

**Capillary extrusion rheometry intercomparison using
polyethylene and glass-fibre filled polypropylene melts:
measurement of shear viscosity and entrance pressure
drop**

M Rides and CRG Allen

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M Rides and CRG Allen
Centre for Materials Measurement and Technology
National Physical Laboratory
Teddington, Middlesex
United Kingdom
TW11 0LW

ABSTRACT

The results of an extensive round robin on the measurement of shear viscosity and entrance pressure drop using capillary extrusion rheometers for a high density polyethylene (HDPE) and a glass-fibre filled polypropylene (GFPP) melt are reported. The round robin was based on the use of the standard 'ISO 11443 Plastics - Determination of the fluidity of plastics using capillary and slit-die rheometers'. A precision statement for inclusion in the standard has been proposed.

In summary, the repeatability of measurements of shear viscosity of HDPE and GFPP was in the range 20 - 24%, and the reproducibility 27 - 35% (95% confidence levels quoted). The repeatability of measurements of extrusion pressure was in the range 20 - 38% and the reproducibility of measurements of entrance pressure drop 42 - 56%. In all cases GFPP had values that were at the upper end of these ranges whereas HDPE had values at the lower end. Analysis of the uncertainties in the measurement method, using the specification of the standard, indicated that the uncertainties were in the range 2.5 - 19% depending on the test conditions used. The analysis indicated that a potentially large contribution to the uncertainty level was due to the pressure transducer which, if used in the lower part of its range, could contribute significantly to the overall level of uncertainty.

These findings have significant implications for testing using this method, whether to compare data obtained on the same instrument for quality control applications, or to compare data obtained on the same material but using different instruments, or using the data for predictive modelling.

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National Physical Laboratory
Teddington, Middlesex, UK, TW11 0LW

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Approved on behalf of Managing Director, NPL
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1 INTRODUCTION

This work was undertaken as part of the Department of Trade and Industry Engineering, Automotive and Metals Division's (EAM) programme on processability, Projects PMP4 on 'The determination of the viscosity of polymers as a function of cure, temperature and pressure', and PMP5 on 'The determination of the elasticity of polymer melts'. These projects are two of a wider range of projects on the processability of materials funded by the EAM.

The aim of this inter-laboratory comparison was to quantify the repeatability and reproducibility of the measurement of shear viscosity and entrance pressure drop of molten polymers using extrusion rheometers. This intercomparison would provide the necessary information to develop a precision statement for inclusion into the standard 'ISO 11443 Plastics - Determination of the fluidity of plastics using capillary and slit-die rheometers' (1), and also to provide recommendations for the further development of the testing procedure of that standard. Currently, the standard contains a precision statement based on a limited intercomparison that was not carried out on the basis of the standard: the standard was drafted after that intercomparison. The repeatability and reproducibility of shear viscosity values were quoted in the ranges 5 - 10% and 10 - 20% respectively although no traceable reference is made to the intercomparison and insufficient details are presented to base judgements reliably on these values (even to the extent that it is not stated that the presented values are 95% confidence levels rather than one standard deviation values). Furthermore, no values for entrance pressure measurements were presented. A recent intercomparison based on the ASTM D3835 (2) yielded repeatability values for shear viscosity in the range 1.8 - 21% and reproducibility values in the range 11 - 49% (95% confidence limits) with the values decreasing within the stated ranges as the shear rate increased. Bafna (3) also presented repeatability results for two capillary rheometers and obtained maximum standard deviations of 8% (95% confidence of 22.4% assuming a factor of 2.8) for a HDPE at low shear rates.

Shear viscosity data are commonly used in quality control applications and also increasingly in flow simulation for mould and process design. Although the use of entrance pressure drop data has been ongoing for many years (4-7), for example for qualitative applications, its use for providing data for flow simulation is in its infancy and there is a need to quantify the repeatability and reproducibility of the measurement method.

2 ISO STANDARD

2.1 SPECIFICATION OF STANDARD

The intercomparison was based on the use of the standard 'ISO 11443: 1995 Plastics - Determination of the fluidity of plastics using capillary and slit-die rheometers' (1). This standard specifies the following tolerances for the measurement of the properties of shear viscosity and entrance pressure drop of plastics.

Capillary rheometry standard ISO 11443 specification:

Capillary die length, L:	± 0.025 mm
Capillary die diameter, D_c :	± 0.007 mm
Barrel diameter D_b :	± 0.007 mm
Pressure measurement, P:	$\pm 1\%$ f.s.d
Flow rate measurement, Q:	$\pm 1\%$

Temperature measurement θ : spatial	$\pm 1\text{ }^{\circ}\text{C}$ for $\theta \leq 200\text{ }^{\circ}\text{C}$ $\pm 1.5\text{ }^{\circ}\text{C}$ for $200\text{ }^{\circ}\text{C} < \theta \leq 300\text{ }^{\circ}\text{C}$ $\pm 2\text{ }^{\circ}\text{C}$ for $\theta > 300\text{ }^{\circ}\text{C}$
Temperature measurement θ : temporal	$\pm 0.5\text{ }^{\circ}\text{C}$ for $\theta \leq 200\text{ }^{\circ}\text{C}$ $\pm 1\text{ }^{\circ}\text{C}$ for $200\text{ }^{\circ}\text{C} < \theta \leq 300\text{ }^{\circ}\text{C}$ $\pm 1.5\text{ }^{\circ}\text{C}$ for $\theta > 300\text{ }^{\circ}\text{C}$

Limit of variation in extrusion pressure with time due to degradation effects etc $\pm 5\%$.

2.2 UNCERTAINTY LIMITS OF TESTING

The uncertainty in the determination of the shear viscosity η was calculated using the equation

$$\eta = \frac{D_c^4}{32 L V_p D_b^2} [P - \Delta P_{ent}] \quad [1]$$

where ΔP_{ent} is the entrance pressure drop, V_p is the piston velocity (proportional to volume flow rate) and other terms are as defined above (also see Appendix 1). This expression is used to calculate shear viscosity values that are corrected for entrance pressure effects but not for the effect of a non-Newtonian velocity profile, the correction for which is commonly known as the Rabinowitsch correction (9, 10). The effect of applying the Rabinowitsch correction on the level of uncertainty is assumed to be small (see Appendix 1). The uncertainty in the shear viscosity U_η is thus given by the equation

$$U_\eta = \eta \sqrt{\left[4 \left(\frac{d_c}{D_c} \right)^2 + \left(\frac{\ell}{L} \right)^2 + \left(\frac{v_p}{V_p} \right)^2 + 2 \left(\frac{d_b}{D_b} \right)^2 + \left(\frac{p^2 + \delta p_{ent}^2}{(P - \Delta P_{ent})^2} \right) + (fd)^2 \right]} \quad [2]$$

where the fractional uncertainty of each of the terms is given as the quotient of the uncertainty in the value of the parameter (lower case) to the absolute value of the parameter (upper case). The subscript 'ent' indicates the entrance pressure drop and 'fd' indicates the fractional uncertainty due to degradation effects (see Appendix 1). Other terms are as defined above and also in Appendix 1. For testing based on the specification of ISO 11443 and using a capillary die of 1 mm diameter and 20 mm length, a rheometer with a 10 mm diameter barrel and the further assumptions presented below, then the uncertainties in the measurement of shear viscosity are given in Table 1. The uncertainties in the measurement of extrusion pressure P and entrance pressure drop ΔP_{ent} were taken to be the same, that is 1% of the full scale range of the pressure transducer, but it was assumed that the magnitude of the entrance pressure drop was one fifth of that of the extrusion pressure. The significant effect of utilising the pressure transducer in only a part of its range is clearly shown in Table 1.

In determining the uncertainty values in the measurement of shear viscosity where degradation may occur it was also assumed, in accordance with the standard, that testing is carried out over a time period during which the extrusion pressure (and hence viscosity) may change by no more than 5%. The uncertainty values calculated assuming a 5% effect of degradation are also shown in brackets in Table 1.

Table 1: Uncertainties in measurement of shear viscosity expressed as percentage values

Temperature dependence of viscosity, %/°C	Temperature error, ± °C	Uncertainty in viscosity measurement due to use of only part of range of pressure transducer and excluding degradation effects (values in brackets includes 5% factor, fd, due to degradation), %			
		using 100% f.s.d of pressure transducer	using 50% f.s.d of pressure transducer	using 20% f.s.d of pressure transducer	using 10% f.s.d of pressure transducer
0	-	2.5 (5.6)	3.9 (6.4)	9.0 (10.3)	17.8 (18.5)
1	1	2.7 (5.7)	4.1 (6.4)	9.1 (10.3)	17.8 (18.5)
1	1.5	2.9 (5.8)	4.2 (6.5)	9.1 (10.4)	17.8 (18.5)
3	1.5	5.1 (7.2)	6.0 (7.8)	10.1 (11.2)	18.3 (19.0)

Obviously the uncertainties in measurement of shear viscosity are related to the temperature dependence of the material being tested. For the HDPE and GFPP materials used in this round robin it was estimated, based on measurements made at different temperatures, that the temperature dependence of the viscosity was of the order of 1 %/°C.

These uncertainties do not take into account errors due to application of the Rabinowitsch correction for the effect of the non-Newtonian velocity profile, viscous heating and pressure dependence of viscosity. These factors will all increase the level of uncertainty of the measurements and the reproducibility of results particularly when different testing conditions are used to obtain viscosities at similar shear rates, for example by using different die dimensions.

3 EXPERIMENTAL TECHNIQUES

3.1 PARTICIPANTS

The participant in the round robin were:

BICC Cables Ltd, UK
 CarnauldMetalbox plc, UK
 Cookson Technology Centre, Cookson Group, UK
 Dynisco Europe GmbH, GERMANY
 Ecole des Mines de Douai, FRANCE
 Elf Atochem, FRANCE
 EniChem Research Centre, ITALY
 Gebrüder Haake GmbH, GERMANY
 ICI Materials, UK
 Moldflow Pty. Ltd., AUSTRALIA
 Montell Polyolefins, ITALY
 National Physical Laboratory, UK
 PCD Polymere Ges.m.b.H, AUSTRIA
 Rapra Technology Ltd, UK
 Renault S.A., FRANCE
 Rhone-Poulenc Industrialisation, FRANCE

Rosand Precision Ltd, UK
 Solvay Polymers Technical Centre, USA
 Solvay SA, BELGIUM
 Toyo seiki Seisaku-Sho Ltd, JAPAN

3.2 TEST MATERIALS

Two materials were selected for testing in the round robin, an unfilled high density polyethylene (HDPE: material A, NPL reference HFU000) and a glass fibre filled polypropylene (GFPP: material B, NPL reference HFQ000). Both materials were commercially available. All samples were supplied to the participants by the National Physical Laboratory (NPL). The HDPE material was the same as that used in a round robin on parallel plate oscillatory rheometry (8).

3.3 PROCEDURE

Twenty laboratories participated in the round robin using the instruments listed in Table 2. Instructions detailing the testing procedure to be used and specifying the results and testing information to be provided by the participating laboratory were sent to all participants along with samples of the materials.

Table 2: Instruments used by each of the laboratories indicated by reference number.

Laboratory No.	Rheometer manufacturer and model
1	CBE ACER 2000
2	Rosand RH7-2 ¹
4	Rosand RH7 ¹
5	Rosand RH7 ¹
6	Rosand RH7-2 ¹
7	Rosand RH7-2C ¹
8	CBE RACER
9	Gottfert Rheograph 2002
10	Gottfert Rheograph 2002
11	Gottfert Rheograph 2002
13	Gottfert Rheograph 2002
15	Kayness Galaxy V
16	Gottfert Rheograph 2001
18	Toyo seiki Capiro Graph 1C ²
19	Gottfert Rheograph 2002
20	Scientific Vimeg ²
21	Gottfert Rheograph 2001
23	Haake Torque Rheometer Rheocord 9000 with single screw extruder
24	Gottfert Rheograph 2001
26	Modified Boy injection moulding-machine ³

Notes ¹: Single barrel, twin bore design.
²: Load cell above piston design.
³: Used with slit die and capillary die configurations.

4 RESULTS AND DISCUSSION

4.1 GENERAL

Results are presented for the two materials: the polyethylene (HDPE) at 190 °C, Figures 1 - 8, and the glass fibre filled polypropylene (GFPP) at 230 °C, Figure 9 - 16. Results of shear viscosity, extrusion pressure and entrance pressure drop measurements are presented. All shear viscosity values were corrected for entrance pressure drop and non-Newtonian velocity profile (Rabinowitsch correction (9, 10)) by the laboratory that performed the testing. Results that were obtained whilst melt fracture occurred were discarded.

