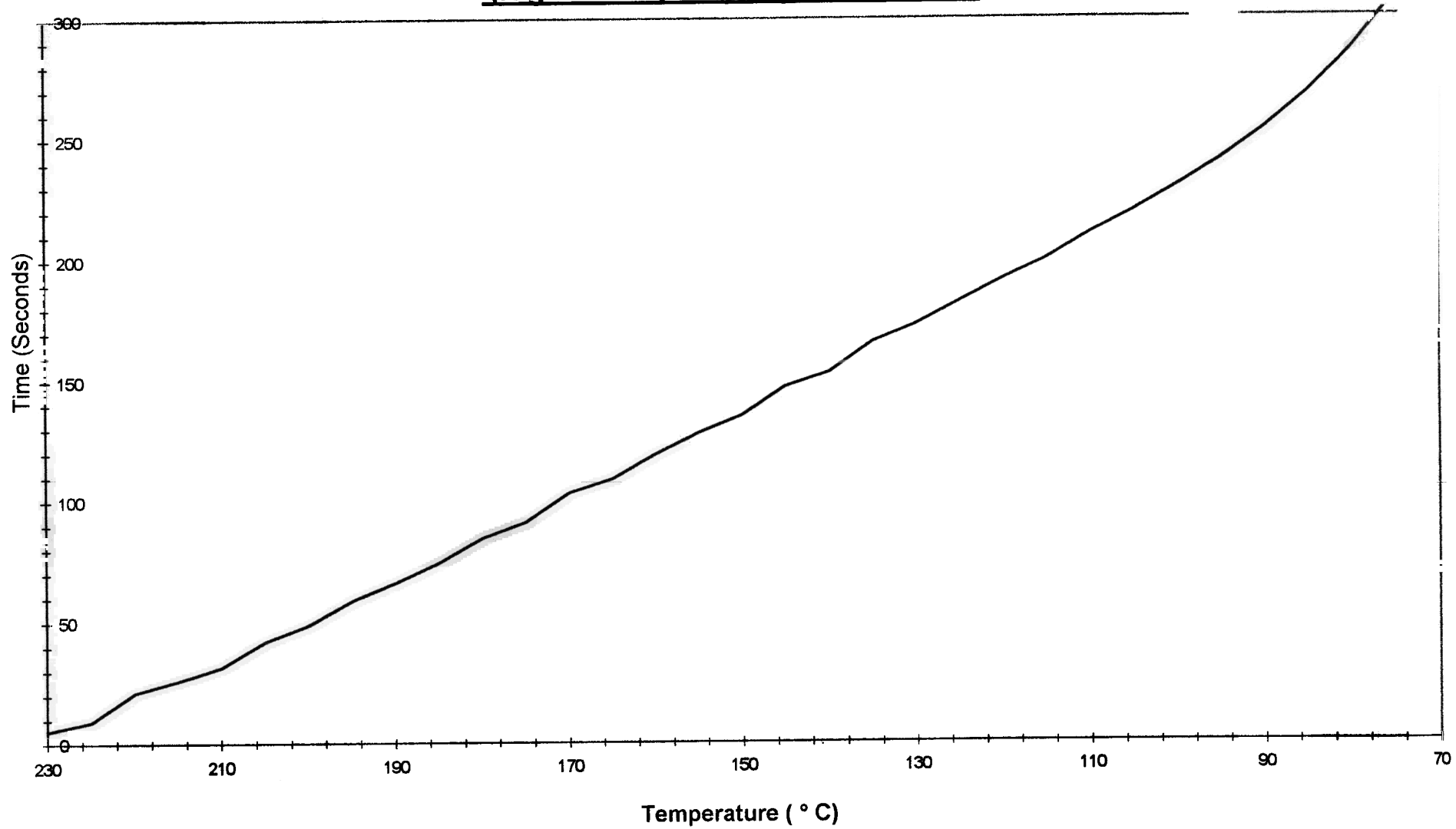


Figure 4

**Temperature Profile of the Sample Compared to the Cell Wall when Ultrafast Cooled
(214 °C/minute) for High Density Polyethylene at 200 bar**

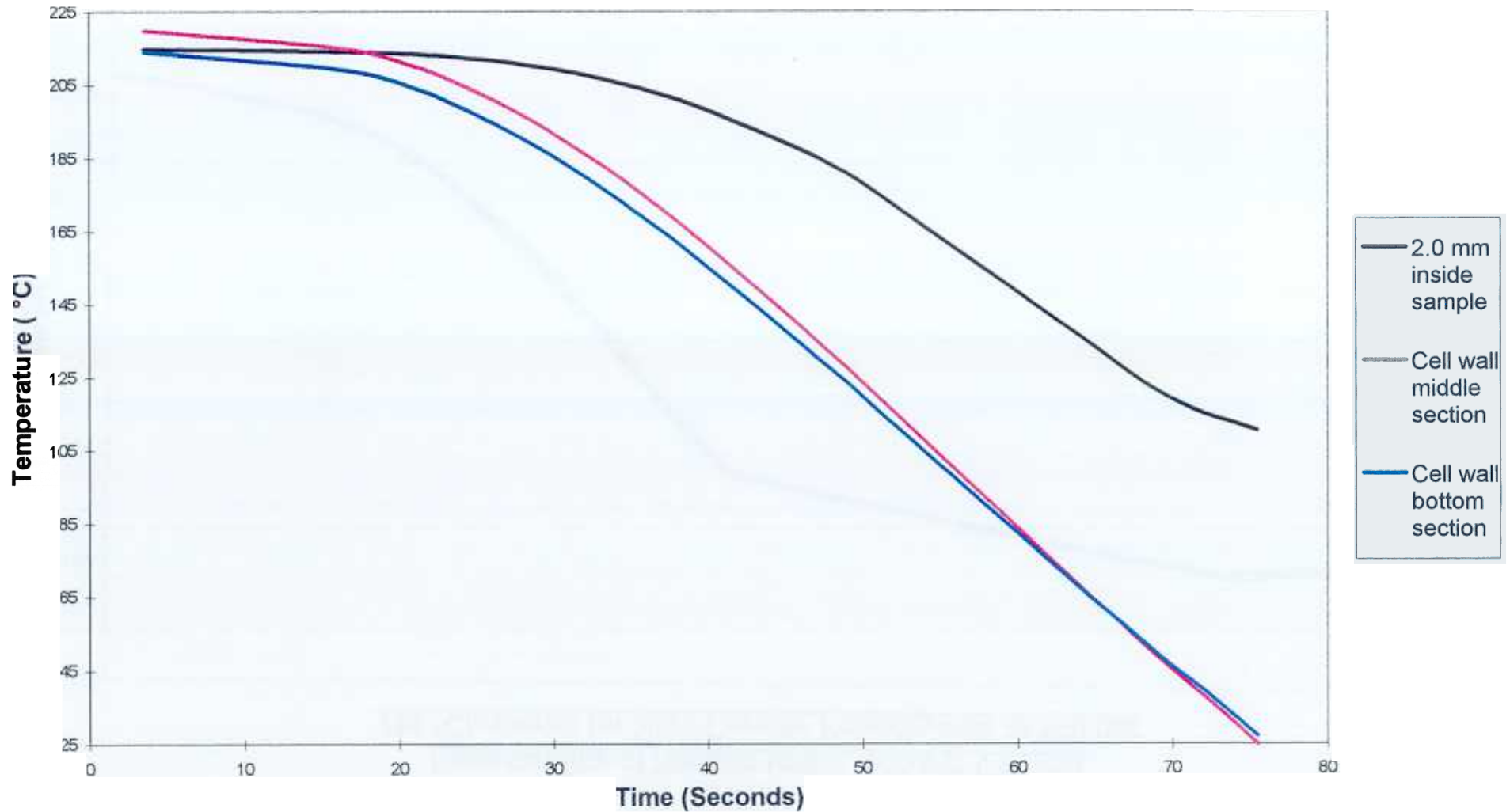


Figure 5

Repeatability of Results under Isobaric Cooling
(35 °C/minute) for High Density Polyethylene at 800 bar

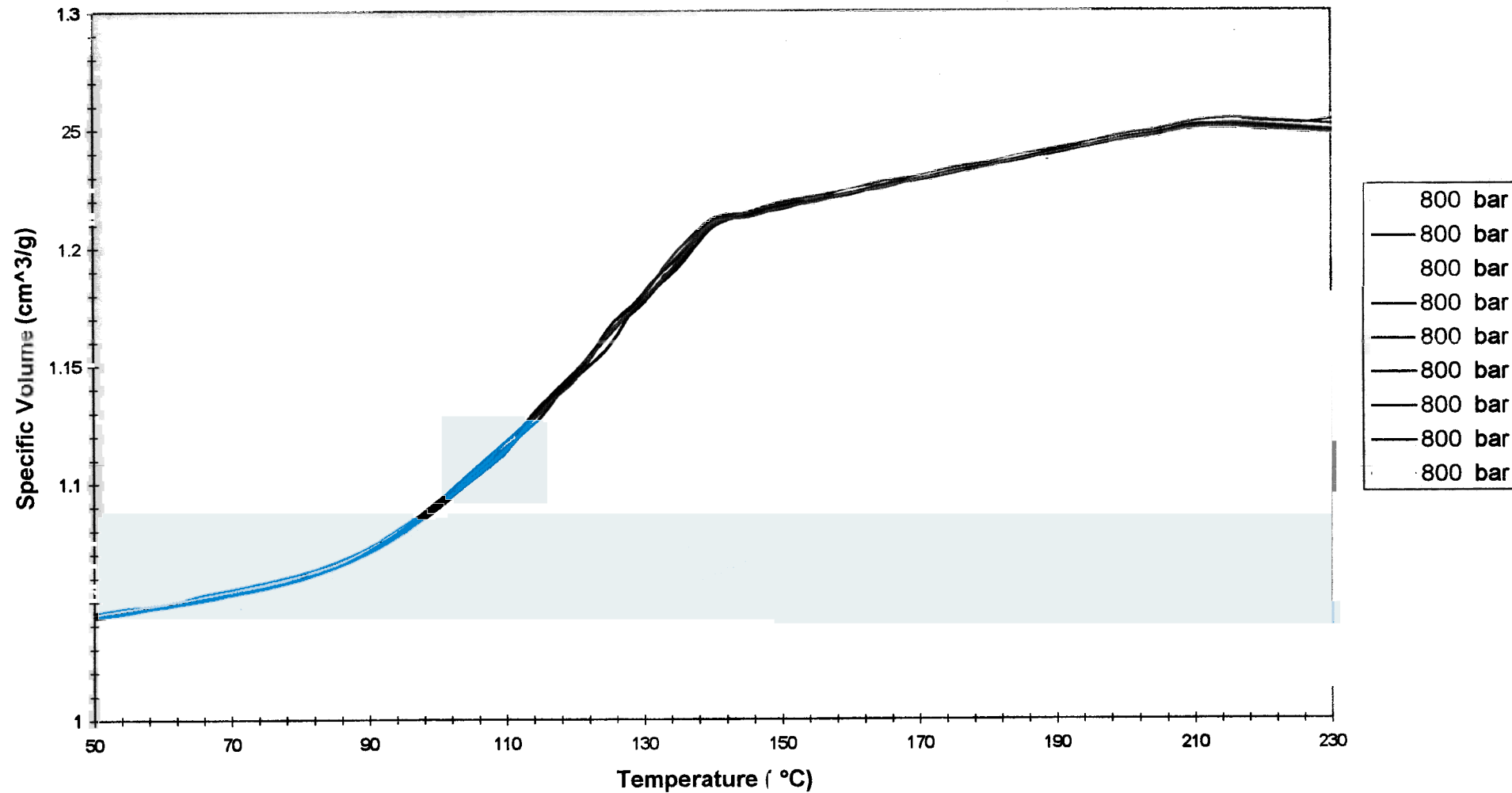


Figure 6

Sample Variability of Results from 5 mm Samples
Isobaric Cooling (35 °C/minute) for High Density Polyethylene at 1600 bar

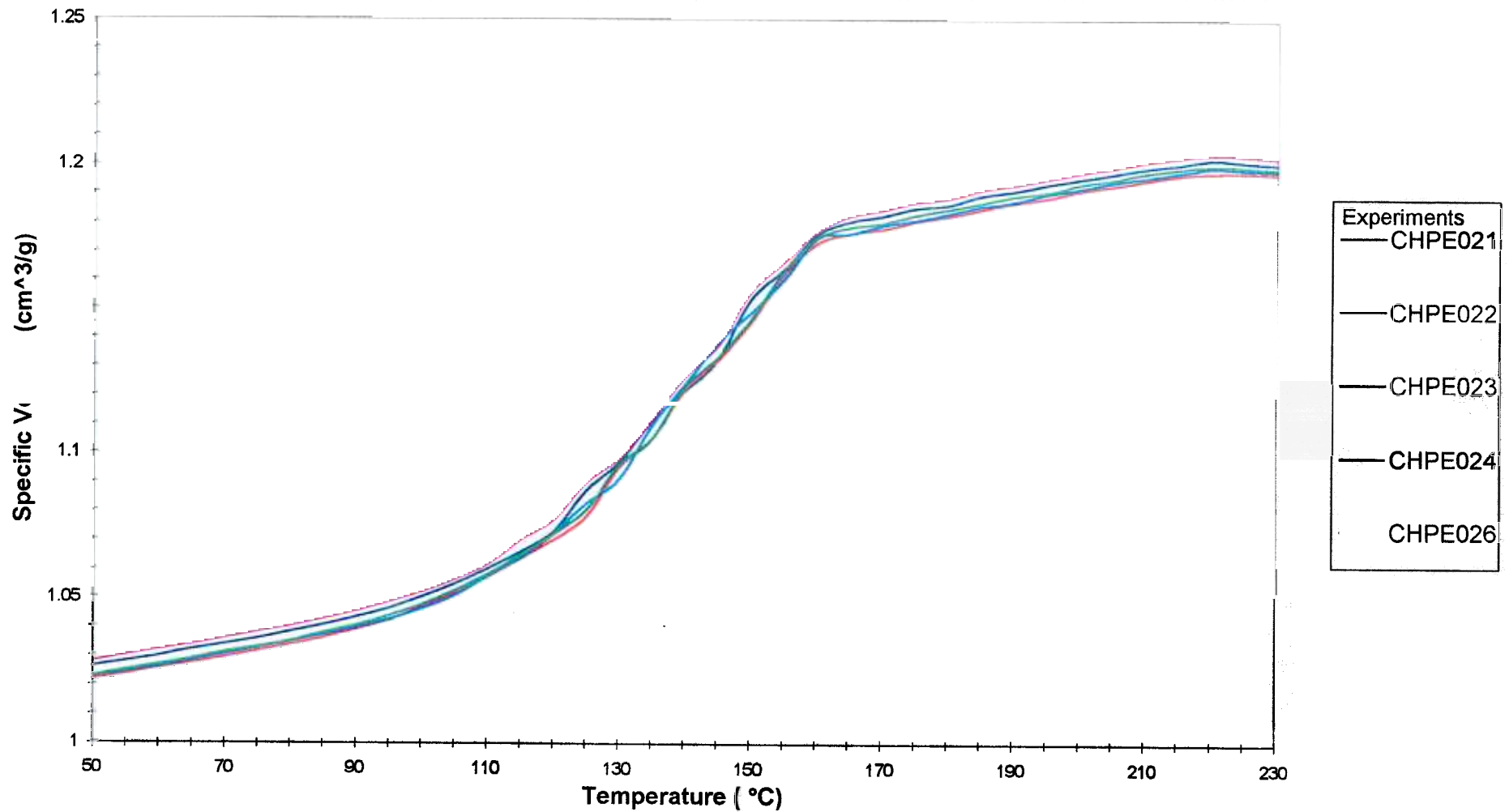


Figure 7

Effect of Cooling Rate on Specific Volume for Polystyrene at 800 bar

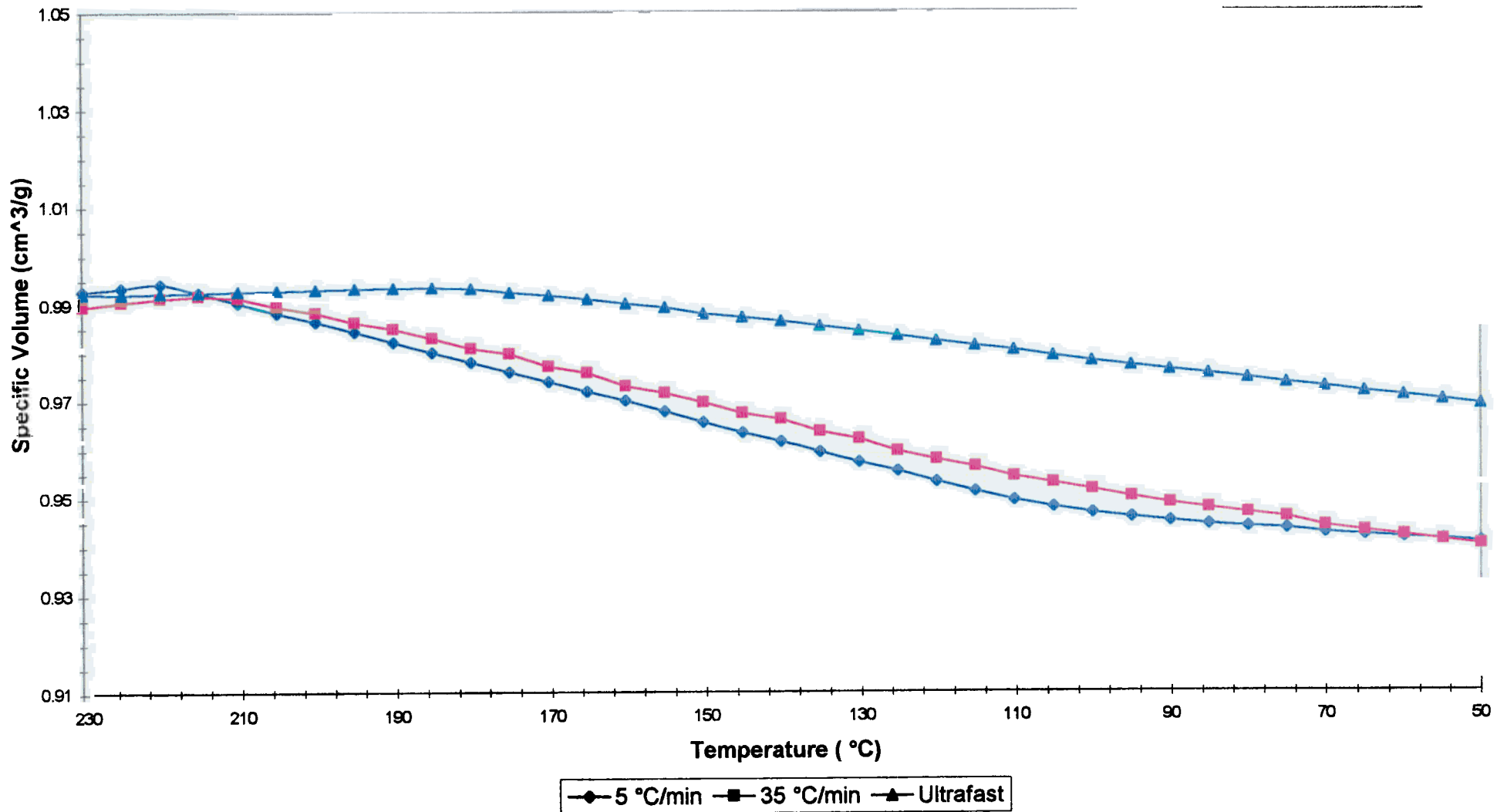


Figure 8

Effect of Cooling Rate on Specific Volume for High Density Polyethylene at 800 bar