4.2 SHEAR VISCOSITY - REPEATABILITY AND REPRODUCIBILITY

Shear viscosity data for HDPE and GFPP are presented in Figures 1 and 9 respectively. The results for GFPP exhibited greater scatter than for HDPE. For example, the results from laboratories 20 and 24 were excluded from the analysis of GFPP data on the basis of their being outliers. For GFPP the data presented in Figure 10 were used in subsequent analyses presented below.

The shear viscosity data were fitted using a second order model of the form

$$\log \eta = A'_{00} + A'_{10} \log \dot{\gamma} + A'_{20} [\log \dot{\gamma}]^2 + A'_{01} \theta + A'_{02} \theta^2 + A'_{11} \theta \log \dot{\gamma} \quad [3]$$

where η is shear viscosity, A'_{00} , A'_{10} , A'_{20} , A'_{01} , A'_{02} and A'_{11} are constants, θ is temperature and $\dot{\gamma}$ the shear rate. For fitting data obtained at a single temperature, as required herein, equation [3] reduces to

$$\log \eta = A_{00} + A_{10} \log \dot{\gamma} + A_{20} [\log \dot{\gamma}]^2 \quad [4]$$

A statistical software package, Fig.P (13), was used to determine the least squares fit of equation [4] to the data. This empirical model is used in commercially available flow simulation software (11, 12) and provided a reasonable fit to the data, Figures 1 and 10. The use of logarithmic values reduced the dependence of the fit to the high shear viscosity end of the data set. The fit of equation 4 to the data yielded the values of the parameters given in Table 3 for the two materials, with 95% confidence levels of the values presented in brackets.

Table 3: Fit of the second order viscosity model to shear viscosity data

Log (shear viscosity) versus Log(shear rate) fit using equation 4.		
Material, temperature	PE, 190 °C	GFPP, 230 °C
A_{00}	3.9121 (0.0386)	3.4768 (0.0544)
A_{10}	-0.0316 (0.0356)	-0.3832 (0.0500)
A_{20}	-0.0651 (0.0077)	-0.0550 (0.0104)
r^2	0.9924	0.9923

Note : r is the correlation coefficient and therefore r^2 the coefficient of determination.
95% confidence values for A_{00} , A_{10} and A_{20} presented in brackets.

This fit was then used to scale all the viscosity data from the laboratories, Figures 2 and 11 for HDPE and GFPP respectively. The scaled viscosity data showed no clear trend of either increasing or decreasing scatter in values with increasing shear rate, Figures 2 and 11. The scaled data were then used to determine repeatability and reproducibility values. Detailed analysis, carried out in accordance with reference 14 (also see Appendix 1) yielded mean, standard deviation and 95% confidence values for each laboratory, Tables 4 and 5 for HDPE and GFPP respectively. The analysis also yielded overall repeatability and reproducibility values for the measurement of shear viscosity, Table 6. For the reproducibility of measurements the values obtained independently using the curve fitting package Fig.P are also presented in brackets in Table 6 for comparison.

Table 4: Analysis of shear viscosity data per laboratory for HDPE at 190 °C

Laboratory number	2	4	5	6	7	8	9	11	13	15	18	19	20	21	23	26 cap	26 slit
Number of measurements	13	14	9	36	16	5	10	7	7	11	21	8	27	9	30	18	9
Mean	0.978	1.009	1.113	0.970	1.055	1.090	0.978	1.032	1.171	1.081	1.036	1.003	0.868	1.029	0.993	1.040	0.924
Maximum value	1.022	1.226	1.364	1.049	1.200	1.161	1.066	1.101	1.255	1.185	1.161	1.073	0.940	1.105	1.180	1.097	0.993
Minimum value	0.931	0.673	0.980	0.834	0.774	1.057	0.908	0.980	1.088	1.032	0.942	0.954	0.834	0.968	0.917	0.979	0.830
Standard deviation	0.032	0.173	0.108	0.045	0.115	0.037	0.053	0.044	0.057	0.052	0.048	0.041	0.026	0.042	0.071	0.035	0.061
95% confidence	0.073	0.388	0.264	0.094	0.254	0.116	0.125	0.117	0.152	0.122	0.103	0.103	0.054	0.104	0.147	0.076	0.148

Table 5: Analysis of shear viscosity data per laboratory for GFPP at 190 °C

Laboratory number	2	5	6	7	8	9	10	11	13	15	18	19
Number of measurements	7	11	9	49	6	10	6	16	11	12	30	9
Mean	0.871	0.983	0.797	1.007	0.912	0.877	1.209	1.072	1.030	1.089	1.038	1.074
Maximum value	1.050	1.100	0.850	1.197	1.001	0.938	1.282	1.153	1.601	1.162	1.171	1.174
Minimum value	0.657	0.932	0.691	0.733	0.818	0.800	1.119	0.994	0.795	1.028	0.889	0.918
Standard deviation	0.134	0.048	0.060	0.082	0.061	0.047	0.061	0.054	0.207	0.047	0.061	0.090
95% confidence	0.327	0.108	0.139	0.165	0.156	0.106	0.129	0.120	0.455	0.097	0.184	0.207

Table 6: Repeatability and reproducibility of shear viscosity values, expressed as percentage values.

Material, test temperature		PE, 190 °C	GFPP, 230 °C
Repeatability	standard deviation	7.2%	8.6%
	r 95% confidence	20.3%	24.0%
Reproducibility	standard deviation (value obtained using Fig.P (13))	9.9% (10.4%)	12.2% (12.8%)
	R 95% confidence	27.7%	34.1%

It is emphasised that the repeatability values were obtained for the measurement of shear viscosity over approximately three decades of shear rate and therefore include a factor due to testing over a range of rates rather than at one specific rate. It is expected therefore that the repeatability values would be higher than had they been determined at a single shear rate. However as a larger number of repeat measurements were consequently made then a more significant statistical analysis could be performed. Furthermore, in practice, testing is normally carried out at several shear rates. This approach was adopted due, in part, to the impossibility of obtaining true shear viscosity data at identical shear rates as the shear rate value is not known until the experiment and analysis of the raw data are completed. The approach was therefore considered reasonable, if not more appropriate to the normal use of this method.

For each materials, the mean of the scaled viscosity values obtained by each laboratory was plotted against the 95% confidence limit for that laboratory, Figures 3 and 12. For testing of HDPE two laboratories (13 and 20) had mean values that differed from the overall mean value of 1 by greater than the 95% confidence level for that laboratory, Figure 3 and Table 4. Similarly, for GFPP three laboratories (6, 9 and 10) were outside the 95% confidence limits. A possible explanation for this is that there might have been systematic errors in the results of these laboratories with the consequence that their results deviated from the intercomparison mean by a value greater than the 95% confidence limit for that laboratory. In Figure 3 the position of laboratory 20 (0.054, 0.868) - its low mean value combined with a small 95% confidence value - was attributed to the fact that the experimental data had been processed and that derived data was presented. It is expected that the derived data exhibited less scatter and therefore a smaller confidence level than the raw data.

4.3 EXTRUSION PRESSURES - REPEATABILITY

Repeat extrusion pressure measurements were carried out to determine the repeatability of measurements. For each set of repeat tests at a given flow rate the 95% confidence values were calculated and plotted against the average shear rate for HDPE, Figure 4, and also against the mean extrusion pressure for both materials, Figures 5 and 13. These results showed that the level of repeatability of measurements varied dramatically. The magnitude of the variation increased with decreasing shear rate and decreasing extrusion pressure. The difficulty in utilising these data is in quantifying the repeatability as a single value, which it clearly is not. To this end 95% confidence levels for repeatability of extrusion pressure measurements were estimated, in accordance with Appendix 1, to be approximately 19.6% for HDPE and 37.5% for GFPP. However these values may be considerably smaller, of the order of 10% for HDPE and 15% for GFPP, for well controlled experimental work.

The high repeatability values of the extrusion pressure data are not incompatible with the lower repeatability values of the shear viscosity data that were derived from the extrusion pressure data for the following argument. The high repeatability values were obtained for the low extrusion pressure measurements that were predominantly obtained using short or 'zero-length' dies. Shear viscosity values corrected for entrance pressure drop effects are calculated using both long and short die data. It can be shown that the repeatability of the shear viscosity values can be less than the repeatability of the short or zero length die extrusion pressure measurements by consideration of the equations used to calculate shear viscosity values corrected for entrance pressure effects (Appendix 1).

4.4 ENTRANCE PRESSURE DROP - REPRODUCIBILITY

Entrance pressure drops were measured either directly using a 'zero-length' die or determined by extrapolation of data to a die length of zero, Figures 6 and 14. For the unfilled HDPE, results obtained using a range of contraction ratios (expressed as the quotient of the barrel diameter to die diameter) from 9.55 to 15.5 exhibited little difference, Figure 6. However, for the GFPP material the scatter in entrance pressure drop values was considerably greater. Consequently only data obtained using a contraction ratio of 15 were analyzed for GFPP. The log(entrance pressure drop) versus log(shear rate) data were fitted using a straight line, Figures 6, 7 and 15, and the quality of the fit determined, Table 7.

Table 7: Fit of the second order viscosity model to entrance pressure drop data

Log(entrance pressure drop) versus log(shear rate) fit using the equation $\log(\Delta P_{ent}) = m \log(\dot{\gamma}) + c$.			
Material, test temperature	PE, 190 °C contraction ratio of 15 only	PE, 190 °C contraction ratios 9.55 - 15.5	GFPP, 230 °C contraction ratio of 15 only
m	0.4954 (0.0209)	0.5054 (0.0168)	0.6457 (0.0217)
c	-0.8739 (0.0477)	-0.8825 (0.0381)	-1.6685 (0.0528)
r^2	0.9749	0.9641	0.9778

Note : r is the correlation coefficient and therefore r^2 the coefficient of determination.
95% confidence values for m and c presented in brackets.

These fits to the data were used to determine the reproducibility of the entrance pressure drop data, Table 8. The variation in scaled entrance pressure (scaled by the value calculated using the parameters given in Table 7) as a function of entrance pressure drop is presented in Figures 8 and 16 for HDPE and GFPP respectively. There is a slight reduction in scatter with increasing entrance pressure drop: the effect is greater for GFPP than for HDPE.

Table 8: Reproducibility of entrance pressure drop values, expressed as a percentage

Material, test temperature		PE, 190 °C contraction ratio of 15 only	PE, 190 °C contraction ratios 9.55 -15.5	GFPP, 230 °C contraction ratio of 15 only
Reproducibility	standard deviation	15.1%	17.8%	19.8%
	R 95% confidence	42.3%	49.8%	55.5%

4.5 SUMMARY DISCUSSION

In summary, this inter-laboratory comparison of capillary extrusion rheometry using an unfilled HDPE and a glass-fibre filled PP has identified the levels of repeatability and reproducibility of shear viscosity measurements using this technique. The reproducibility of extrusion pressure drop measurements could not be assessed due to the wide range of geometries used: there were variations in the barrel diameter, die diameter, die length and also flow rate. However, for entrance pressure drop measurements, scaled as a function of shear rate at the die wall, these factors were either conveniently removed by the scaling process or were assumed to have negligible effect. Consequently the reproducibility values could be determined. The repeatability of entrance pressures drop measurements can be assumed, as a first approximation, to be equal to the repeatability of the extrusion pressure measurements.

The repeatability and reproducibility values of GFPP were higher than those of HDPE for several reasons. The presence of the fibres is a cause of increased scatter in measurements (16). More significantly, the viscosity of GFPP was lower than that of HDPE by a factor of approximately three. Consequently the errors due to the measurement of extrusion pressure were greater (the extrusion pressures would be a factor of approximately three lower for the GFPP). The calculation of the uncertainties for shear viscosity measurement clearly indicated that the errors arising from the use of pressure transducer are potentially the greatest source of uncertainty in the measurement technique. Improvement to the specification of the standard and increased awareness of the importance of the appropriate use of pressure transducers and their calibration over the range in which they are to be used is required to limit the magnitude of this effect on the accuracy of measurements.

5 PROPOSED PRECISION STATEMENT FOR ADOPTION IN ISO 11443

The following precision data have been determined during a test program made in 1995 - 1996, comprising 20 laboratories in total on polyethylene and glass-fibre filled polypropylene samples.

Extrusion pressure measurement

Material, test temperature		PE, 190 °C	GFPP, 230 °C
Repeatability	standard deviation	7.0%	13.4%
	r 95% confidence	19.6%	37.5%

Shear viscosity measurement (corrected for entrance pressure drop and non-Newtonian velocity profile (Rabinowitsch))

Material, test temperature		PE, 190 °C	GFPP, 230 °C
Repeatability	standard deviation	7.2%	8.6%
	r 95% confidence	20.3%	24.0%
Reproducibility	standard deviation	9.9%	12.2%
	R 95% confidence	27.7%	34.1%

Entrance pressure drop measurement

Material, test temperature		PE, 190 °C contraction ratio of 15 only	PE, 190 °C contraction ratios 9.55 -15.5	GFPP, 230 °C contraction ratio of 15 only
Reproducibility	standard deviation	15.1%	17.8%	19.8%
	R 95% confidence	42.3%	49.8%	55.5%

The difference between two individual results obtained on an identical material using this test method with "repeatability conditions" will not exceed the repeatability limit *r* on average more than 5 times out of 100 when the method is applied normally and correctly.

Individual results obtained on an identical material submitted to a test by two laboratories will not exceed the reproducibility limit *R* on average more than 5 times out of 100 when the method is applied normally and correctly in reproducibility conditions.

6 CONCLUSIONS

On the basis of the work reported here the following conclusions are made (all repeatability and reproducibility values quoted are for 95% confidence levels):

- Repeatability of shear viscosity measurements were approximately 20% for HDPE and 24% for GFPP.
- Reproducibility of shear viscosity measurements were approximately 28% for HDPE and 34% for GFPP.
- The repeatability and reproducibility of shear viscosity measurements of GFPP were approximately 20% higher than HDPE.
- Reproducibility of entrance pressure drop measurements were approximately 42% for HDPE and 56% for GFPP.

- The single major sources of error was considered to be due to accuracy of pressure measurement and utilisation of the pressure transducer in the appropriate range.
- A precision statement for the standard ISO 11443 detailing repeatability and reproducibility limits for measurement of shear viscosity and entrance pressure drop has been proposed, section 6.
- In testing in accordance with the specification of the standard ISO 11443 the uncertainties in the measurement of shear viscosity and entrance pressure drop were estimated to be in the range 2.5 - 19% for the polyethylene and polypropylene materials, and depended most significantly on the range over which the pressure transducer was being used.

In summary, the repeatability and reproducibility levels have been quantified. Potentially, they have significant implications for testing using this method, whether to compare data obtained on the same instrument for quality control applications, or to compare data obtained on the same material but using different instruments, or using the data for predictive modelling. The levels of repeatability and reproducibility must be taken into account in assessing the value of test results.

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 Montell Polyolefins, ITALY
 Montell UK
 PCD Polymere Ges.m.b.H, AUSTRIA
 Rapra Technology Ltd, UK
 Renault S.A., FRANCE
 Rhone-Poulenc Industrialisation, FRANCE
 Rosand Precision Ltd, UK
 Solvay SA, BELGIUM
 Solvay Polymers Technical Centre, USA
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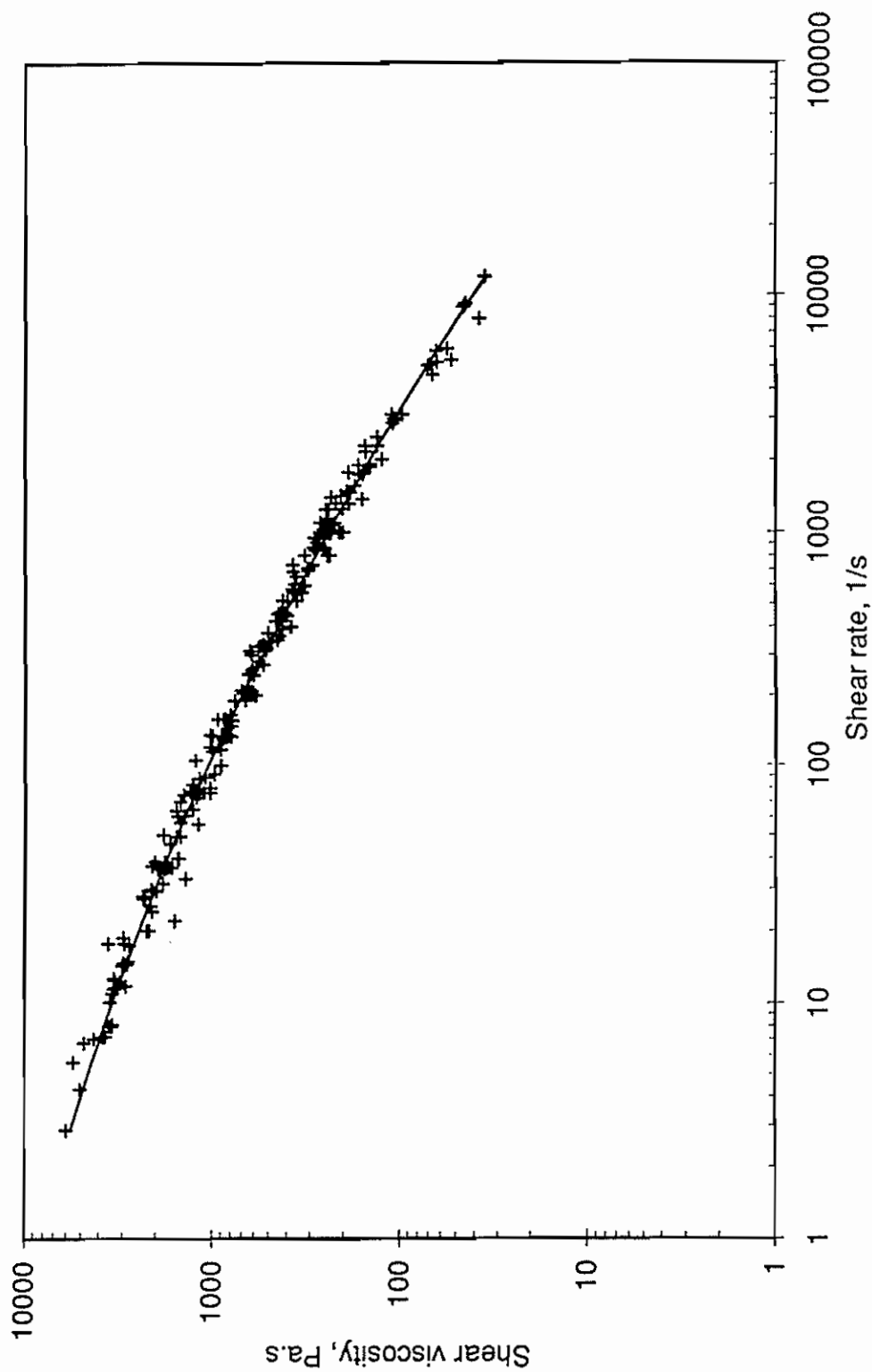


Figure 1. Shear viscosity data for PE at 190 °C obtained by 16 laboratories with a best-fit second order model (see equation 4 and table 3 for the model and the values of the parameters).

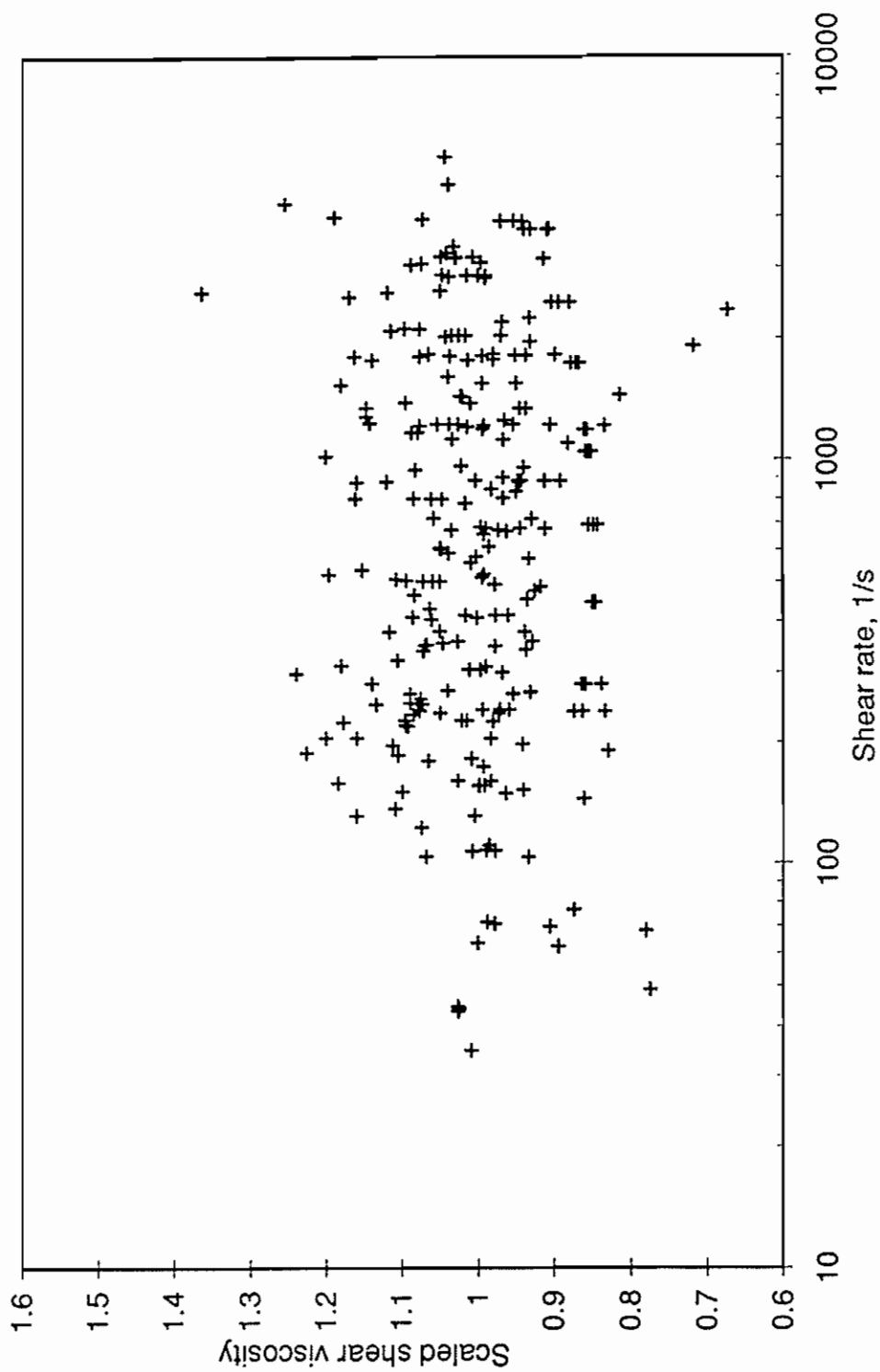


Figure 2. Scatter in scaled viscosity values with shear rate for PE at 190 °C (viscosity values scaled using the shear viscosities calculated using equation 4 and the values of the parameters given in table 3).