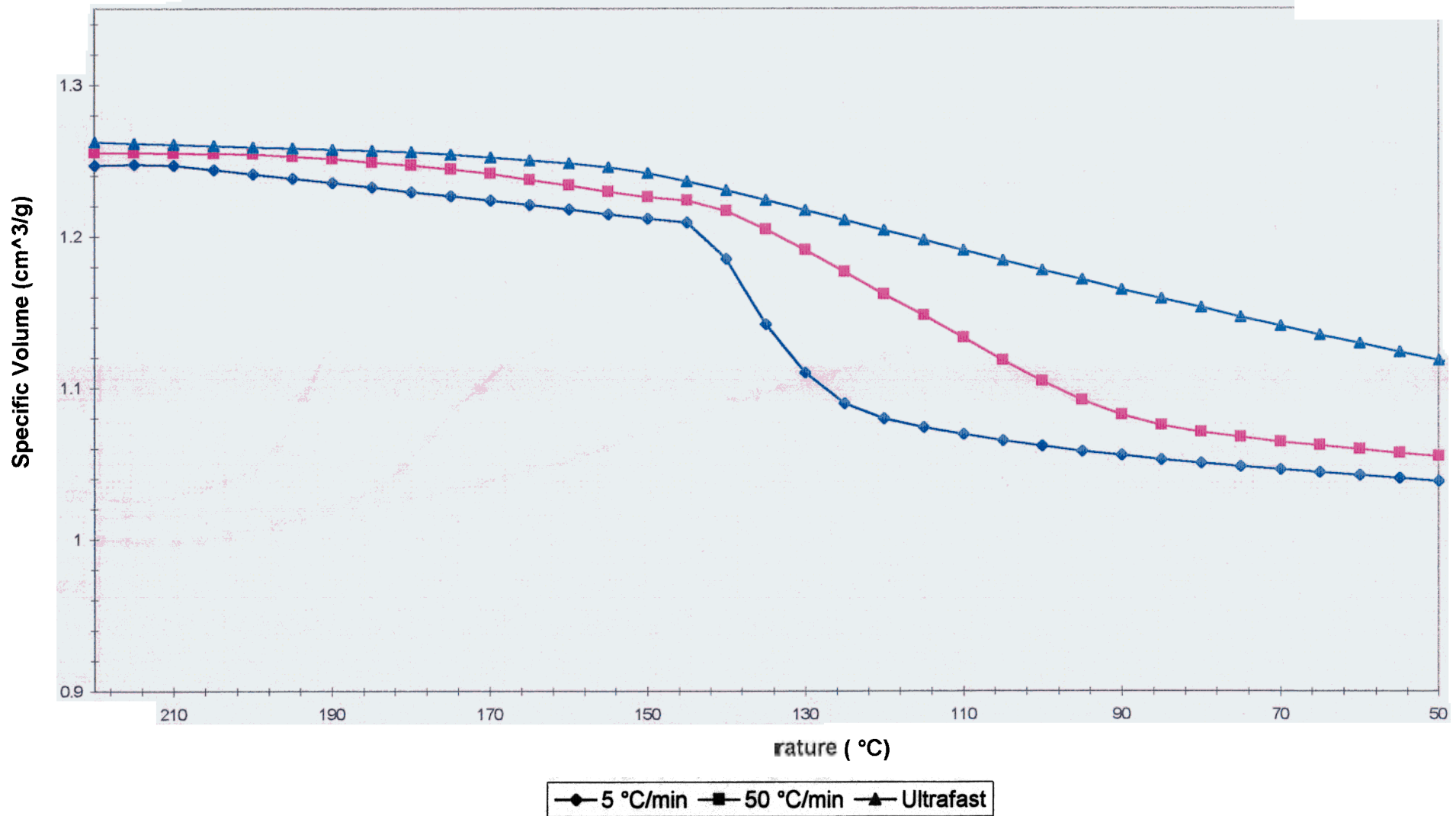


Figure 9

Effect of Cooling Rate on Specific Volume for Polyphenylene Sulphide at 800 bar

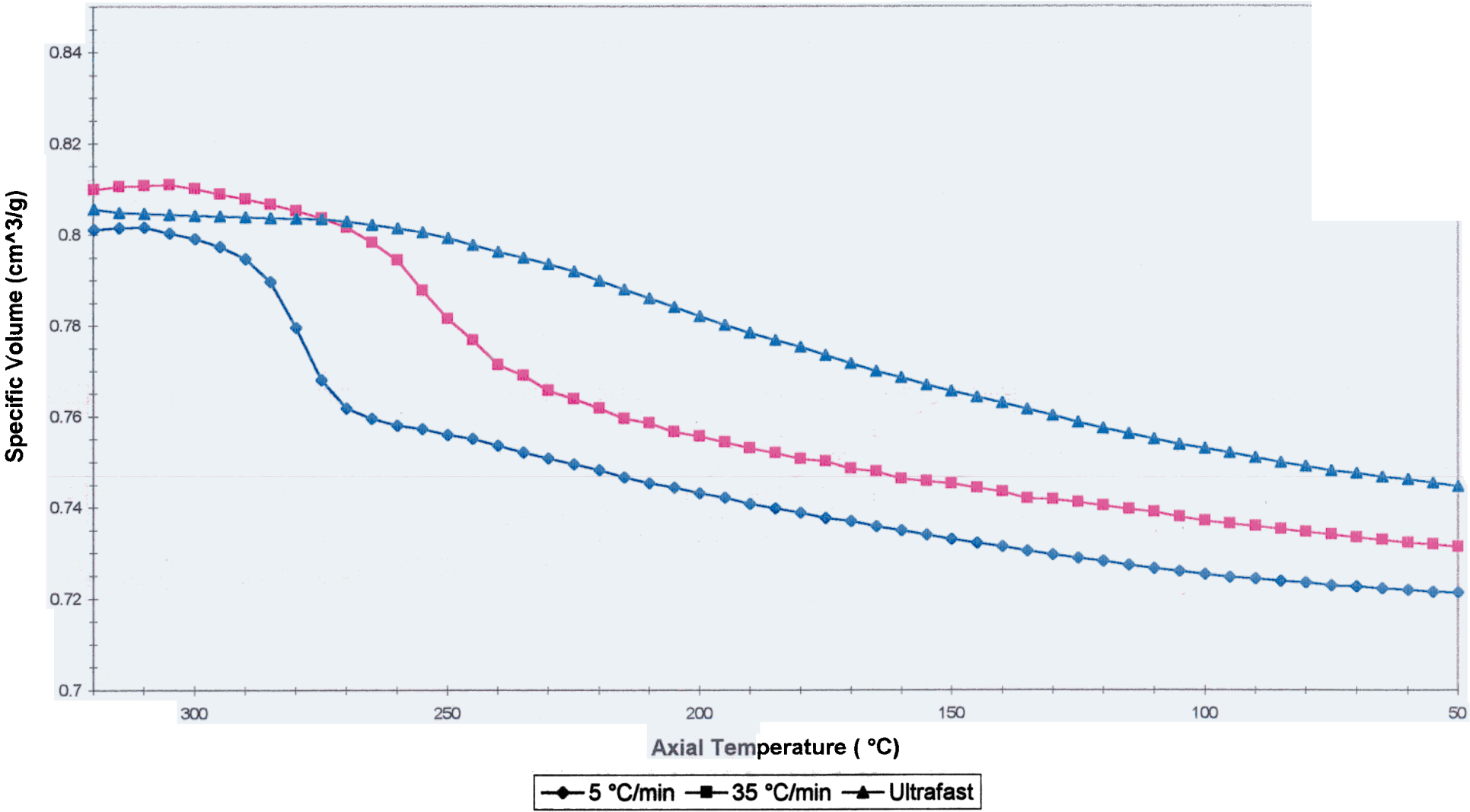


Figure 10

Effect of Pressure on High Density Polyethylene Cooled at 5 °C/minute
(Change in Specific Volume with Axial Temperature)

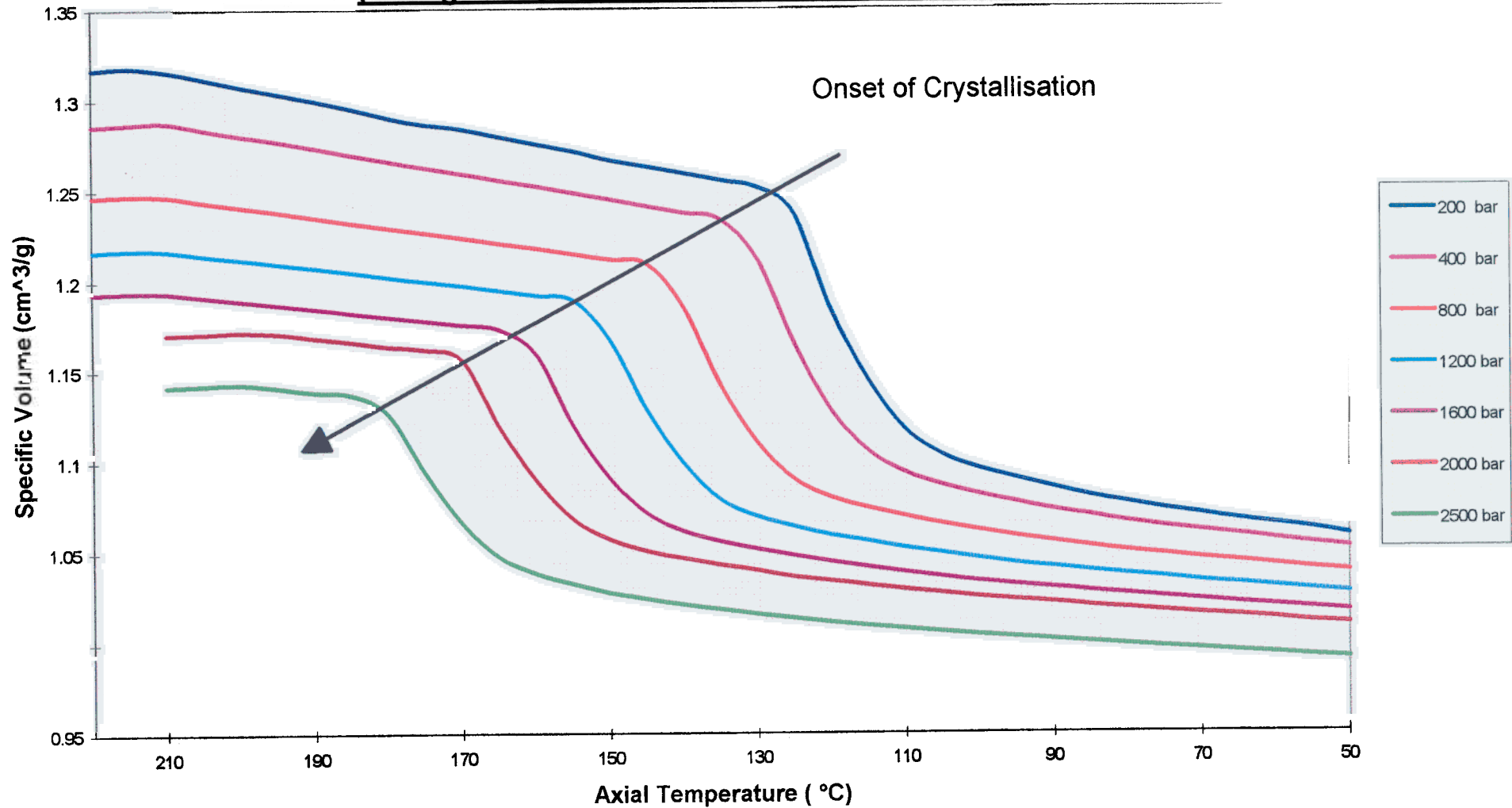


Figure 11

**Effect of Pressure on High Density Polyethylene Cooled at 5 °C/minute
(Change in Specific Volume with Radial Temperature)**