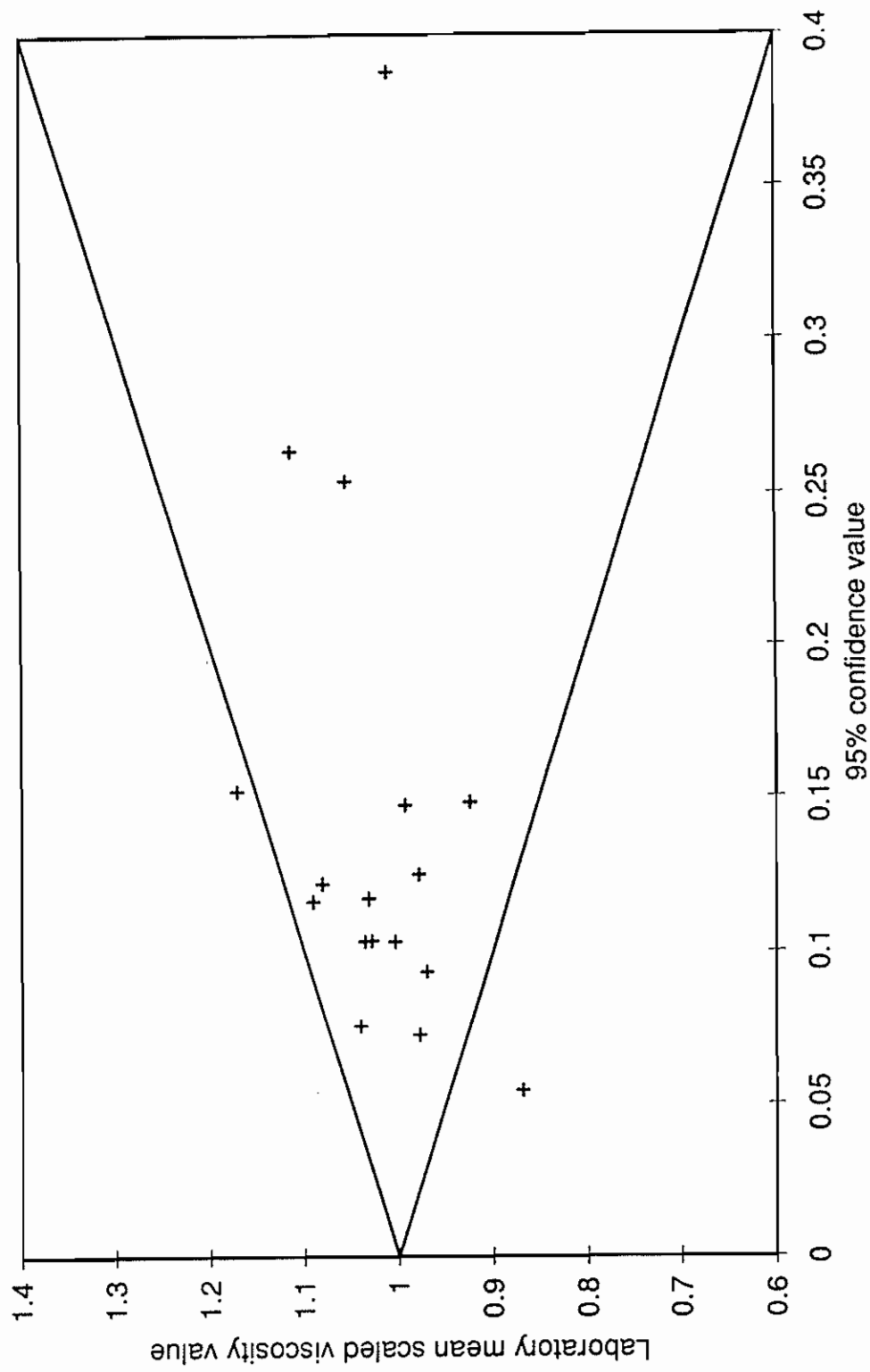


Figure 3. Variation in mean scaled viscosity values for PE at 190 °C for each laboratory as a function of the repeatability of the values for that laboratory.

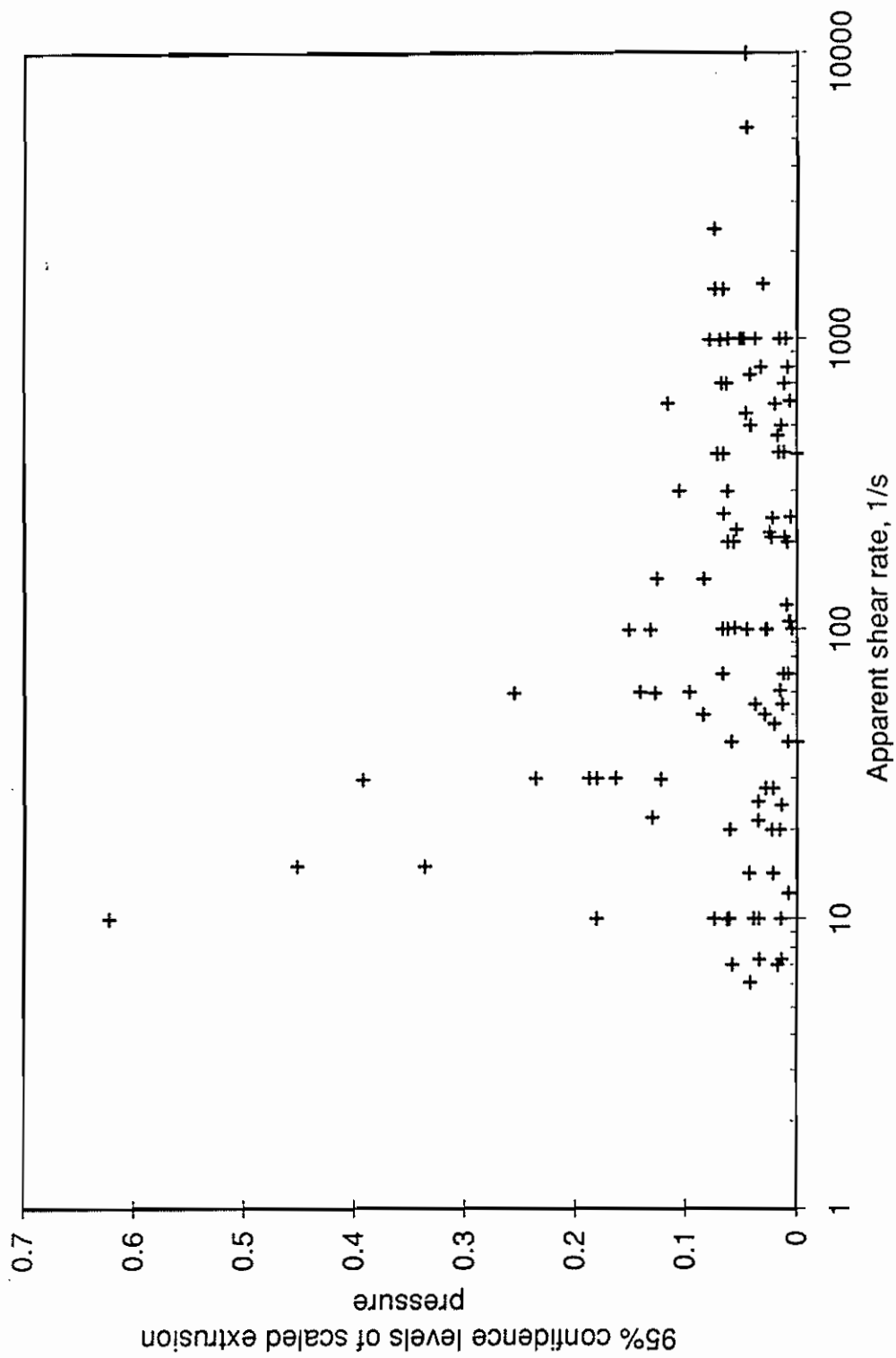


Figure 4. Repeatability of extrusion pressures as a function of shear rate for PE at 190 °C (extrusion pressure scaled using the average extrusion pressure for that set of conditions).

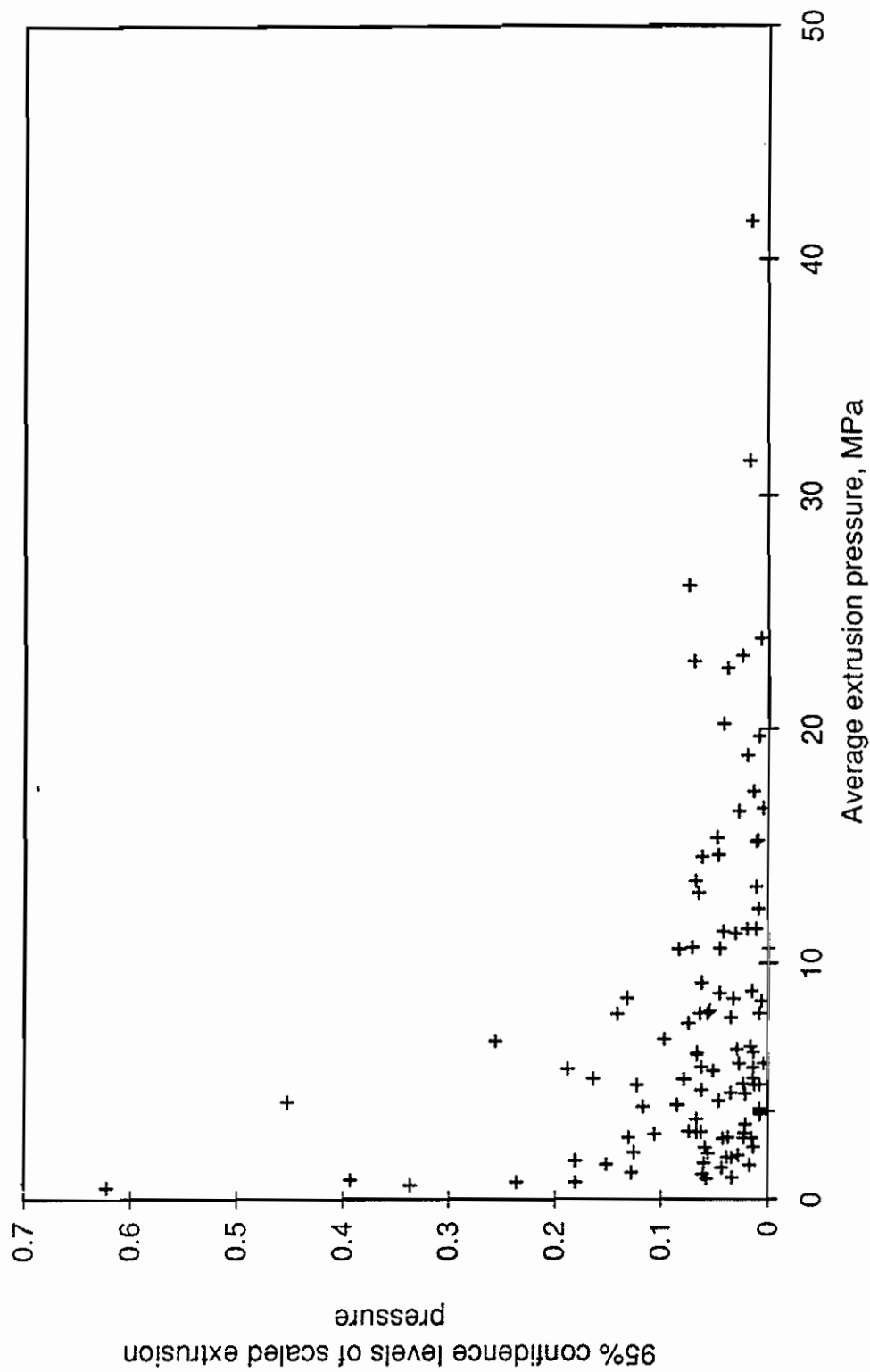


Figure 5. Repeatability of extrusion pressures as a function of extrusion pressure for PE at 190 °C (extrusion pressure scaled using the average extrusion pressure for that set of conditions).

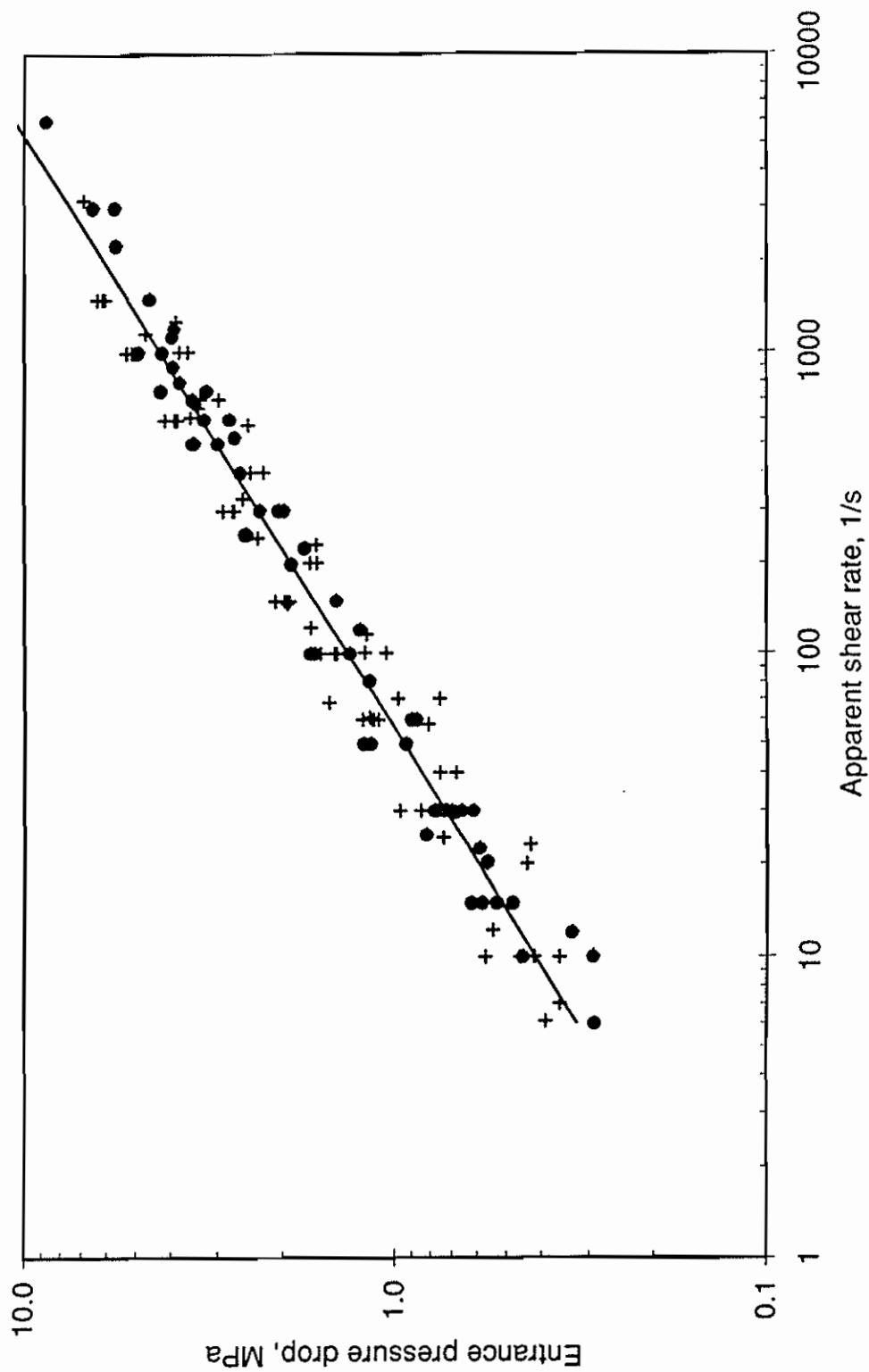


Figure 6. Scatter in entrance pressure drop values for PE at 190 °C with apparent shear rate using various barrel to die diameter contraction ratios in the range 9.55 - 15.5, with best-fit straight line to the data (see table 7). Legend: Contraction ratios: + 9.55 - 12, • 15 - 15.5.

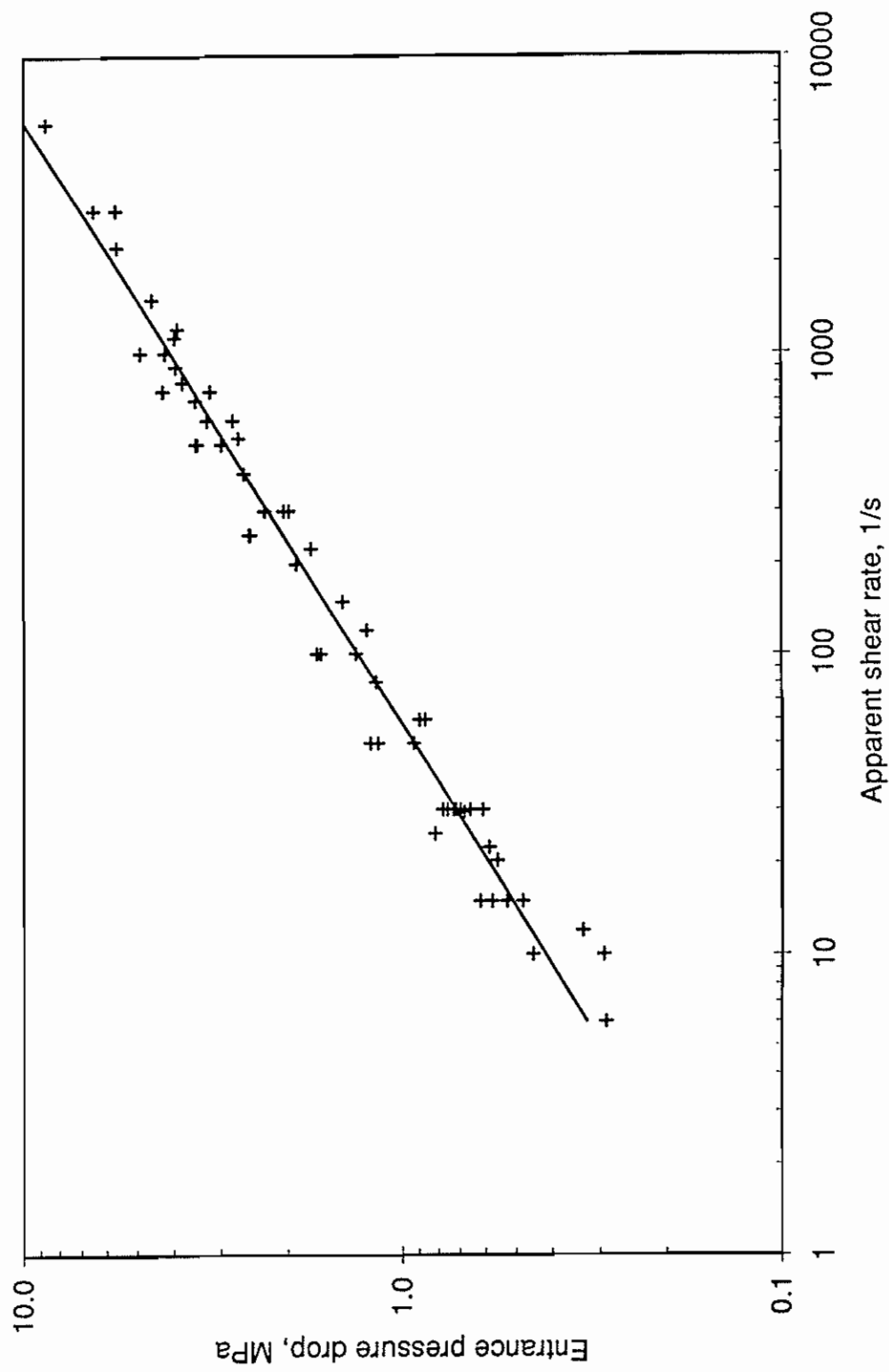


Figure 7. Scatter in entrance pressure drop values for PE at 190 °C with apparent shear rate using a barrel to die diameter contraction ratio of 15 only, with best-fit straight line to the data (see table 7).

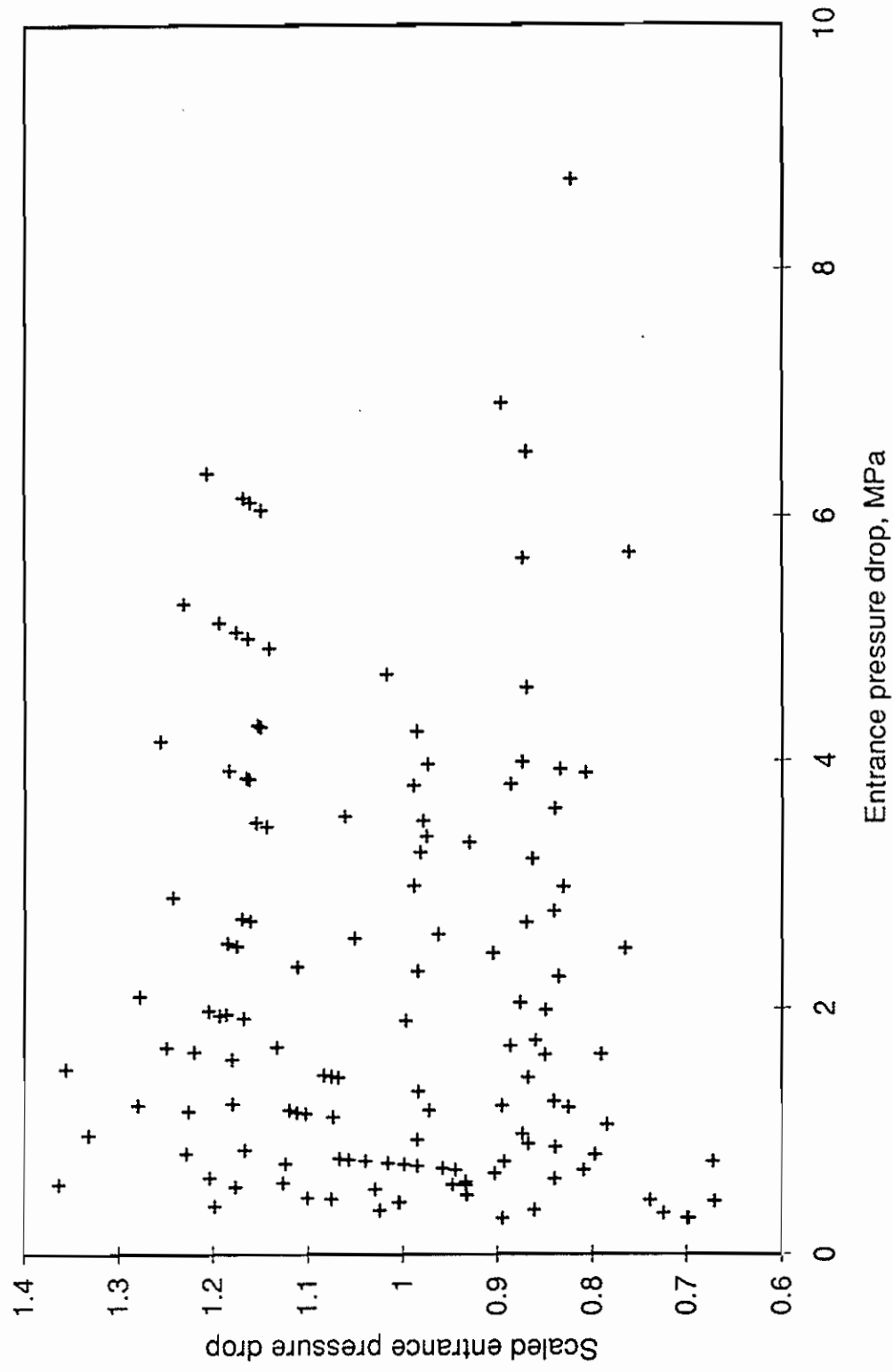


Figure 8. Scatter in scaled entrance pressure drop values as a function of entrance pressure drop for PE at 190 °C (entrance pressures scaled using entrance pressure drop values calculated using the parameters presented in table 7).