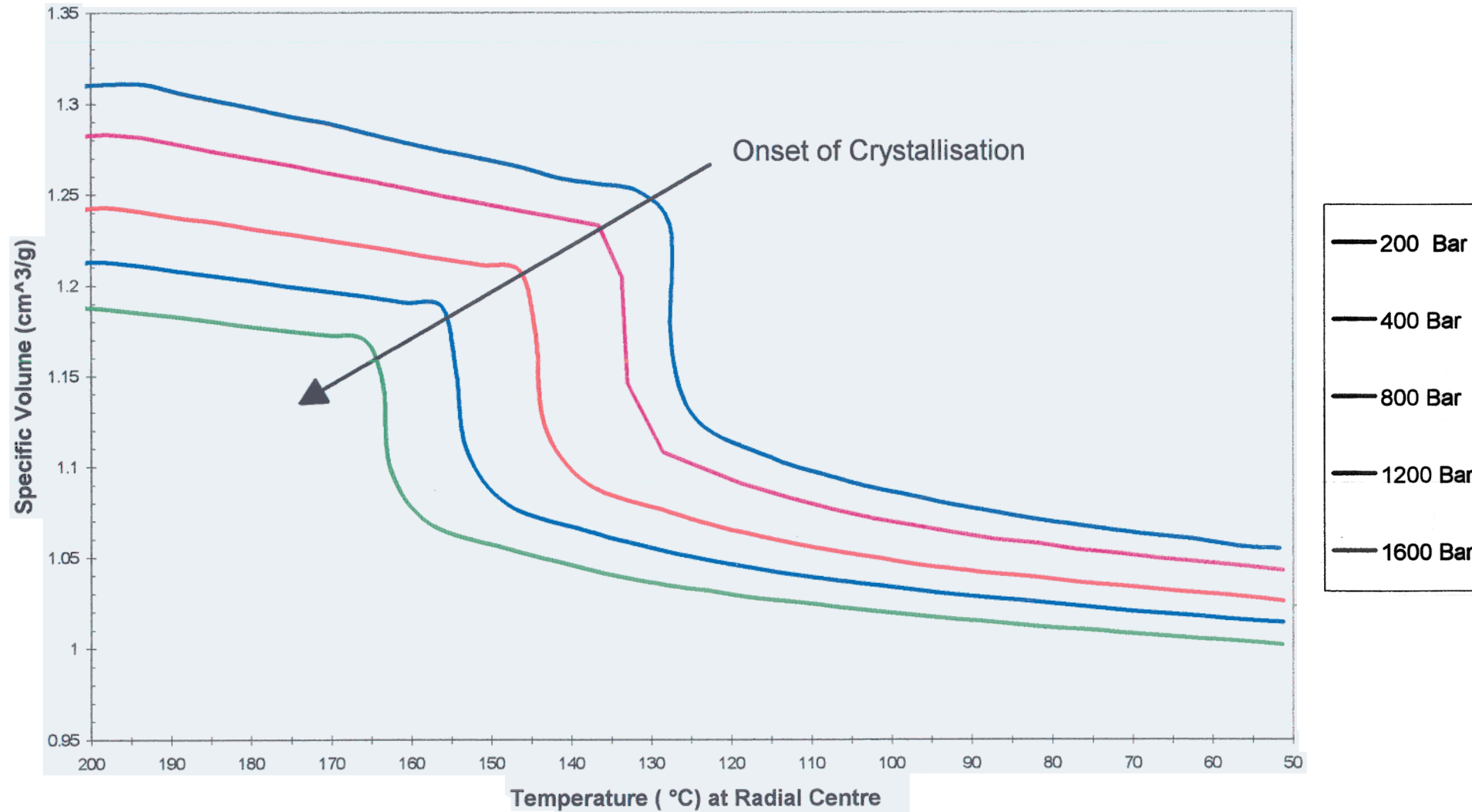
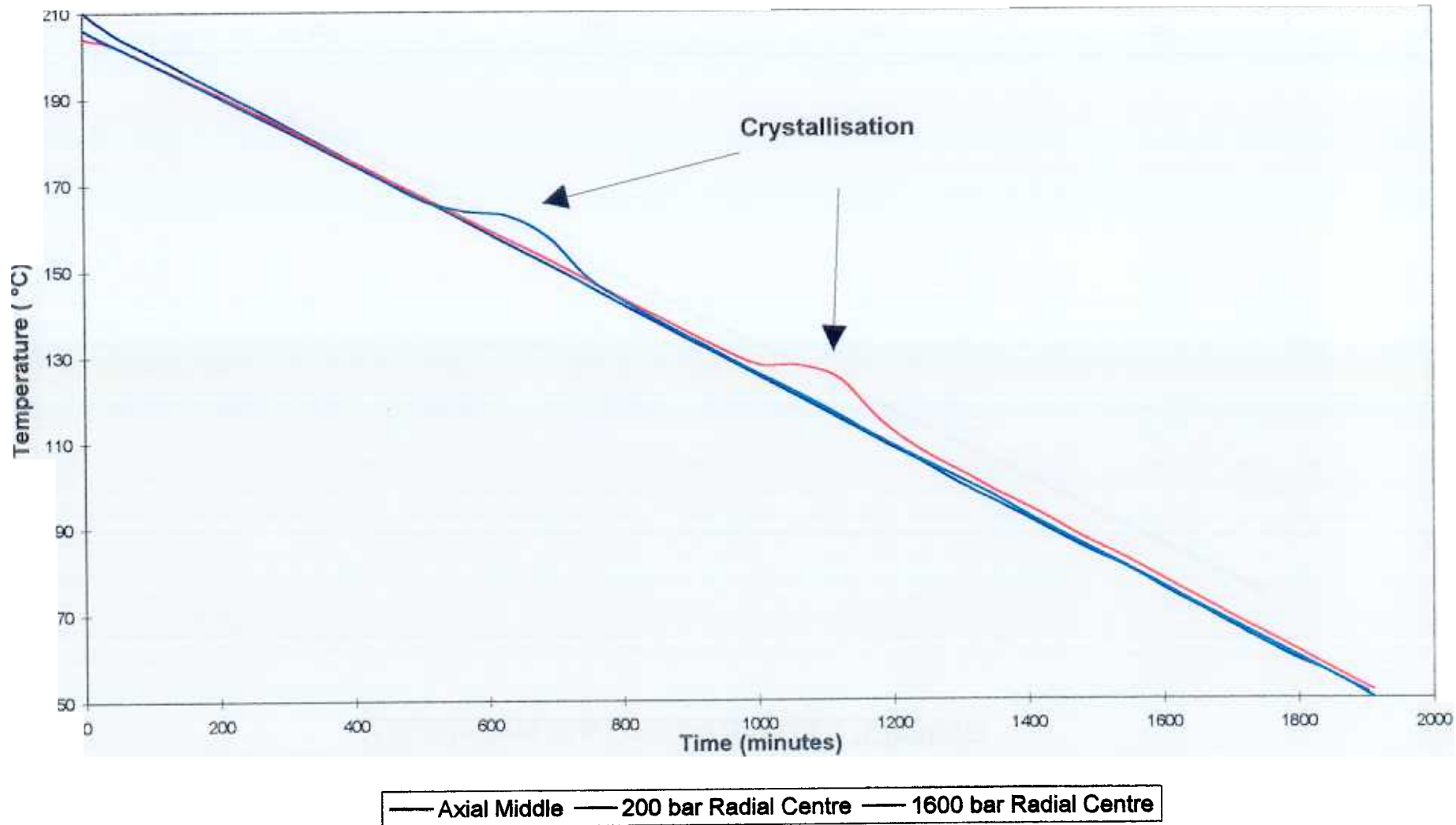


Figure 12

Effect of Pressure on Crystallisation Temperature for High Density Polyethylene at 200 and 1600 bar
Cooled at 5 °C/minute



PVT/7.8mmcell/7.8mmcool/CHPE038cool

Figure 13

Effect of Pressure on the Crystallisation Onset Temperature of High Density Polyethylene at a Cooling Rate of 5 °C/minute

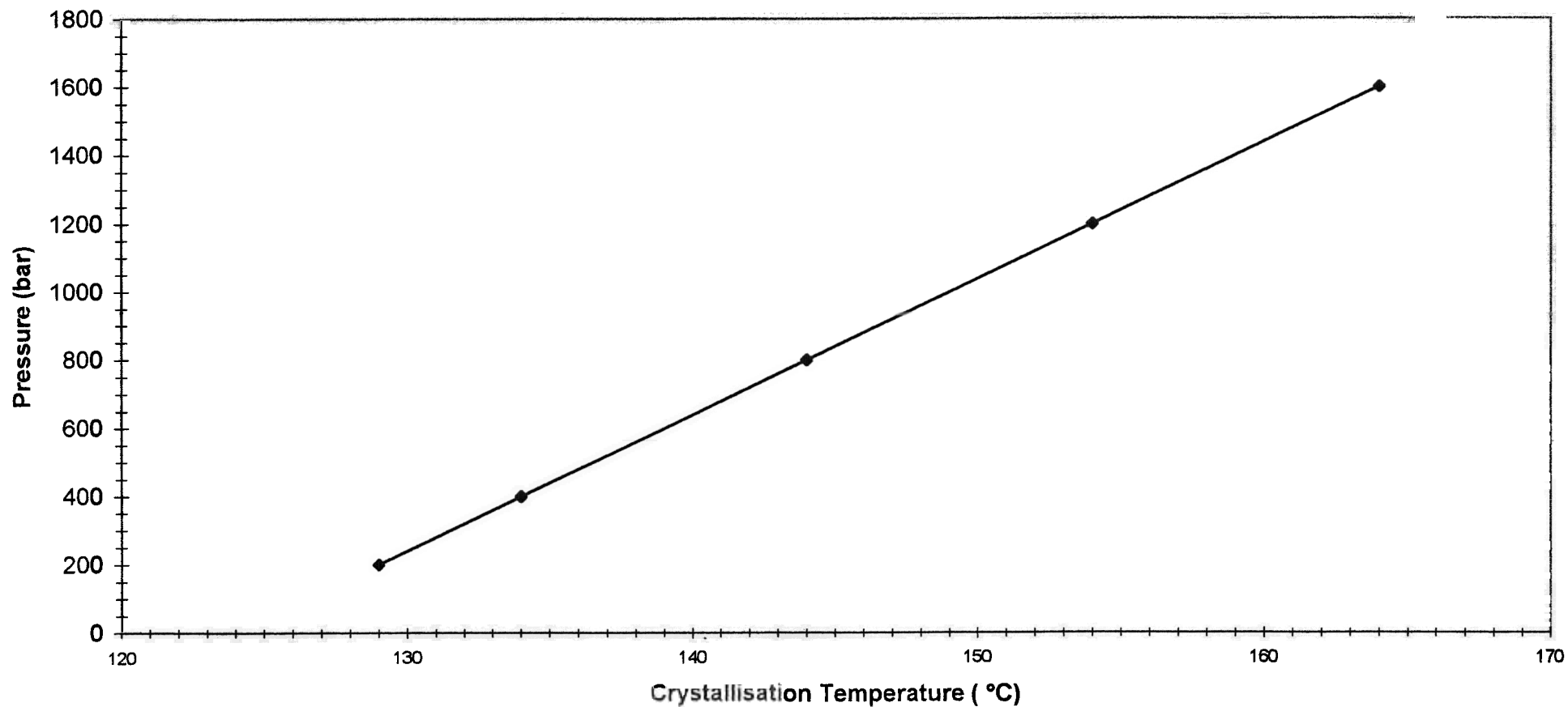


Figure 14

Effect of Pressure on Ultrafast Isobaric Cooling of High Density Polyethylene
(Change in Specific Volume with Axial Temperature)

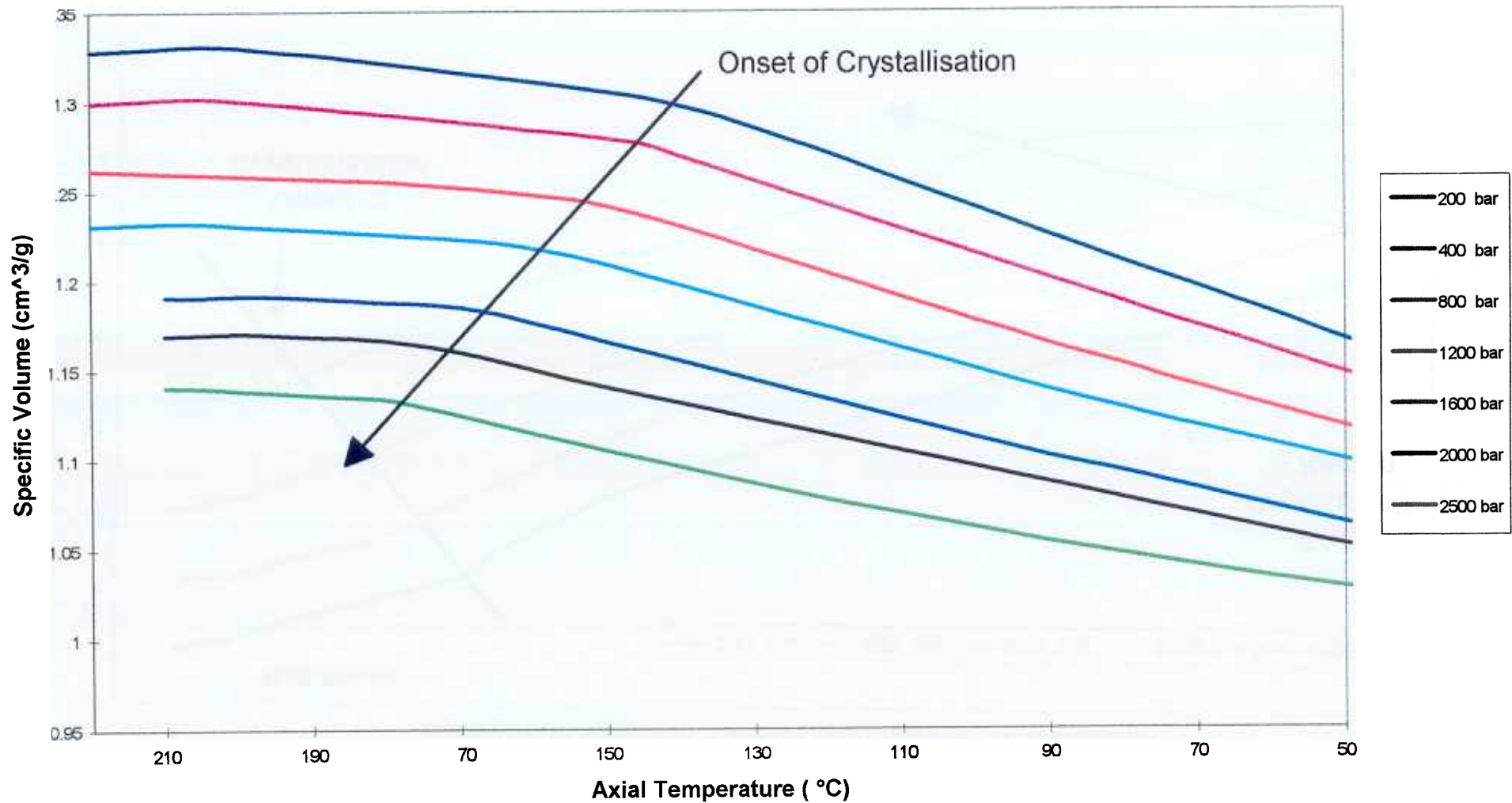


Figure 17

**Contributions to the Overall Shrinkage of High Density Polyethylene at 200
bar Cooled at 5 °C/minute**

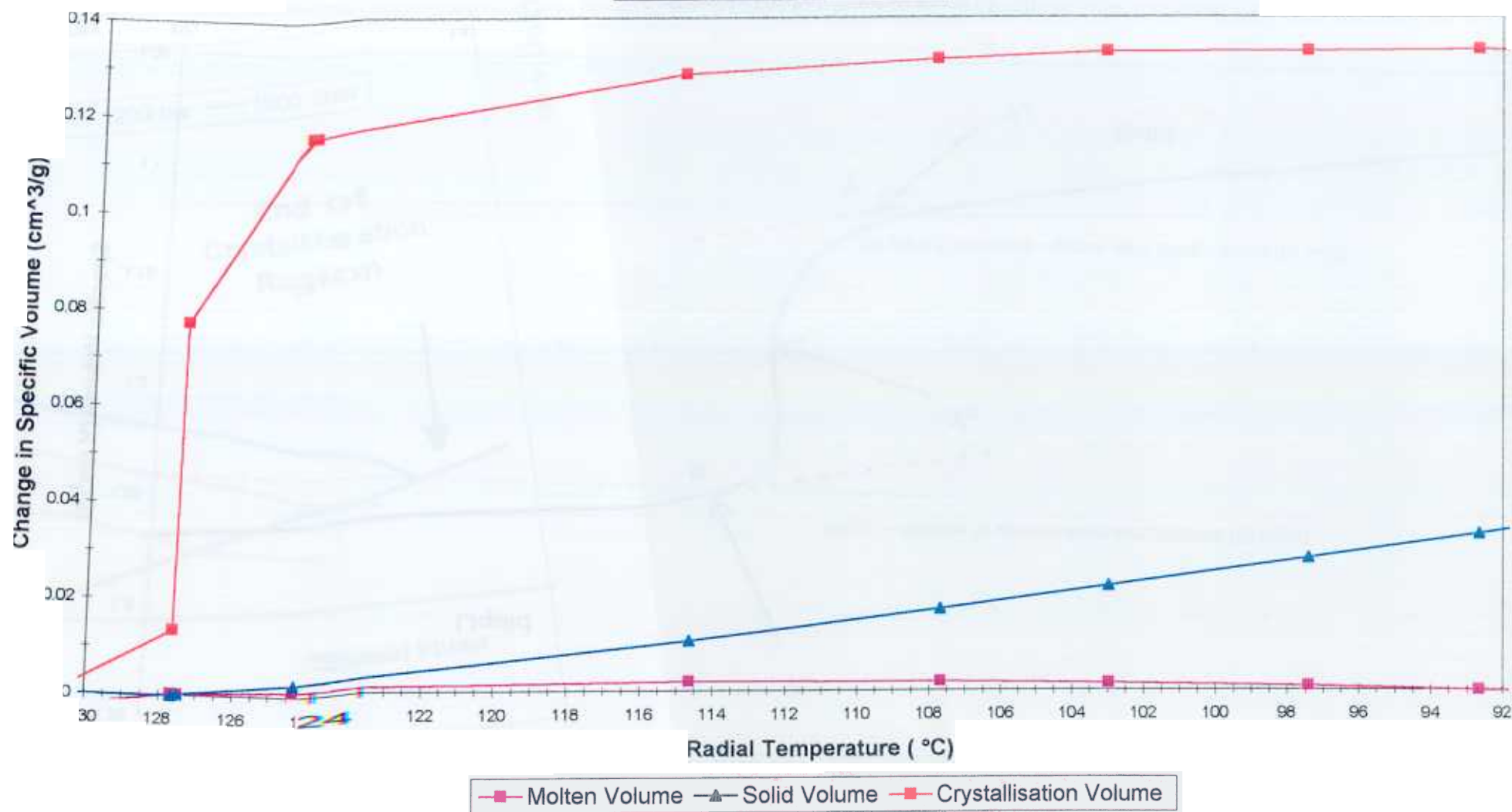
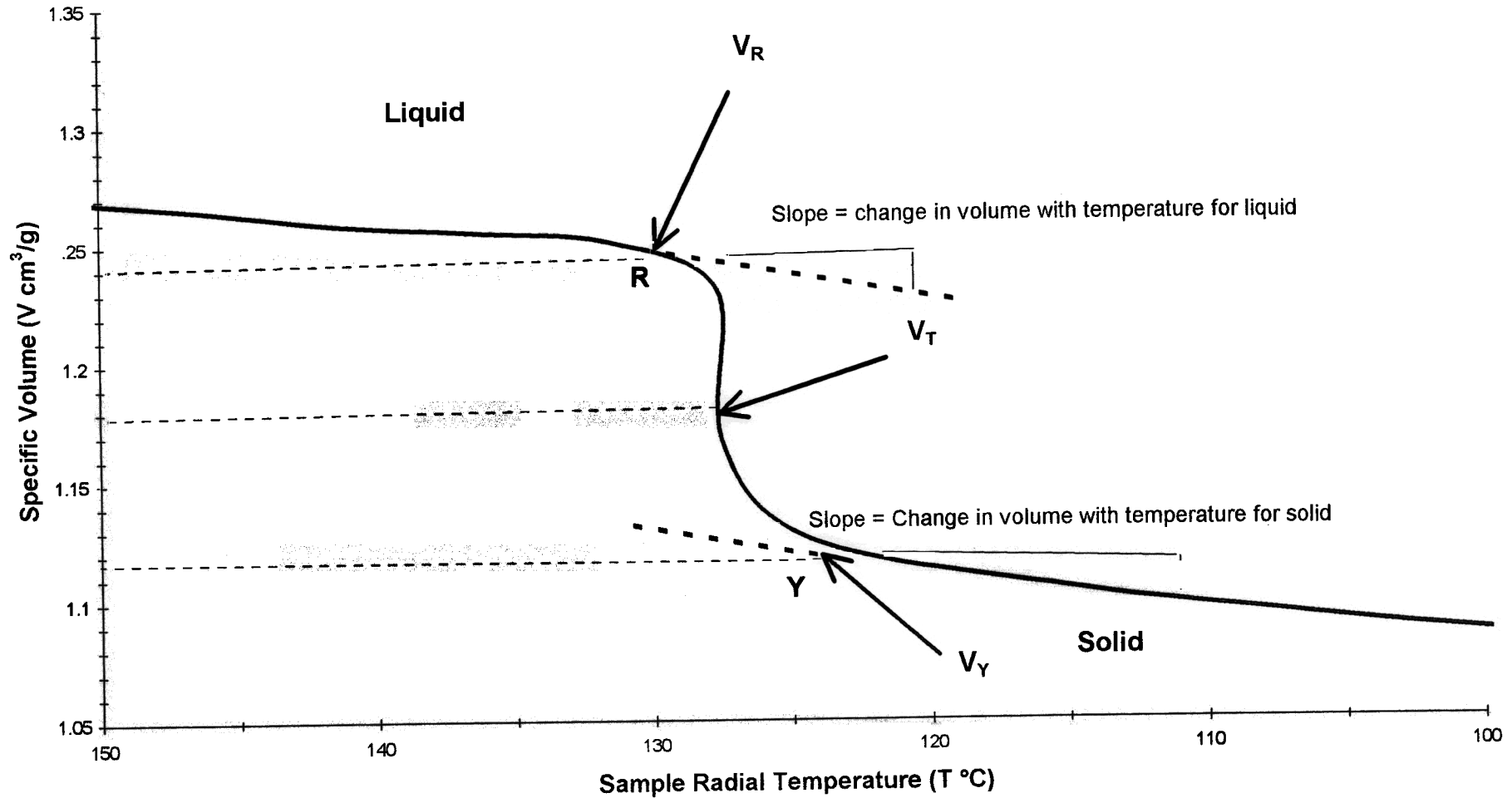