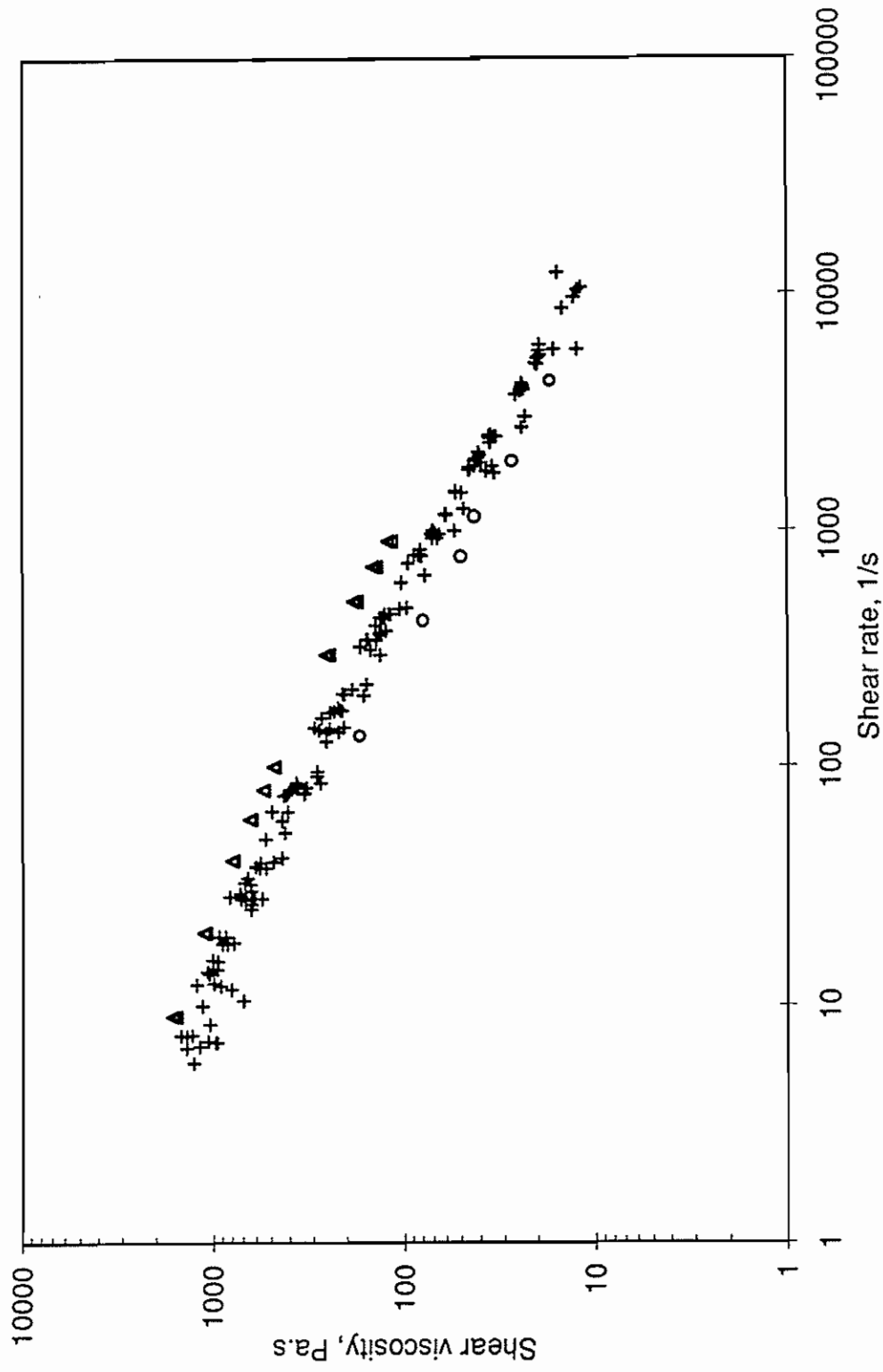


Figure 9. Shear viscosity data for GFPP at 230 °C obtained by 14 laboratories.

Δ - lab 20, o lab 24

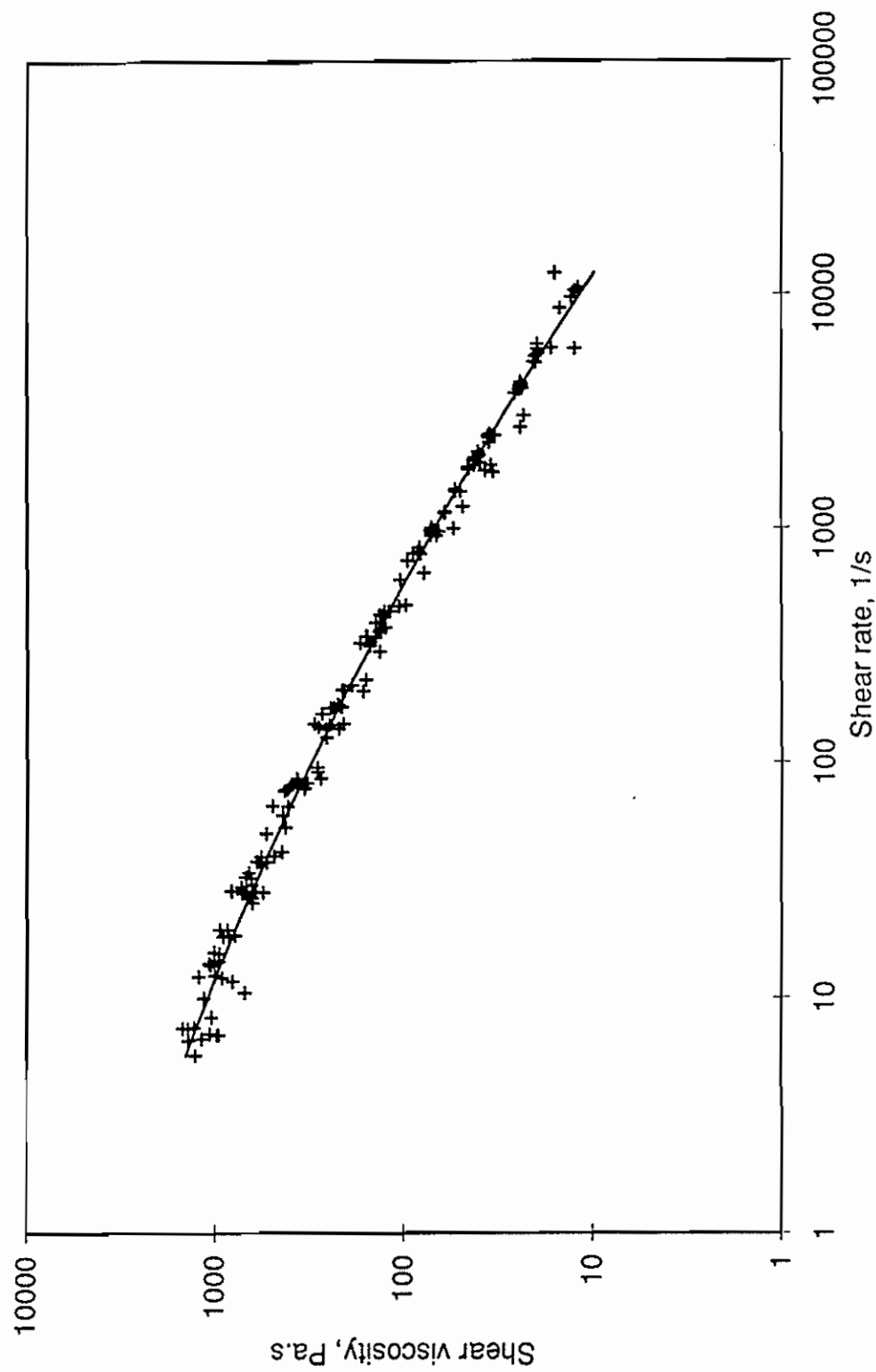


Figure 10. Shear viscosity data for GFPP at 230 °C obtained by 12 laboratories with a best-fit second order model (see equation 4 and table 3 for the model and the values of the parameters).

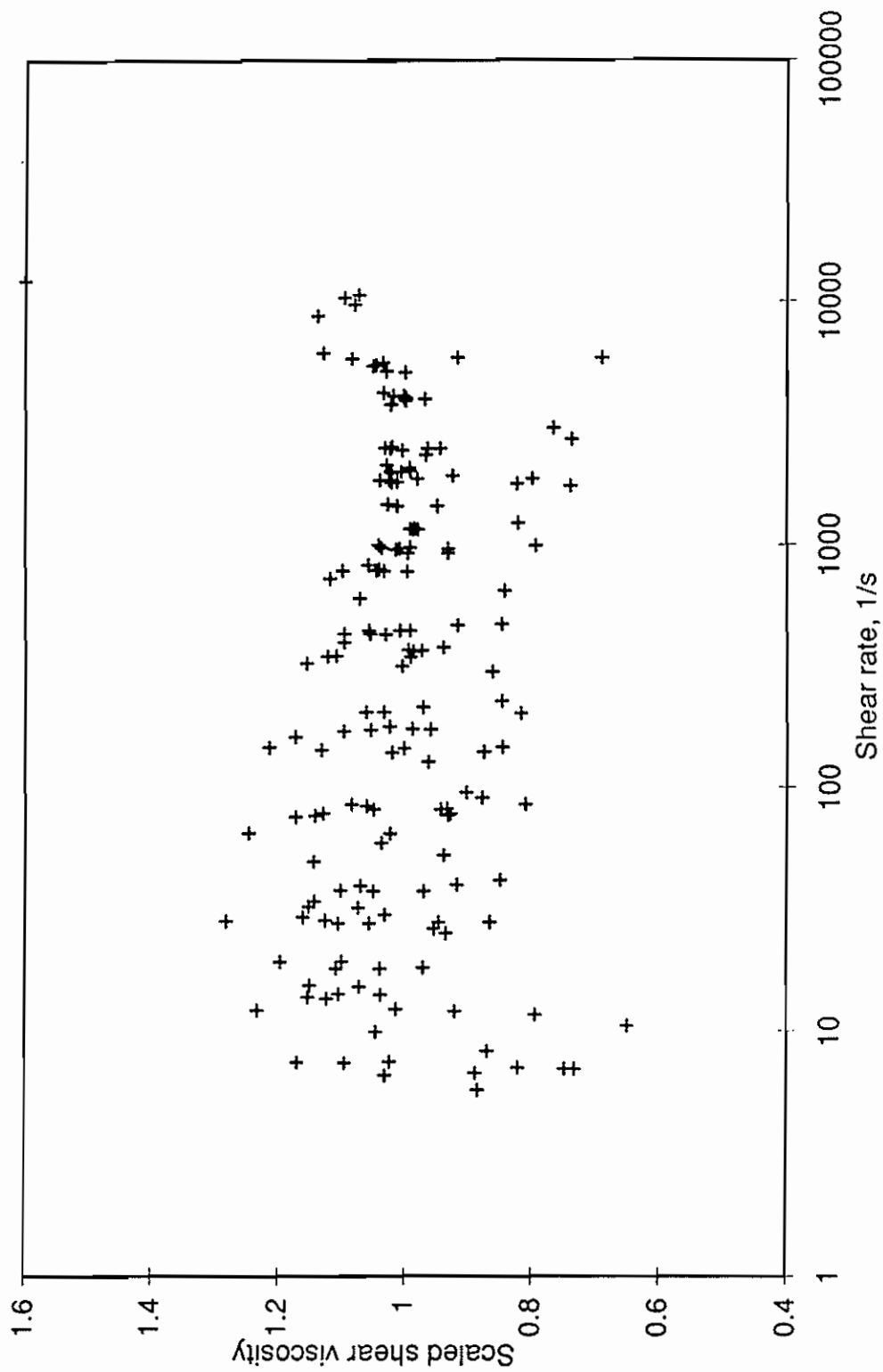


Figure 11. Scatter in scaled viscosity values with shear rate for GFPP at 230 °C (viscosity values scaled using the shear viscosities calculated using equation 4 and the values of the parameters given in table 3).