Figure 16

Isobaric Cooling at a Rate of 5 °C /minute for High Density Polyethylene at 200 Bar



Schematic PVT curve (for one pressure only) indicating the extrapolation procedure to determine the contribution to the total volume reduction from the thermal contraction of the liquid phase and the solid phase. See text for details.

Figure 19

**Effect of Sample Height for High Density Polyethylene at 1600 bar and 5 °C/minute
Cooling Rate (standard cell)**

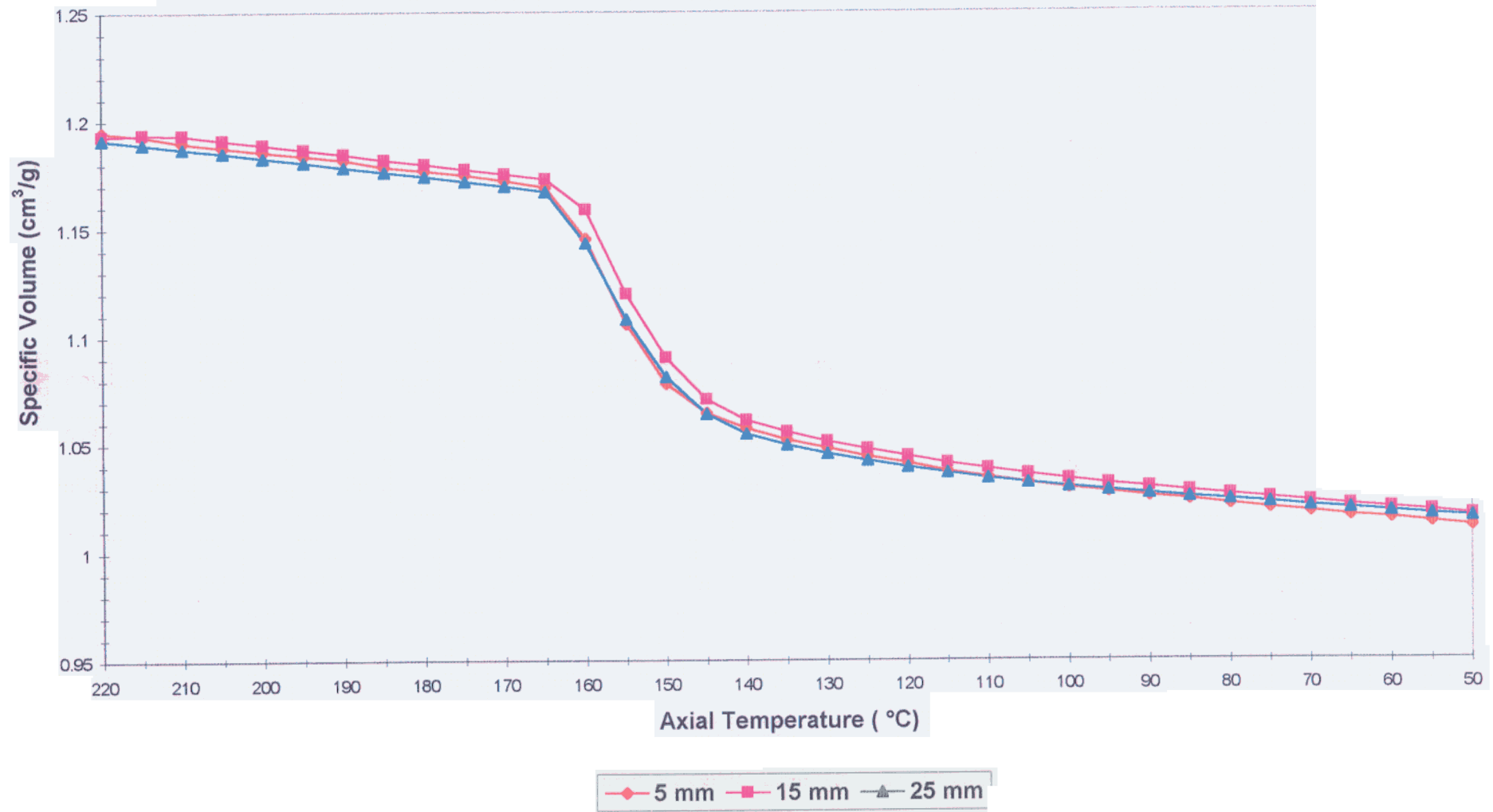


Figure 18

Contribution to the Overall Shrinkage of High Density Polyethylene at 1600 bar Ultrafast Cooled

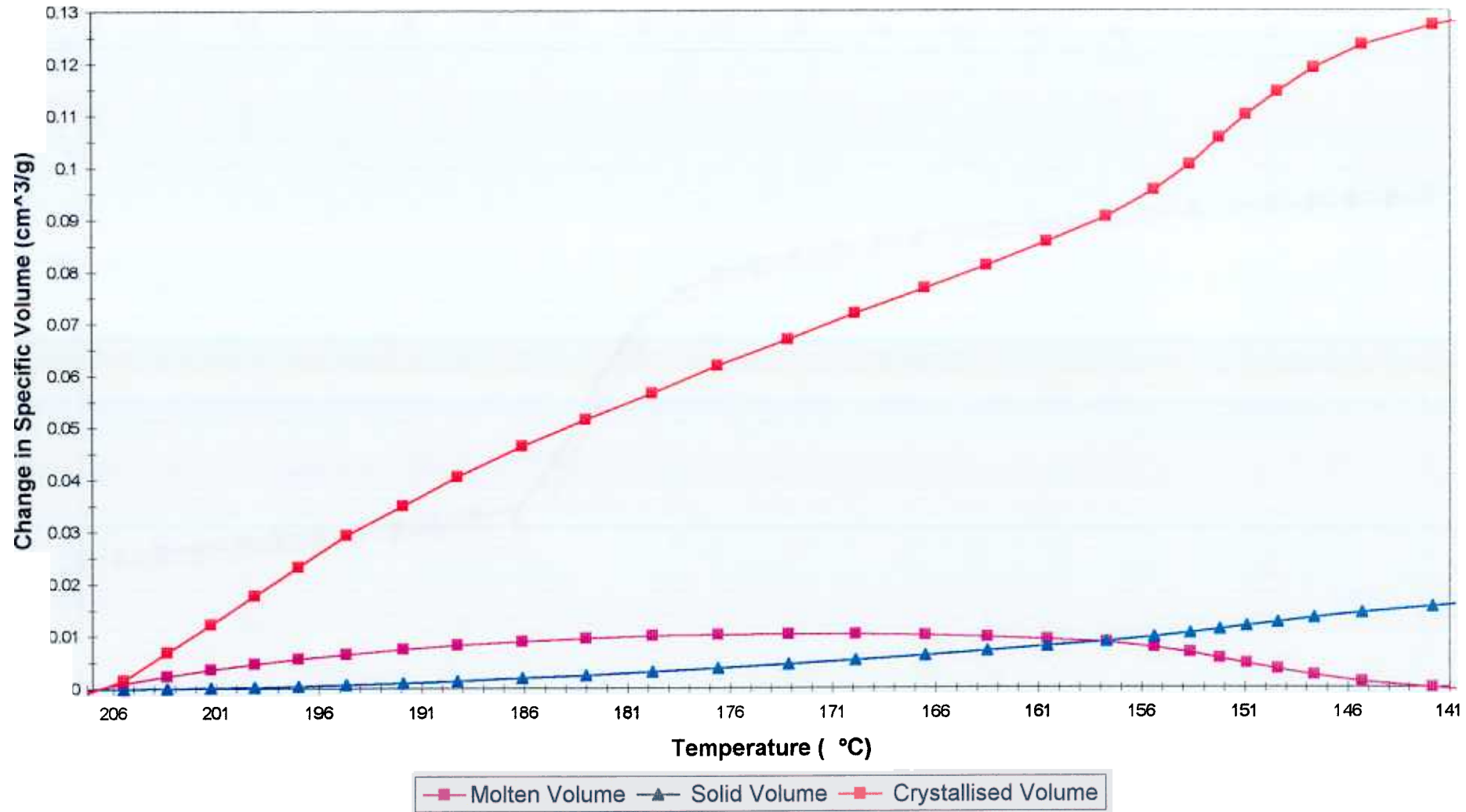


Figure 21

Effect of Sample Height for Polystyrene at 1600 bar Cooled at 5 °C/min (standard cell)

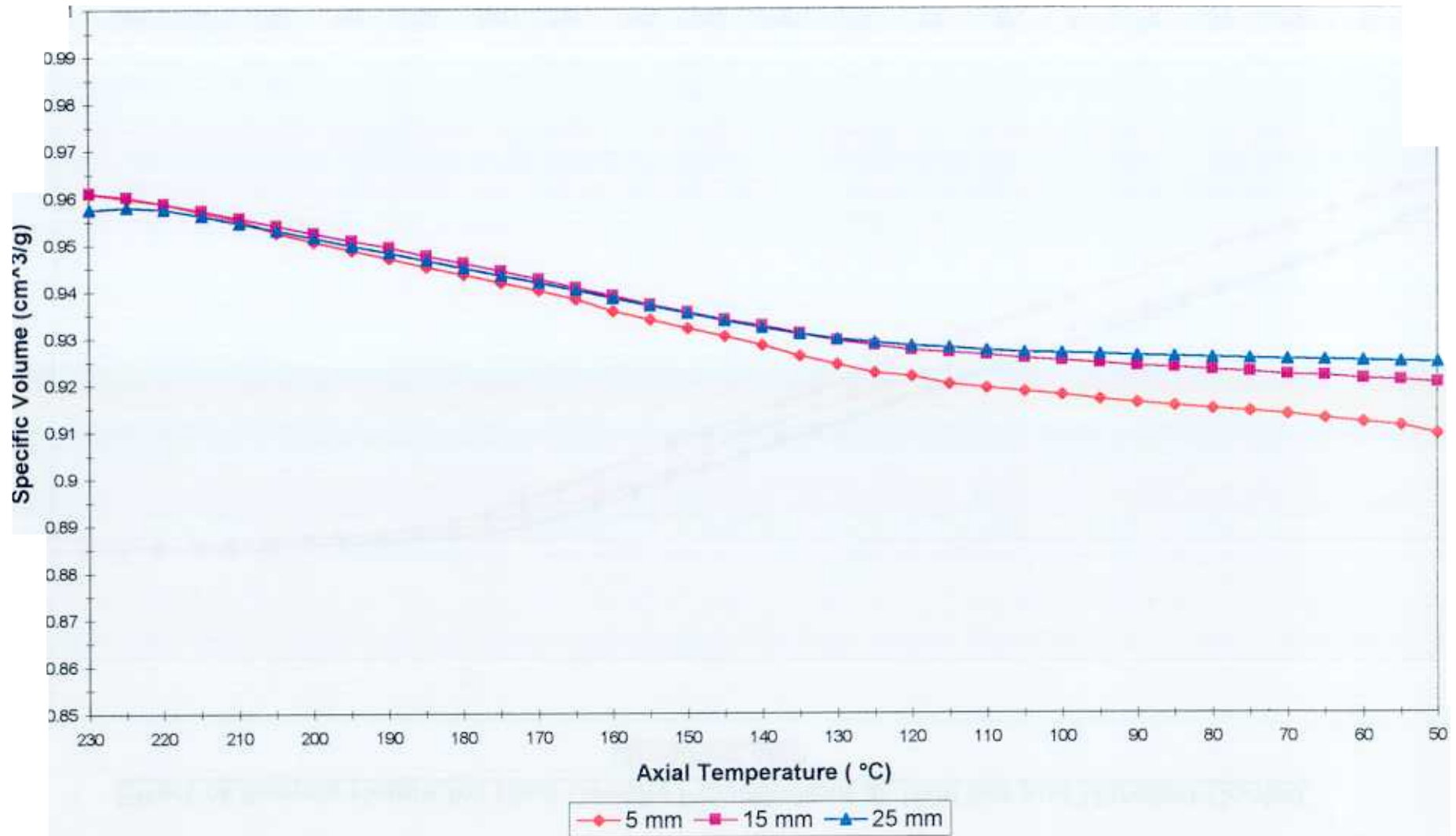


Figure 20

Effect of Sample Height for High Density Polyethylene at 1600 bar and Ultrafast Cooled
(standard cell)

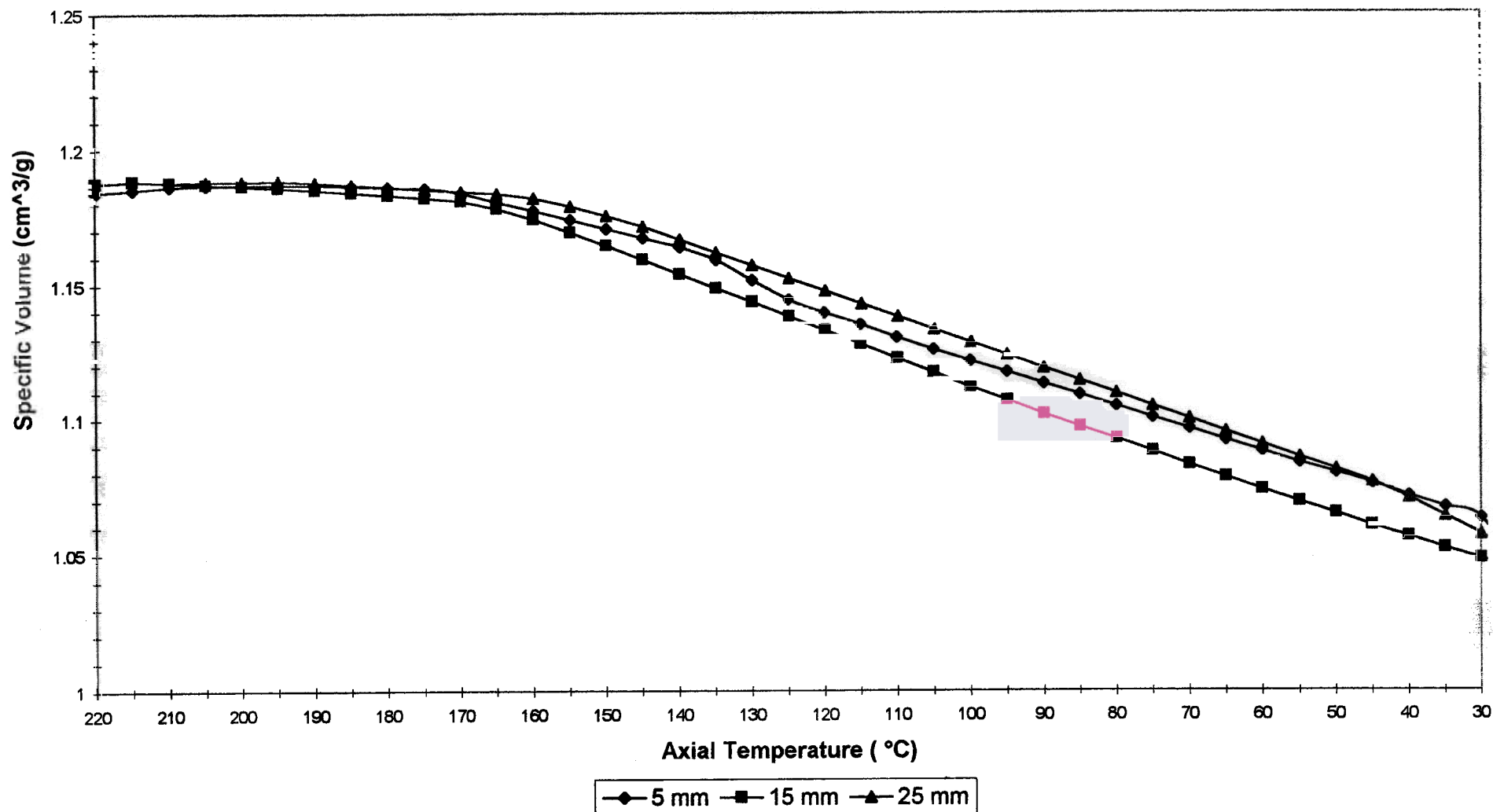
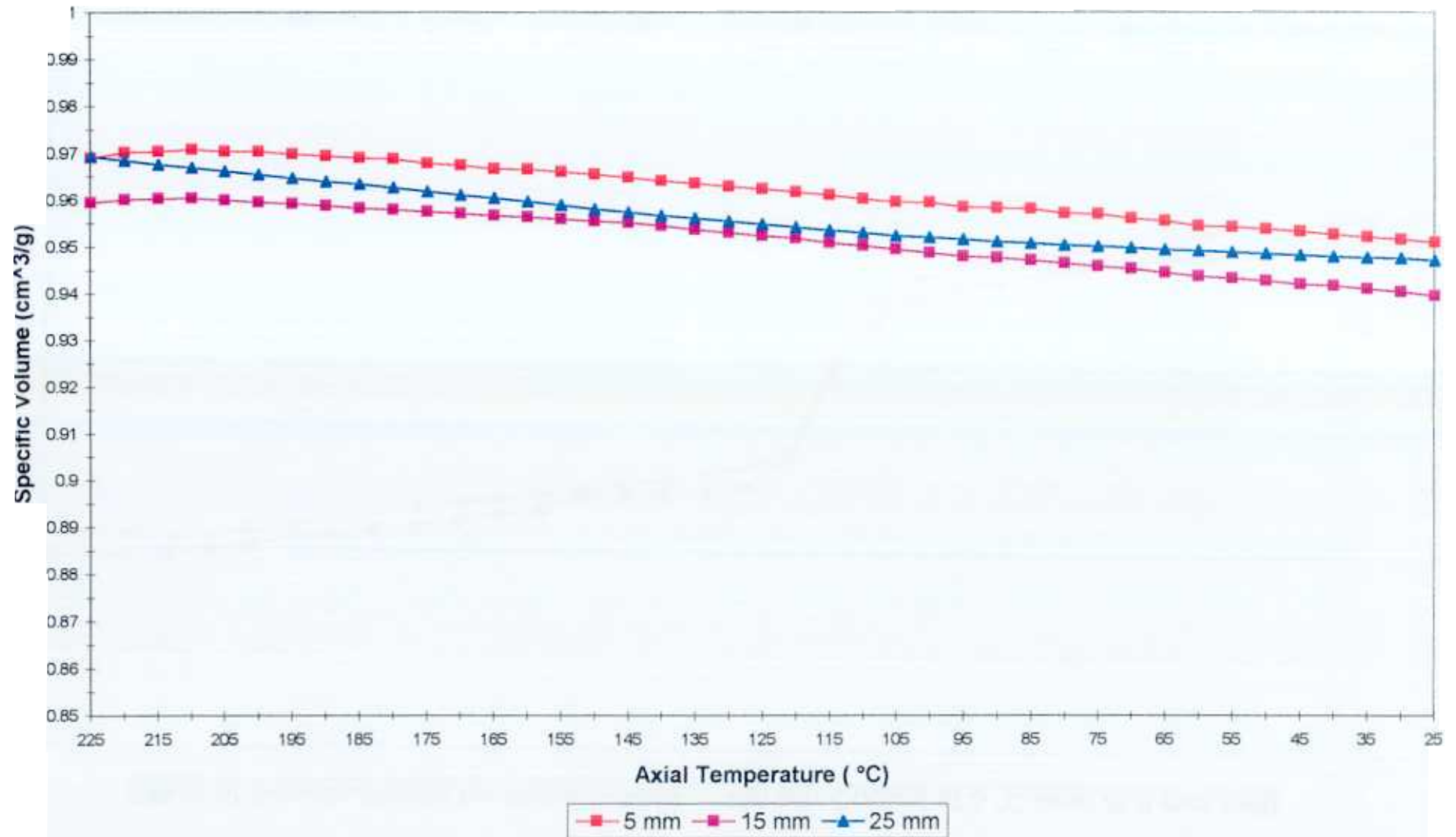


Figure 22

Effect of Sample Height for Polystyrene at 1600 bar and Ultrafast Cooled (standard cell)



PVT/CompheightPS

Figure 23

Effect of Sample Height for Polyethylene at 400 bar Cooled at 5 °C /min (6.0 mm cell)

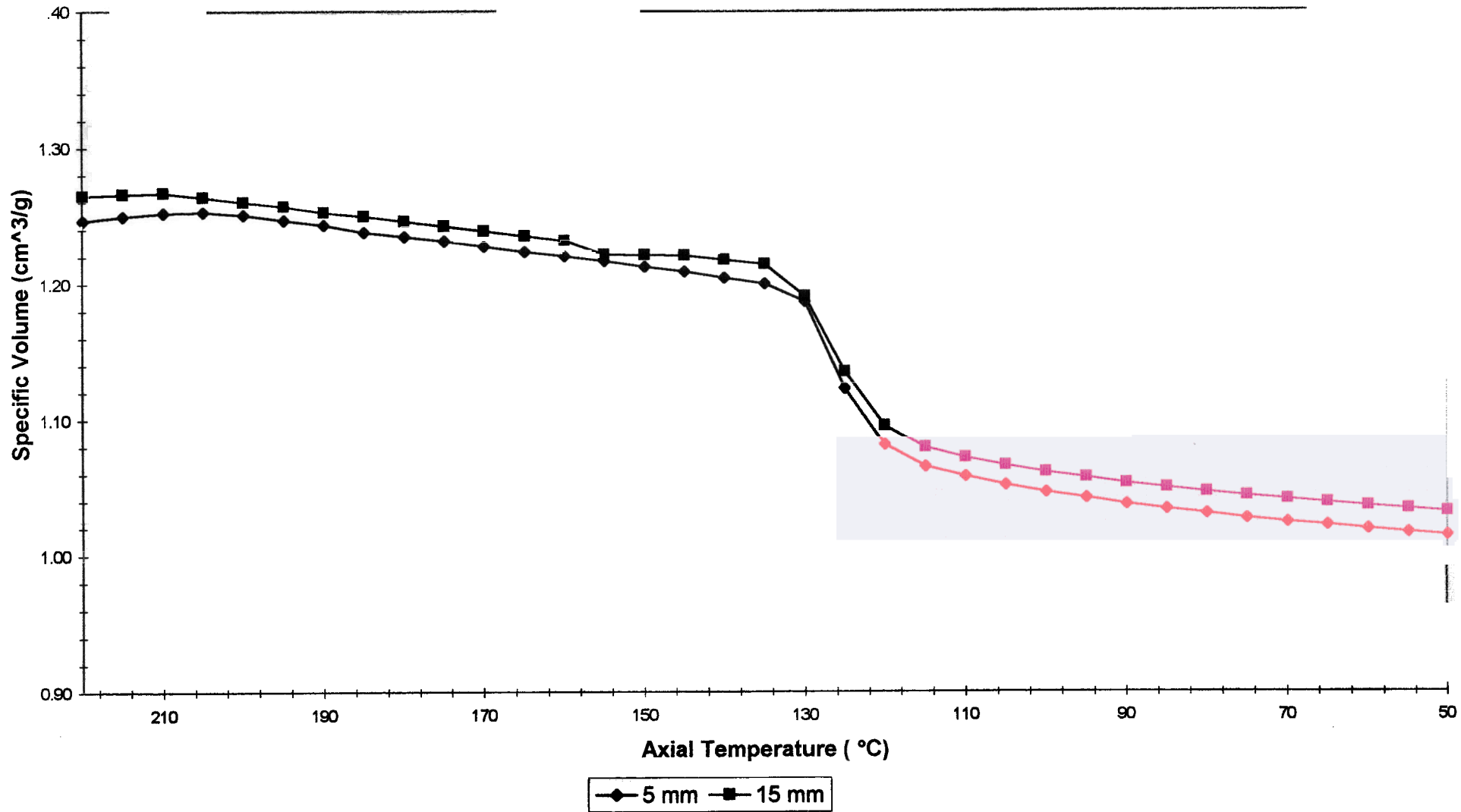
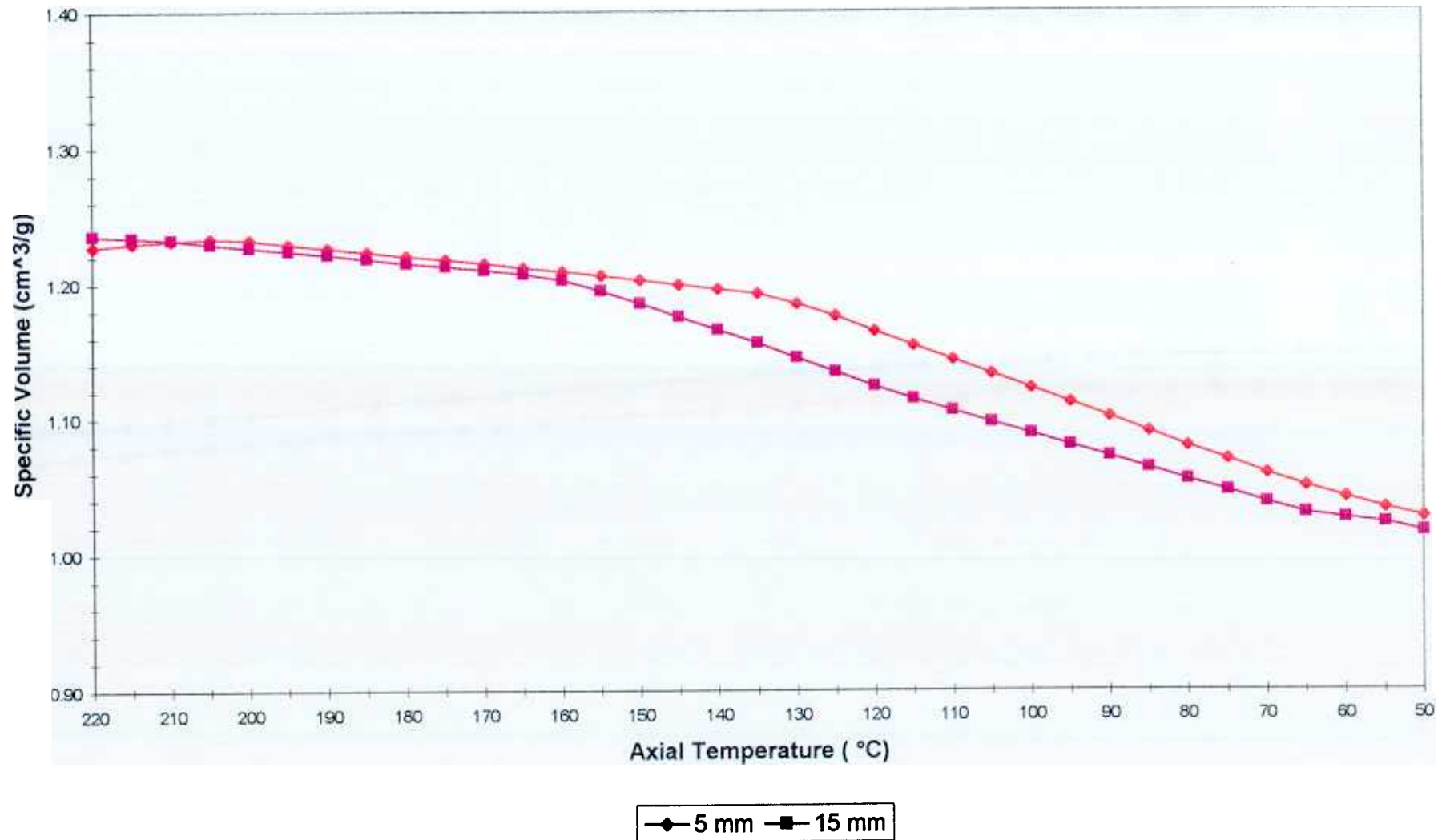


Figure 24

Effect of Sample Height for Polyethylene at 400 bar and Ultrafast Cooled (6.0 mm cell)



PVT/CompheighPE/6mm

Figure 25

Effect of Sample Height for Polystyrene at 400 bar and Cooled at 5°C/min (6 mm cell)

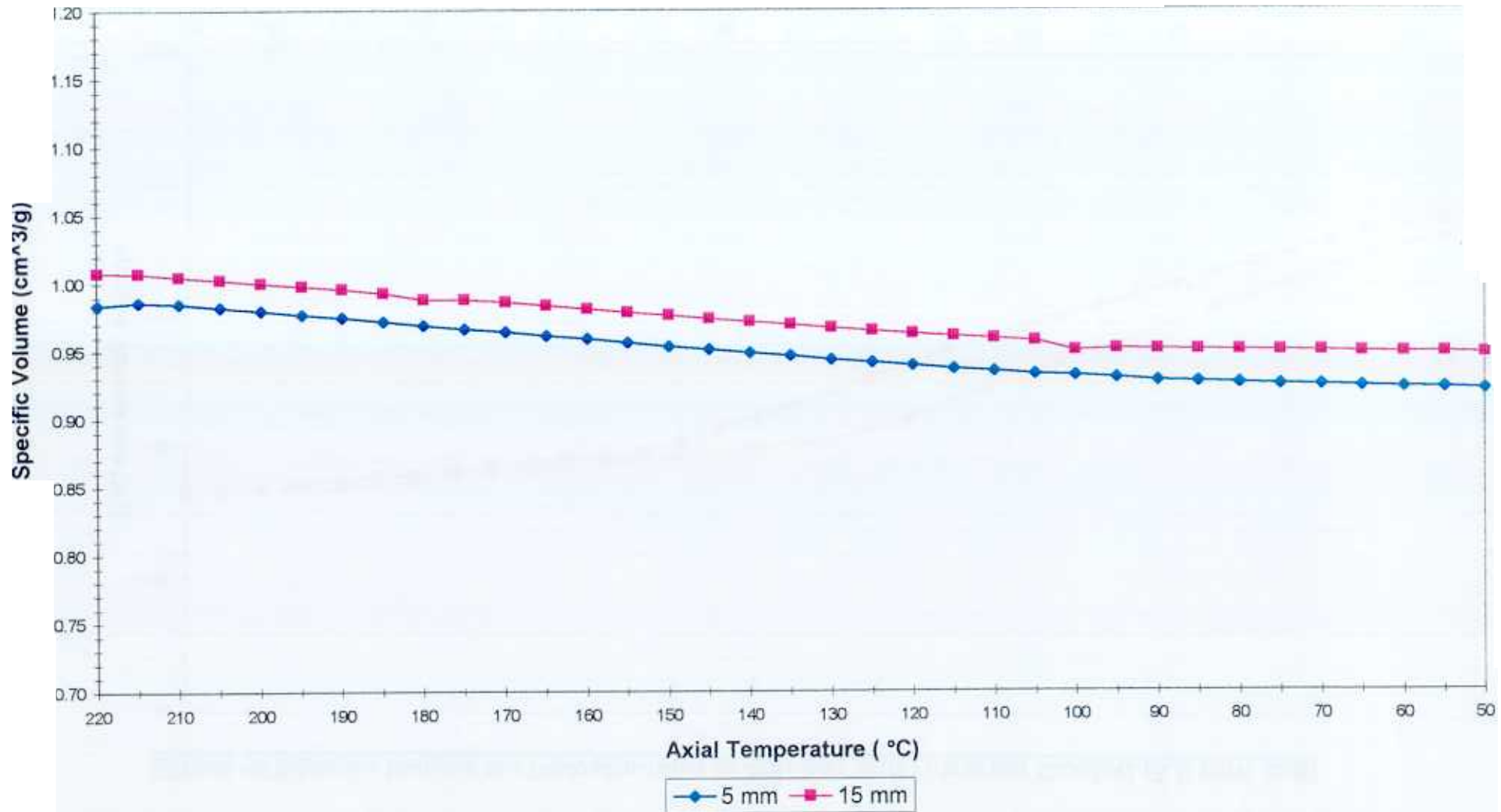
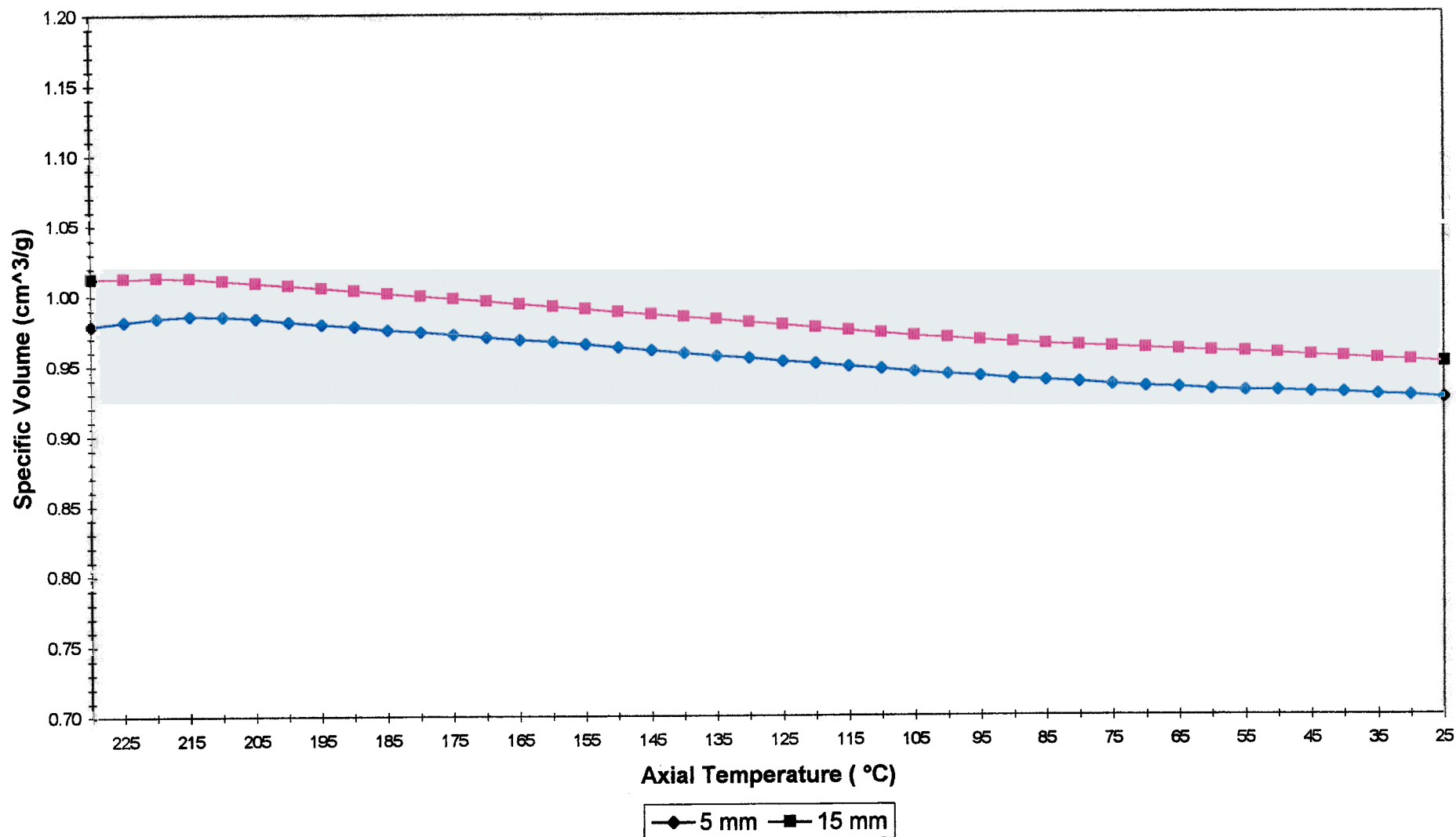