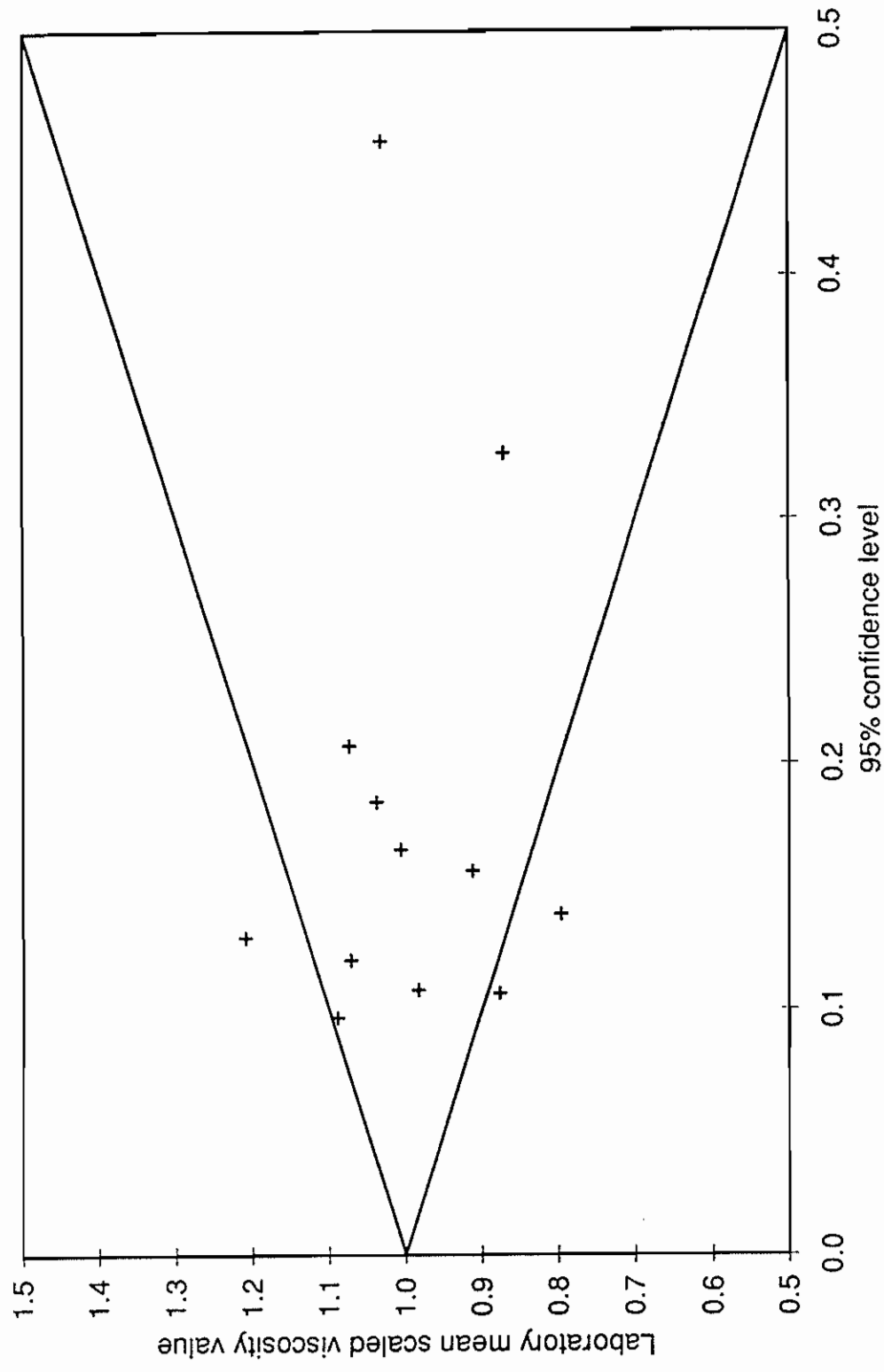


Figure 12. Variation in mean scaled viscosity values for GFP at 230 °C for each laboratory as a function of the repeatability of the values for that laboratory.

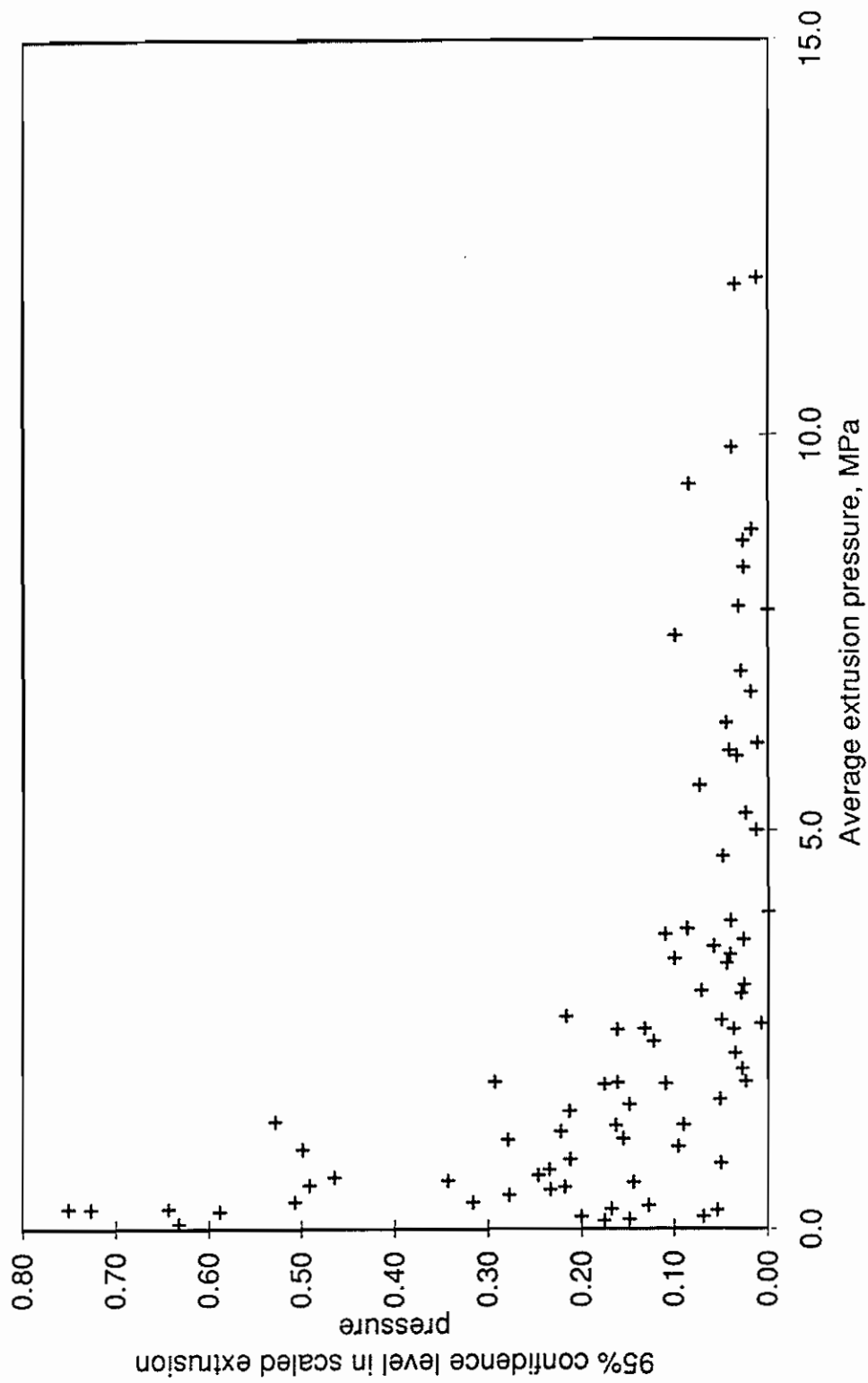


Figure 13. Repeatability of extrusion pressures as a function of extrusion pressure for GFPP at 230 °C (extrusion pressure scaled using the average extrusion pressure for that set of conditions).

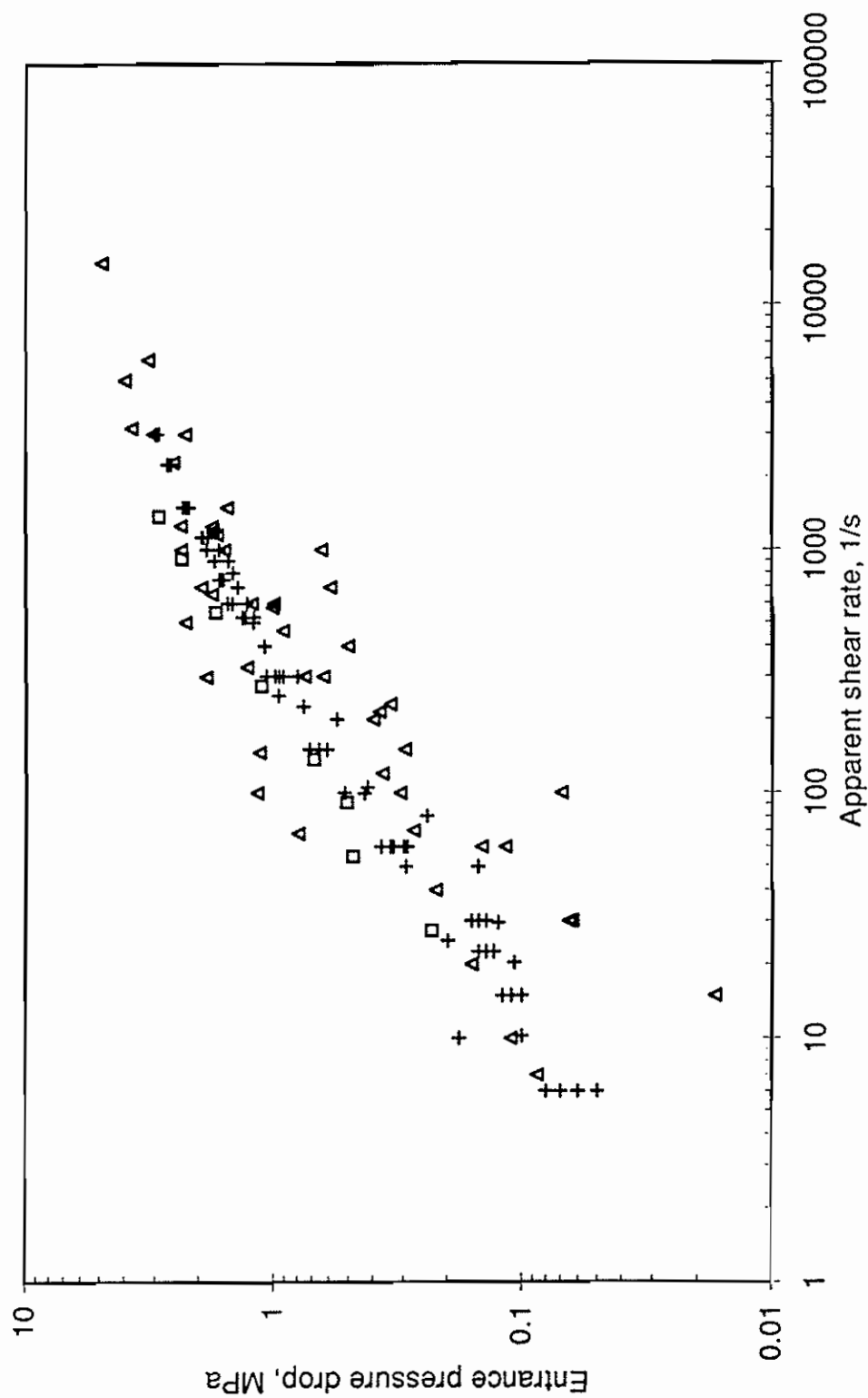


Figure 14. Scatter in entrance pressure drop values for GFPP at 230 °C with apparent shear rate using various barrel to die diameter contraction ratios in the range 9.55 - 15.5. Contraction ratios: $+$ 15, Δ 1.55 - 12.5, $\square$ 15 - 15.5.