Figure 26

Effect of Sample Height for Polystyrene at 400 bar and Ultrafast Cooled (6 mm cell)



PVT/ComheightPS6mm

Figure 27

Effect of Sample Height for High Density Polyethylene at 400 bar Cooled at 5 °C/min
(14.0 mm cell)

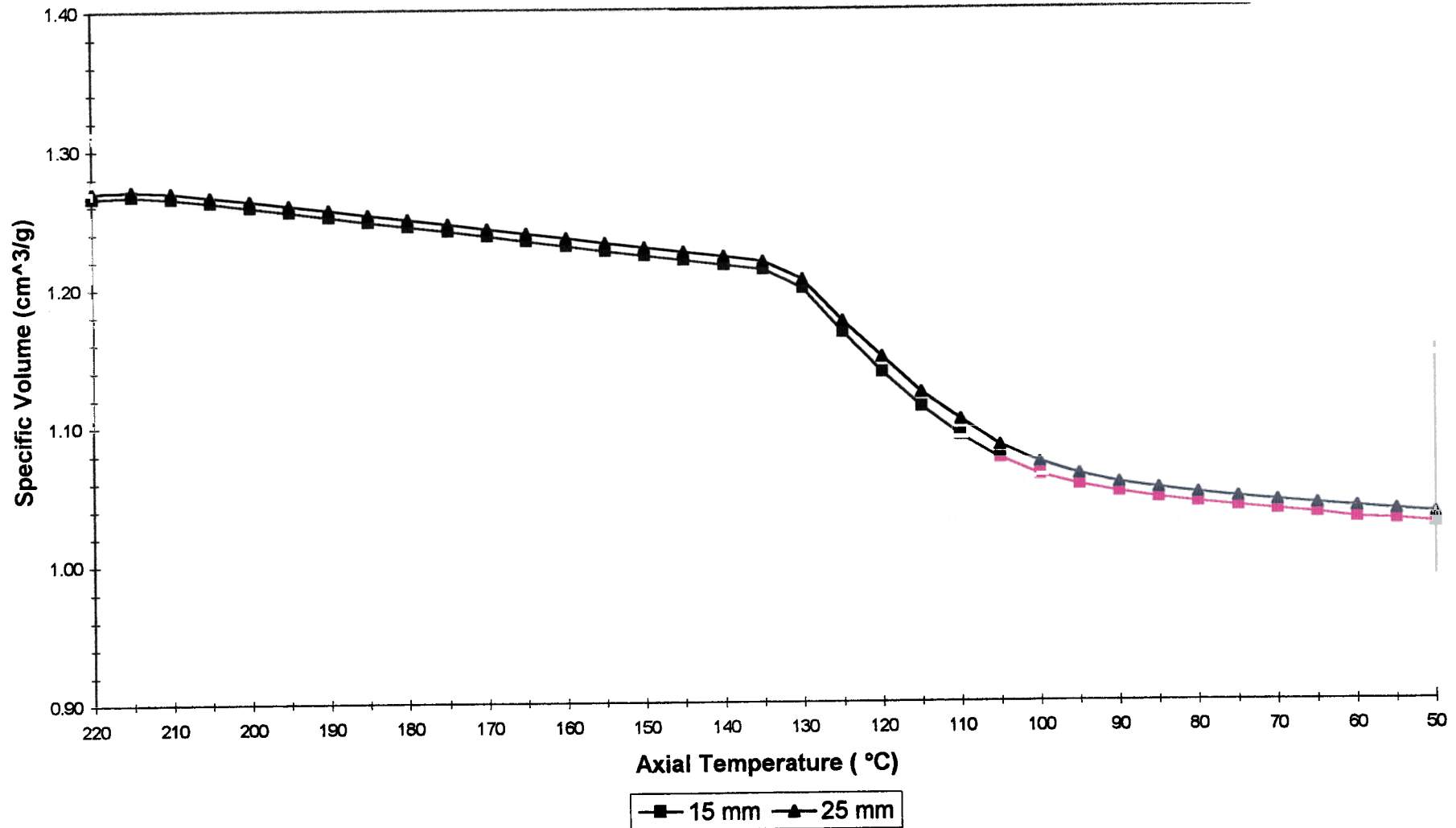
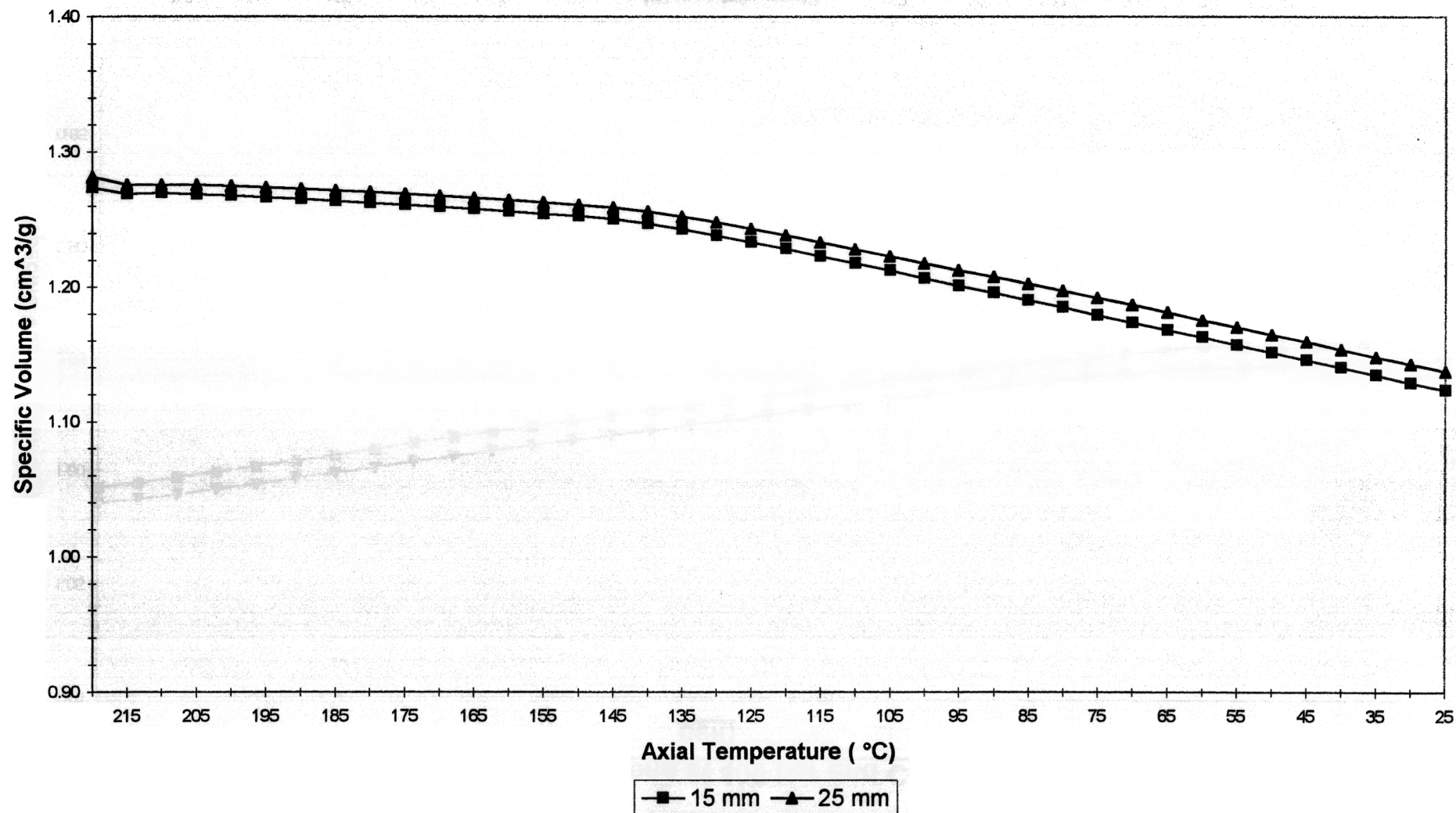


Figure 28

Effect of Sample Height for High Density Polyethylene at 400 bar and Ultrafast Cooled
(14.0 mm cell)



PVT/comparheightPE6mm

Figure 29

Effect of Sample Height for Polystyrene at 400 bar and Cooled at 5 °C/min (14.0 mm cell)

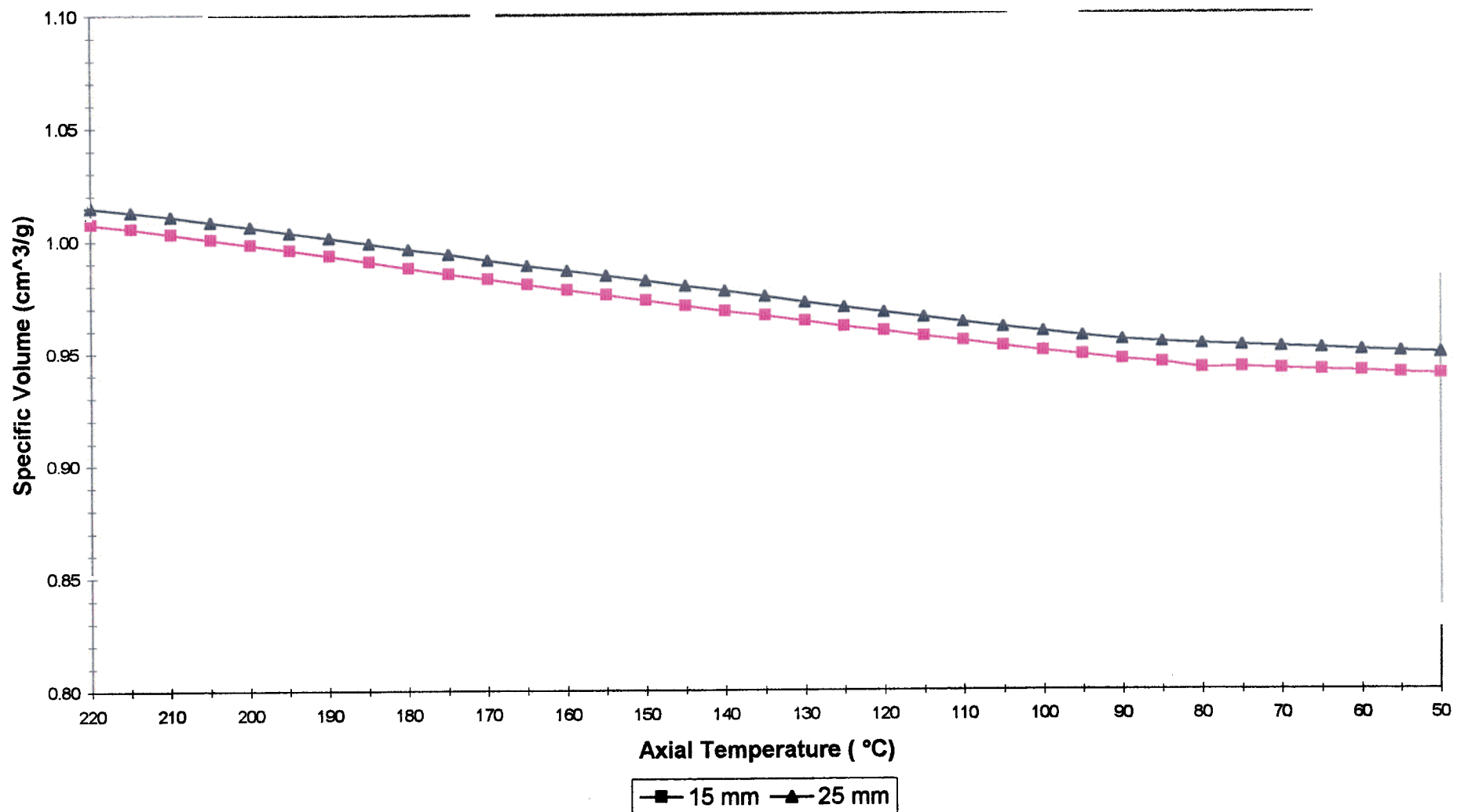
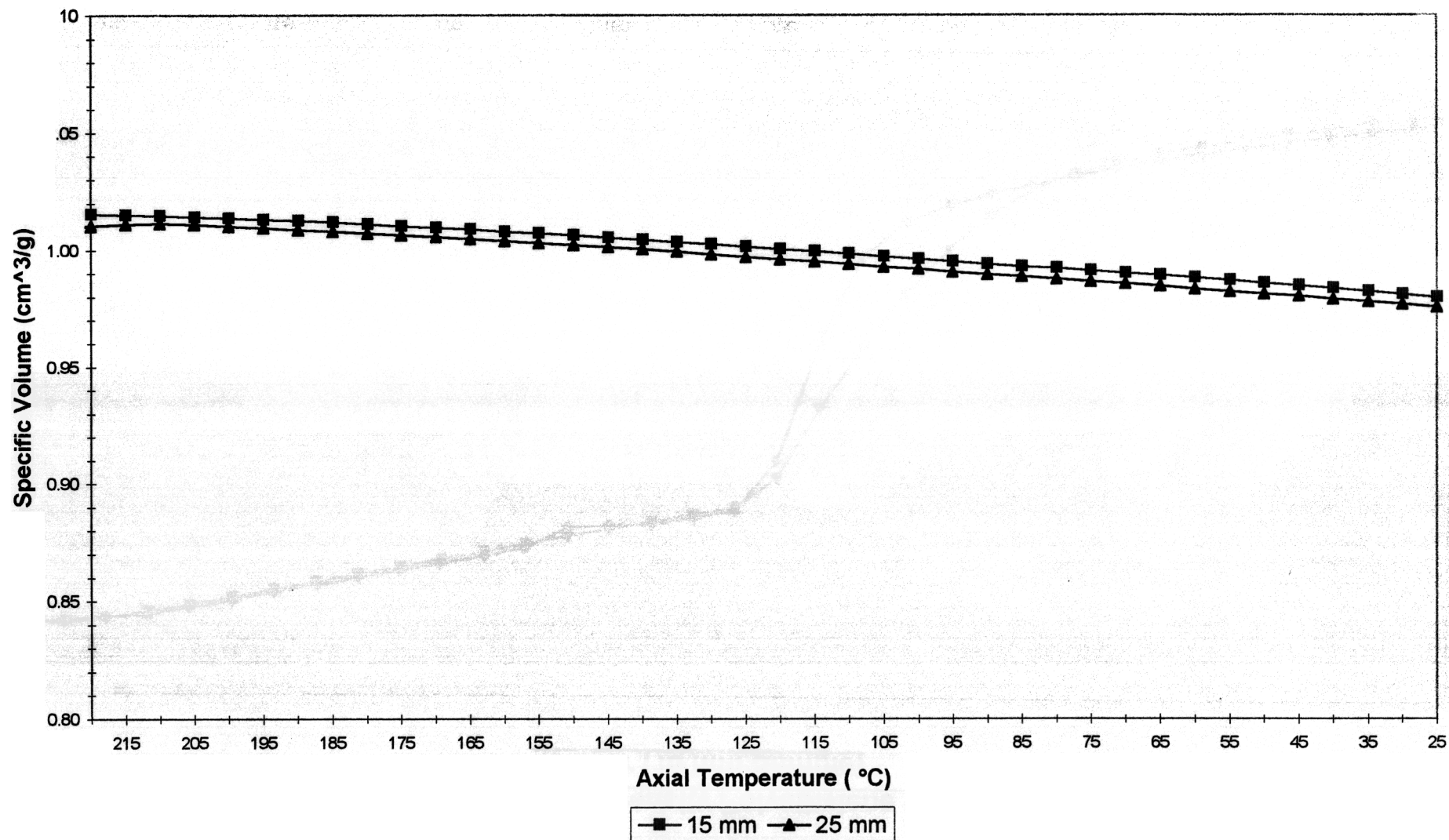


Figure 30

Effect of Sample Height for Polystyrene at 400 bar and Ultrafast Cooled (14.0 mm cell)



PVT/ComheightPS6mm

Figure 31

Effect of Test Cell Diameter for High Density Polyethylene Cooled at 5 °C/minute under 400 bar (15 mm Sample)

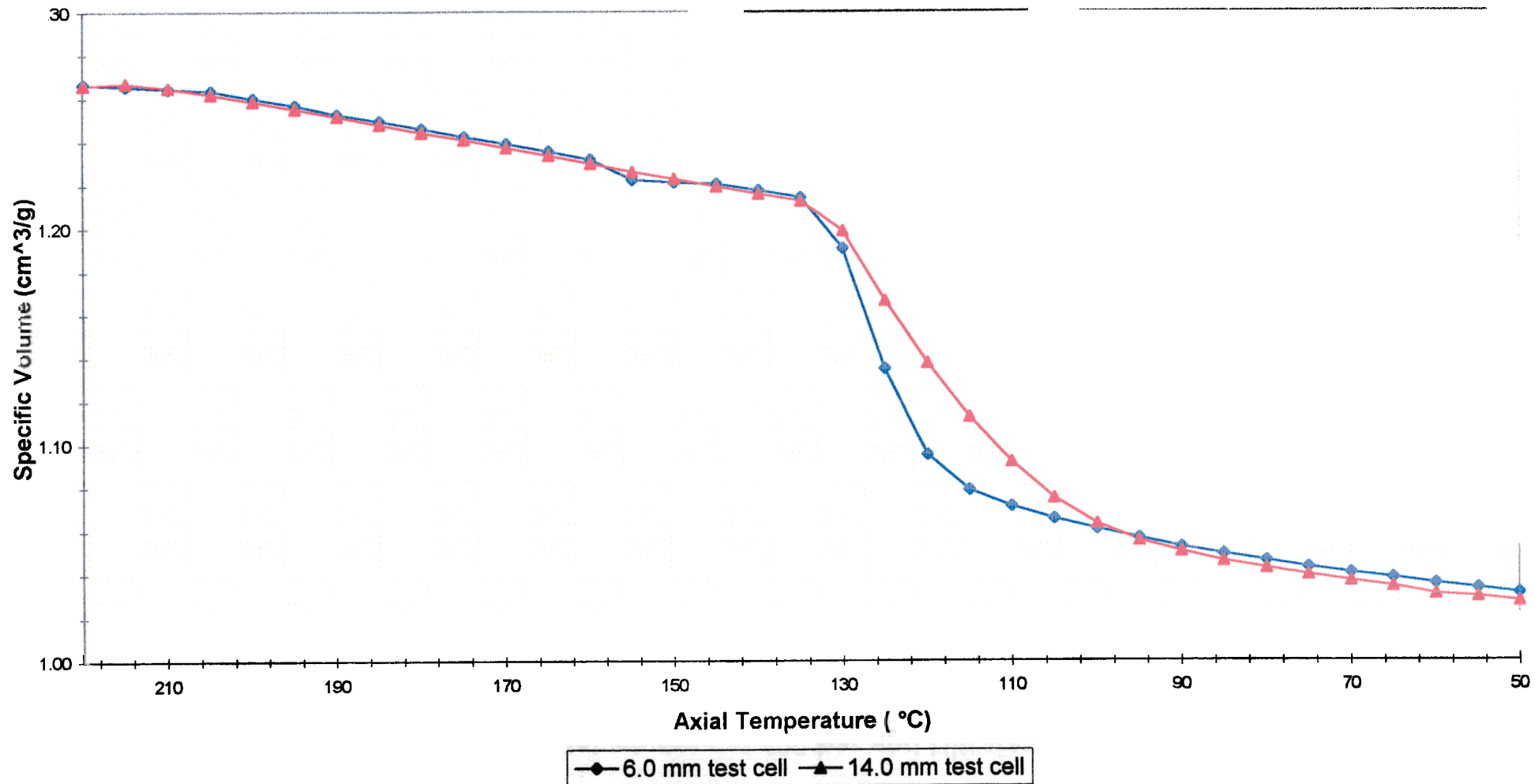


Figure 32

Effect of Test Cell Diameter for High Density Polyethylene Ultrafast Cooled under 400 bar (15 mm Sample)

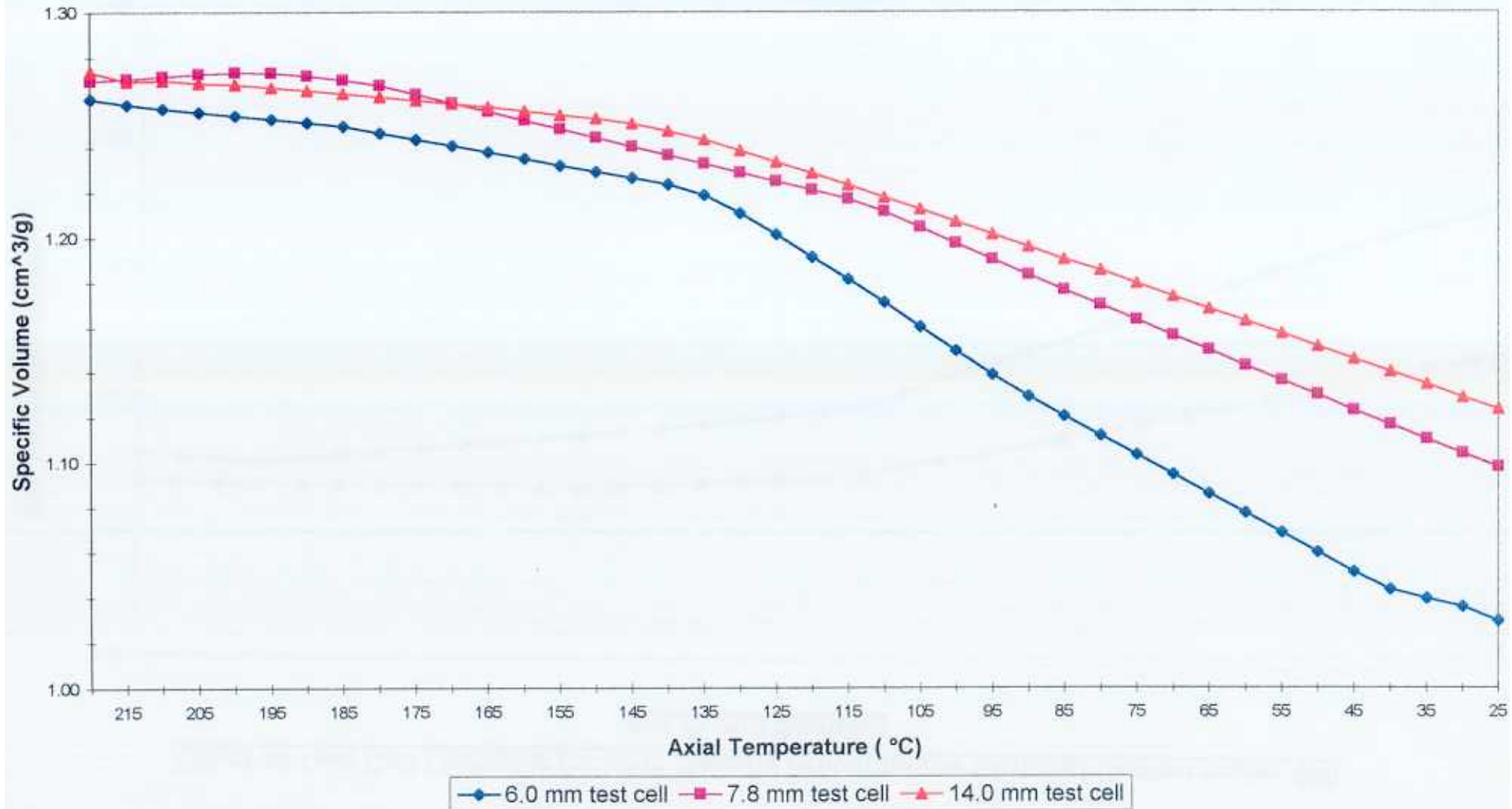


Figure 33

Effect of Test Cell Diameter for High Density Polyethylene Ultrafast Cooled under 400 bar (5 mm Sample)

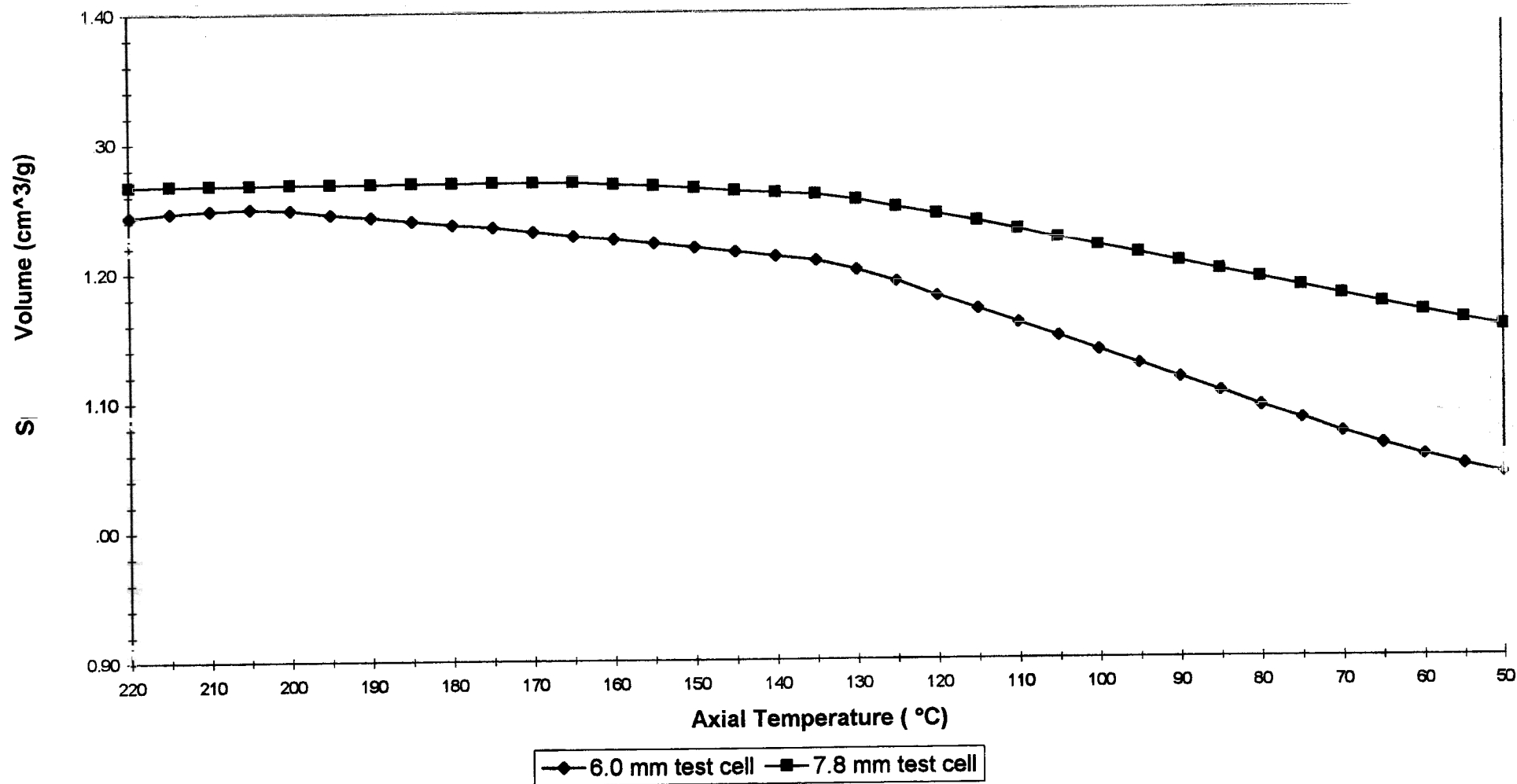
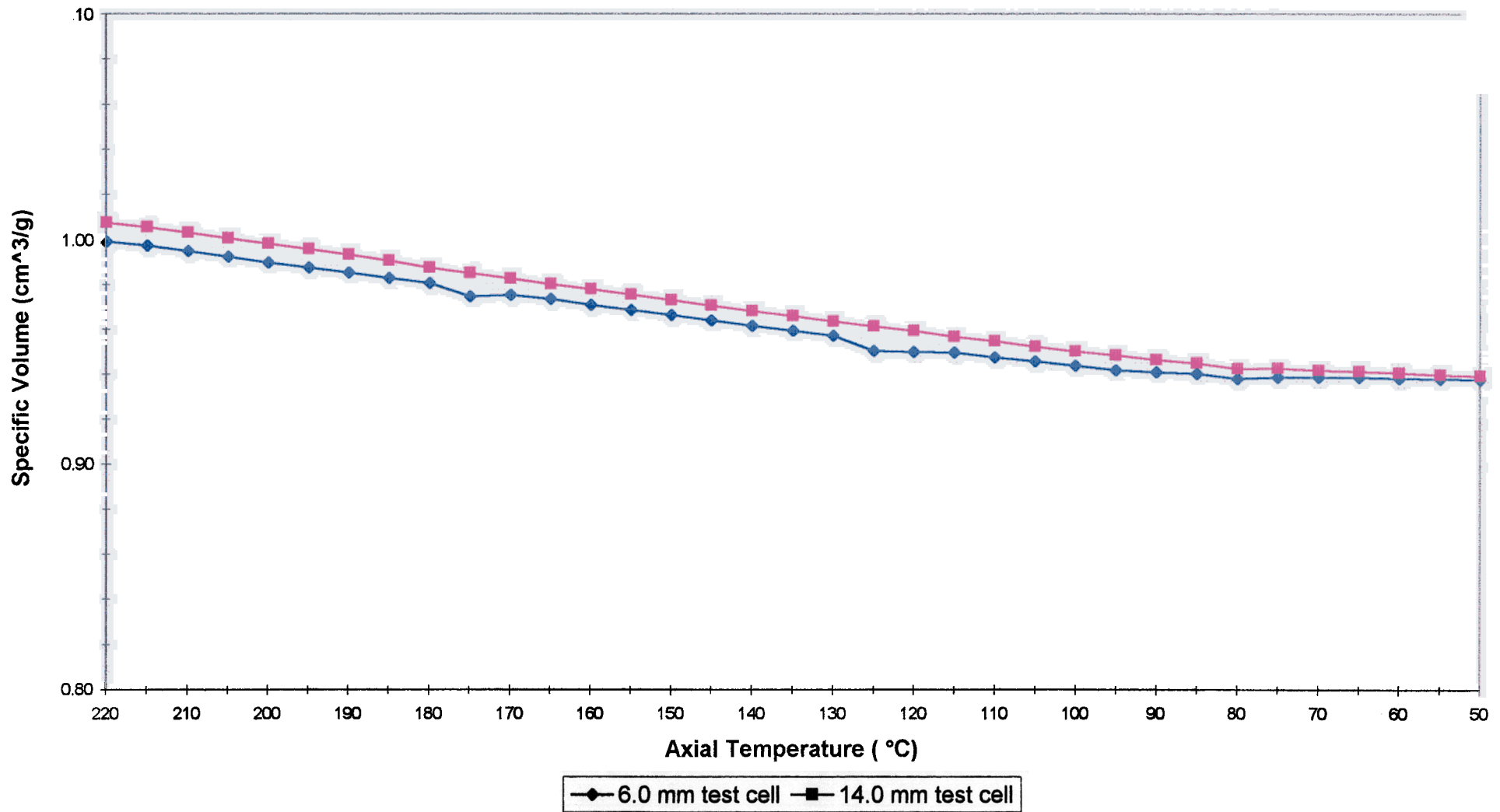