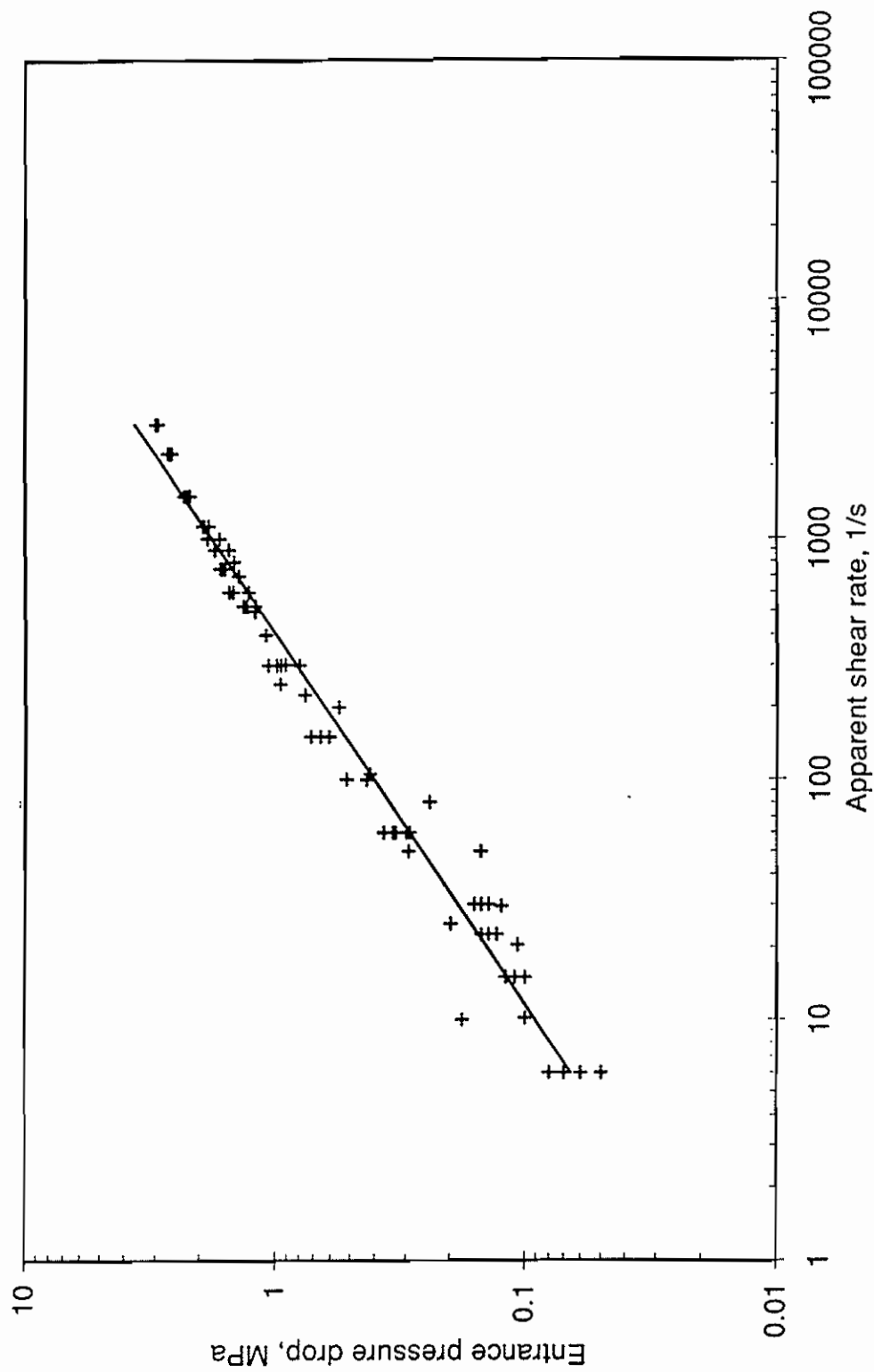


Figure 15. Scatter in entrance pressure drop values for GFPP at 230 °C with apparent shear rate using a barrel to die diameter contraction ratio of 15 only, with best-fit straight line to the data (see table 7).

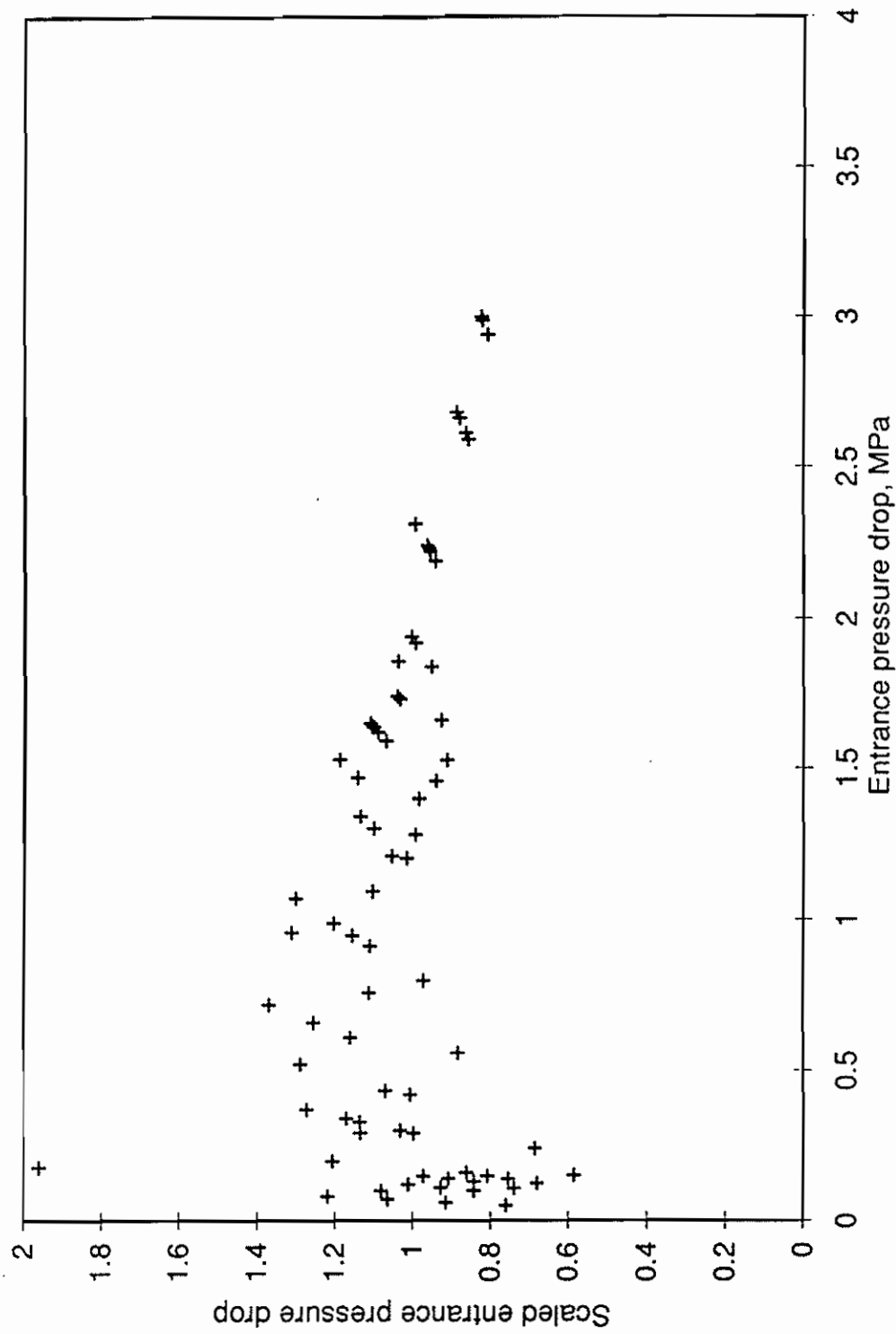


Figure 16. Scatter in scaled entrance pressure drop values as a function of entrance pressure drop for GFPP at 230 °C (entrance pressures scaled using entrance pressure drop values calculated using the parameters presented in table 7).

APPENDIX 1 DETERMINATION OF THE UNCERTAINTY BUDGET FOR CAPILLARY EXTRUSION RHEOMETRY

The following uncertainty budget was determined in accordance with NPL procedure DMM/B/130 (17) and covers the measurement of shear viscosity of polymers.

For the following equations for calculating shear viscosity see references 1, 8 and 16. The subscript 'app' indicates terms that have not been corrected for non-Newtonian velocity profile effects (Rabinowitsch correction (9, 10)) but have been corrected for entrance pressure drop effects. Although the application of the Rabinowitsch correction may introduce further variation in results between laboratories the effect on uncertainties is considered to be small in comparison with other sources of error. Variability due to the application of the Rabinowitsch correction may occur due to the method of determination of the gradient of the log(apparent shear viscosity) versus log(apparent shear rate) curve at given apparent shear rates. For the purpose of this exercise the uncertainties in Rabinowitsch corrected shear viscosities are assumed to be equal to the uncertainties in apparent shear viscosities.

Using the following definitions:

L	=	capillary die length
D _c	=	capillary die diameter
D _b	=	barrel diameter
V _p	=	piston speed
Q	=	volume flow rate
P	=	extrusion pressure
ΔP _{ent}	=	Entrance pressure drop
γ _{app}	=	apparent shear rate.
η _{app}	=	apparent shear viscosity (entrance pressure drop corrected, not Rabinowitsch corrected)

and from analysis of the forces acting in the capillary rheometer (1, 10, 16) then

$$\begin{aligned}
 P &= \frac{4L}{D_c} \tau_{app} + \Delta P_{ent} \\
 &= \frac{4L}{D_c} \eta_{app} \dot{\gamma}_{app} + \Delta P_{ent}
 \end{aligned}$$

or re-arranged

$$\begin{aligned}
 \eta_{app} &= \frac{(P - \Delta P_{ent})}{\left[\frac{4L}{D_c} \times \frac{4Q}{\pi R_c^3} \right]} \\
 &= \frac{(P - \Delta P_{ent})}{\left[\frac{4L}{D_c} \times \frac{8V_p \pi D_b^2}{\pi D_c^3} \right]}
 \end{aligned}$$

where $\dot{\gamma}_{app} = 4Q/\pi D_c^3$ and $Q = V_p \pi D_b^2/4$.

Thus

$$\eta_{app} = \frac{D_c^4}{[32LV_p D_b^2]} [P - \Delta P_{ent}]$$

The fractional uncertainty in the term $P - \Delta P_{ent}$ is given by the equation

$$u^2 (P - \Delta P_{ent}) = (p^2 + \delta p_{ent}^2) / (P^2 - \Delta P^2)$$

and thus the uncertainty in measurement of apparent shear viscosity U_η by

$$U_\eta = \eta_{app} \sqrt{\left[4 \left(\frac{d_c}{D_c} \right)^2 + \left(\frac{\ell}{L} \right)^2 + \left(\frac{v_p}{V_p} \right)^2 + 2 \left(\frac{d_b}{D_b} \right)^2 + \left(\frac{p^2 + \delta p_{ent}^2}{(P - \Delta P_{ent})^2} \right) \right]} \quad [1]$$

The fractional uncertainty in the measurement of η_{app} is estimated, using [1] and the following values of the fractional uncertainties for each of the terms

$$\frac{d_c}{D_c} = 0.007$$

$$\frac{\ell}{L} = 0.00125$$

$$\frac{v_p}{V_p} = 0.01$$

$$\frac{d_b}{D_b} = 0.0007$$

$$\frac{P}{P} = 0.01$$

$$\frac{\delta P_{ent}}{\Delta P_{ent}} = 0.01$$

and also $\Delta P_{ent} = 0.2 \times P$. The effect of degradation (permitted to a level of 5% in accordance with ISO 11443) can be incorporated into equation 1 as an additional term, thus

$$U_\eta = \eta_{app} \sqrt{\left[4 \left(\frac{d_c}{D_c} \right)^2 + \left(\frac{\ell}{L} \right)^2 + \left(\frac{v_p}{V_p} \right)^2 + 2 \left(\frac{d_b}{D_b} \right)^2 + \left(\frac{p^2 + \delta p_{ent}^2}{(P - \Delta P_{ent})^2} \right) + (fd)^2 \right]} \quad [2]$$

where 'fd' in the fraction uncertainty due to degradation and has the maximum value of 0.05. Equations 1 and 2 were used to obtain values for the uncertainties in the measurement of shear viscosity, Table 1, where values are presented with and without a contribution due to degradation effects.

APPENDIX 2 Computation of mean, standard deviations, repeatability and reproducibility limits.

Repeatability and reproducibility can be defined (18) as:

REPEATABILITY: The closeness of agreement between successive results obtained with the same method on identical test material, under the same conditions (same operator, same apparatus, same laboratories and/or same times).

REPRODUCIBILITY: The closeness of agreement between individual results obtained with the same method on identical test material, but under different conditions (different operator, different apparatus, different laboratories and/or different times).

In accordance with ISO document TC61 SC5 GT 21 N18E (14) 'Determination of the precision of a test method - practical guide' the mean, standard deviations and repeatability and reproducibility limits (95% confidence values) are determined as follows (see also (15)), where:

- n_i = number of tests carried out by laboratory i ,
- Y_i = mean of the n_i tests,
- S_i = standard deviation of the n_i tests,
- m = mean of all laboratories,
- S_r = standard deviation within a laboratory per level,
- S_R = standard deviation for the total deviation between the laboratories per level,
- r = repeatability limit ($= 2.8 S_r$), 95% confidence value,
- R = reproducibility limit ($= 2.8 S_R$), 95% confidence value,
- p = number of laboratories.

Given that

$$\begin{aligned} T_1 &= \sum n_i \bar{Y}_i \\ T_2 &= \sum n_i Y_i^2 \\ T_3 &= \sum n_i \\ T_4 &= \sum n_i^2 \\ T_5 &= \sum (n_i - 1) S_i^2 \end{aligned}$$

then

$$S_r^2 = \frac{T_5}{(T_3 - p)}$$

$$S_L^2 = \left[\frac{T_2 T_3 - T_1^2}{T_3(p - 1)} - S_r^2 \right] \left[\frac{T_3(p - 1)}{T_3^2} - T_4 \right]$$

$$S_R^2 = S_L^2 + S_r^2$$

and

$$\begin{aligned} m &= T_1 / T_3 \\ r &= 2.8 S_r \\ R &= 2.8 S_R \end{aligned}$$