Figure 34

Effect of Test Cell Diameter for Polystyrene Cooled at 5 °C/minute under 400 bar
(15mm Sample)



PVT/CelldiamPS

Figure 35

The Effect of Test Cell Diameter for Polystyrene Ultrafast Cooled under 400 bar (15 mm Sample)

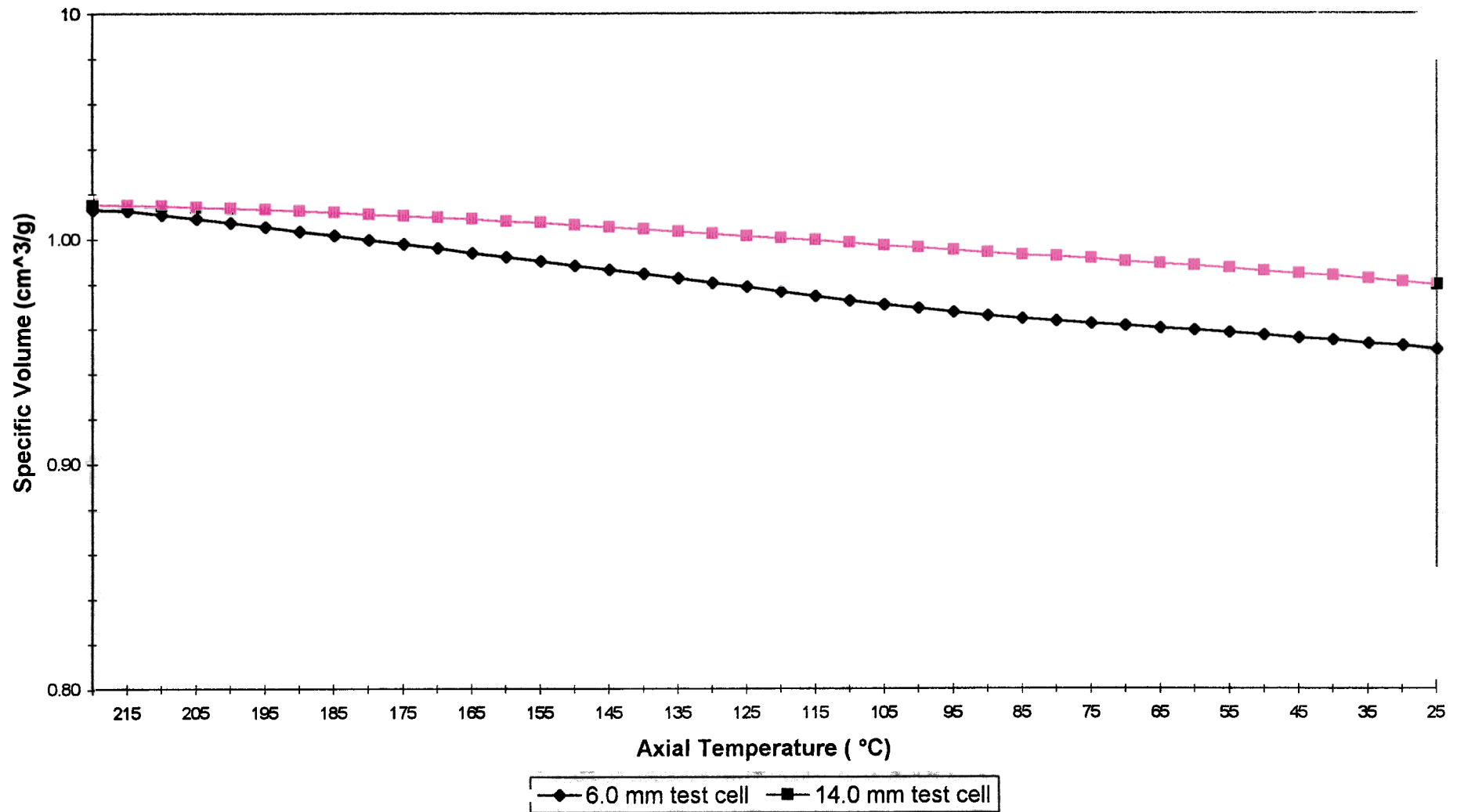
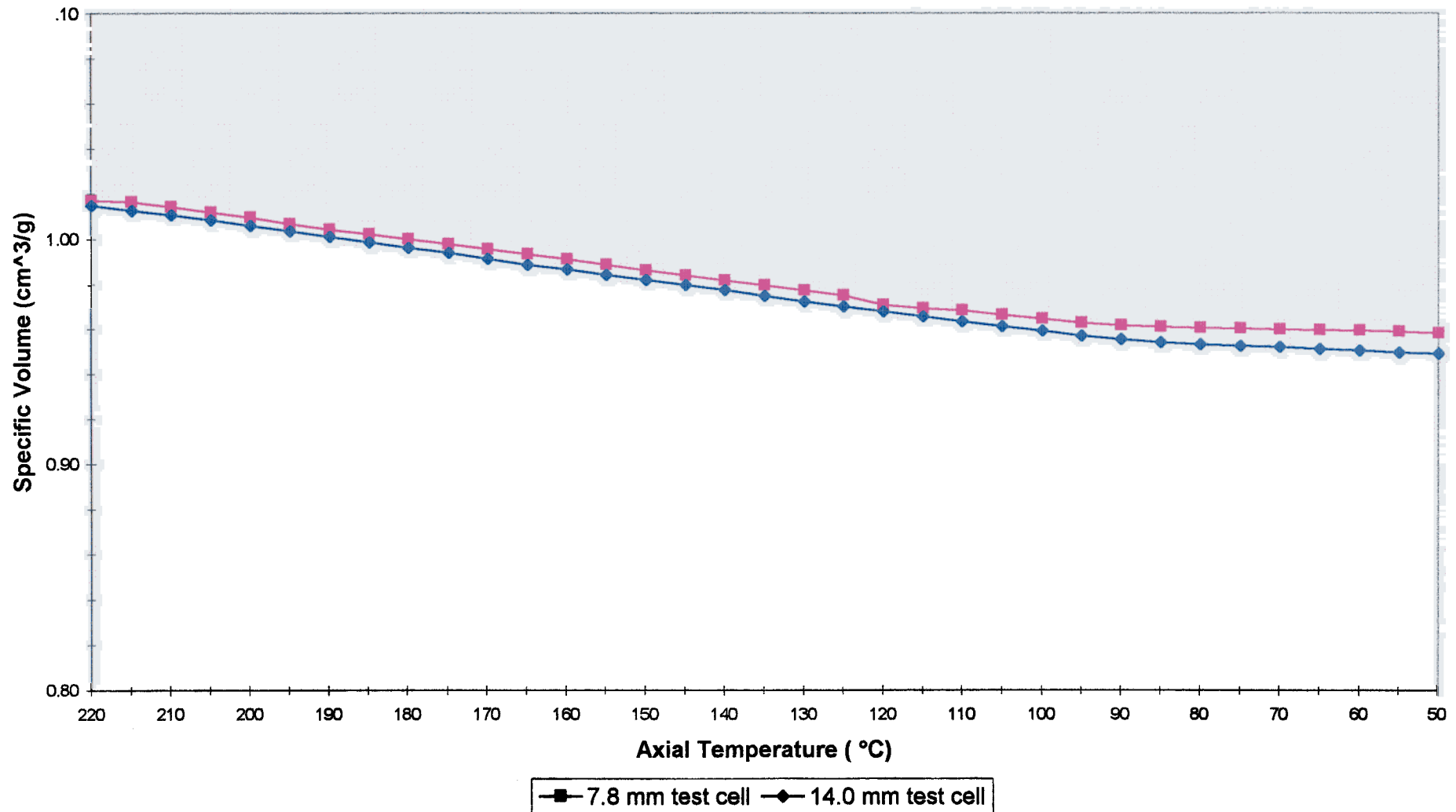


Figure 36

Effect of Test Cell Diameter for Polystyrene Cooled at 5 °C/minute under 400 bar (25 mm Sample)



PVT/CelldiamPS

Figure 37

Effect of Test Cell Diameter for Polystyrene Ultrafast Cooled under 400 bar (25 mm Sample)

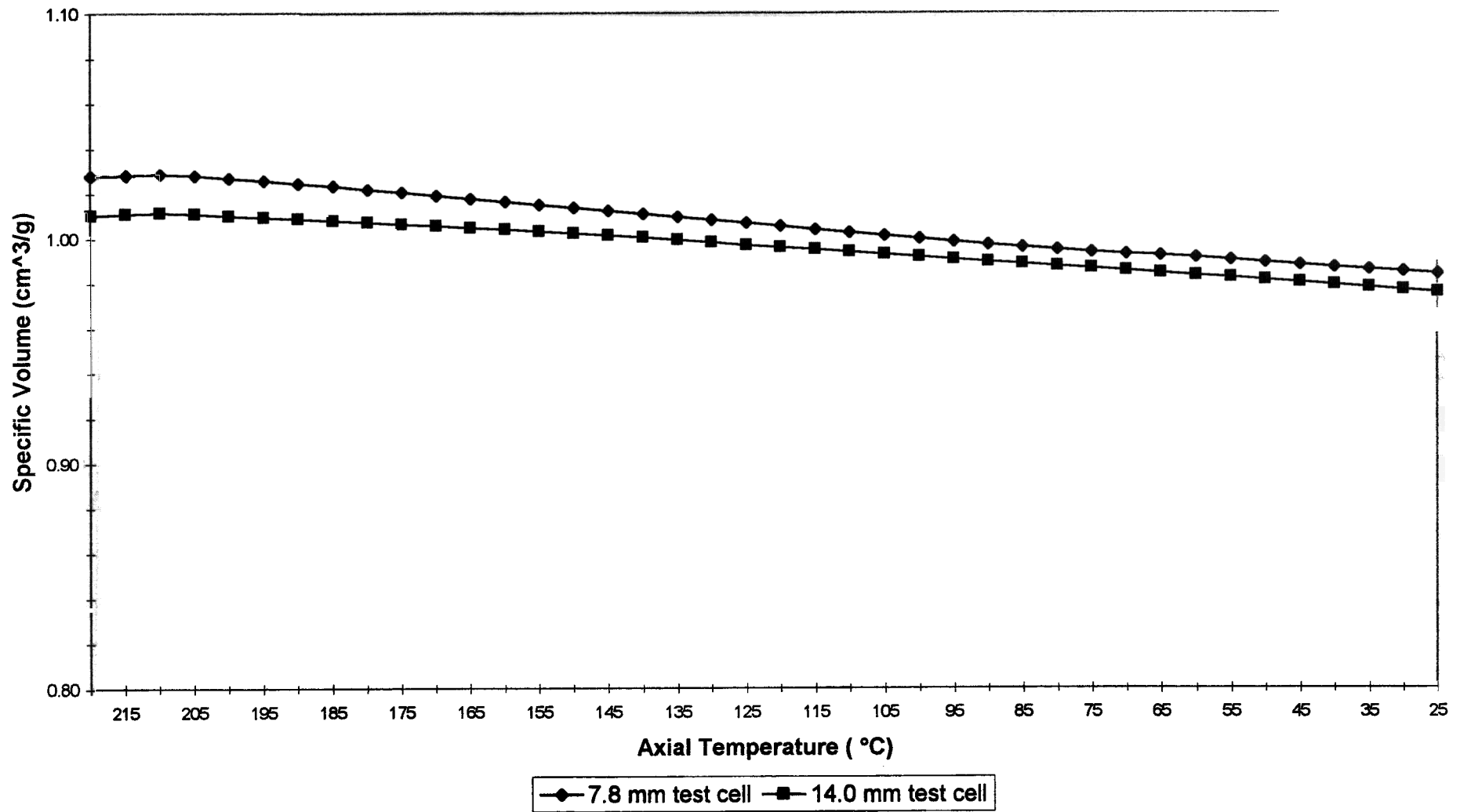
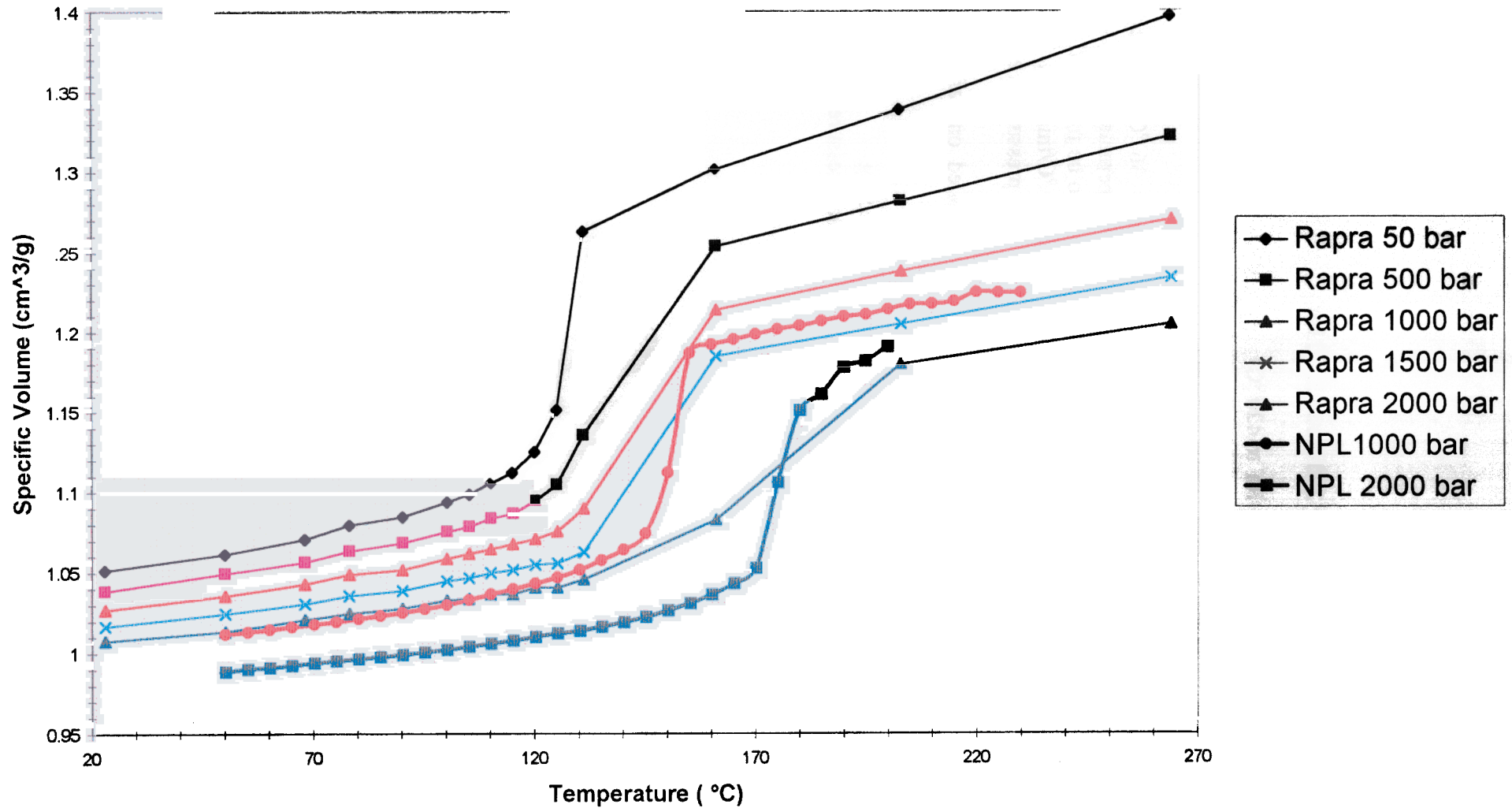


Figure 38

Comparison of NPL PVT Data with Rapra Data for High Density Polyethylene



PVT/7.8mmcell/7.8mmfamily/rapra hca

APPENDIX 1

TECHNICAL DATA:

Pressure range:	200 bar to 2500 bar
Temperature range:	RT to 420 °C
Measurement modes:	
* isobaric cooling	Cooling gradients: 1 °C/min - 36 °C/min (dependent on the used cooling liquid, the temperature level and the thermal conductivity of the materials to be measured). For simple air cooling gradients between 1 °C/min and 20°C/min can be reached. A minimum of 2 bar pressurised air is required.
* isobaric heating	0.05 °C/sec - 1 °C/sec
* isothermal	the pressures will be controlled one after another with no defined gradient
Measuring accuracy:	* specific volume: < 0.001 ccm/g * pressure: ± 1% of the actual pressure (sensitivity ± 0.5%) * temperature: ± 0.3 °C * length: ± 1 µm
Reproducibility:	1.5%
Filling time for cylinder:	about 15 minutes
Measuring time for 5 isobars:	depends on the temperature range
Power supply:	380 Volt / 6 kW / 16 A
Water supply:	fresh water for cooling of hydraulic system
Dimensions:	Width: 130 cm; height: 190 cm; depth: 80 cm
Weight:	700 kg