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REFERENCE MATERIALS

Certification report for a pyrex glass reference material for thermal conductivity between -75°C and 195°C

CRM 039

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1 INTRODUCTION

In recent years provisions have been introduced throughout the EC to encourage the more efficient use of fuel through improved thermal insulation of buildings. Regulatory and administrative actions, which are currently being harmonised under Council Directive 89/106, require constructional and insulating materials to comply with product standards and with technical criteria which call for third party verification of their thermal conductivity and thermal resistance values.

Commercially sensitive measurements of this kind are required to be undertaken using standard guarded hot-plates or heat flow meters which are subjected to regular calibration checks as specified in national and international standards. There is a requirement, therefore, particularly as the constructional and insulating materials of interest have conductivities ranging over two orders of magnitude (0.02 to 2 W/m.K), for a range of well-characterised thermal conductivity reference materials for use by industrial and commercial testing laboratories.

To meet this requirement the Community Bureau of Reference (BCR) initiated a collaborative programme involving a number of leading European laboratories to select and characterise reference materials of the type needed. For the low end of the thermal conductivity range a resin bonded glass fibre board was chosen and for the other end, Pyrex glass. The certification of the former was accomplished with little difficulty using conventional 300 mm and 500 mm square guarded hot-plates and the material is now available as a BCR Certified Reference Material (RM No. 64) [1]. The certification programme on the Pyrex glass, undertaken by the same laboratories, proved far more problematic, in that considerable attention had to be directed towards improving the methodology before results of the required accuracy could be produced.

The accuracy of the guarded hot-plate method depends critically on the establishment of linear heat flow in the specimens. This presents few problems with soft materials but can be extraordinarily difficult to achieve when the specimens are rigid solids, and increasingly so as their thermal resistance decreases (ie the higher their thermal conductivity). Measurements on such materials are particularly prone to errors arising from thermal contact and temperature measurement problems since now compressible material such as soft rubber has to be introduced

to establish uniform thermal contact at the interfaces and temperature differences have to be measured with thermocouples mounted on specimen surfaces.

These practical difficulties were, of course, well recognised by the participants in the certification programme, but when the work was started there was little guidance either in standards or the scientific literature as to how they might be overcome. The early measurements were therefore made with each laboratory adopting an individual approach. Unfortunately, these proved not to be equally effective and the results, although in the main falling within 6% of a weighted mean, were too divergent for reliable certification.

This led to a subsidiary investigation being carried out by NPL aimed at defining and authenticating an optimised technique capable of producing results of the required accuracy. The investigation comprised essentially a series of carefully executed thermal conductivity measurements in which many of the critical parameters were changed systematically. Two techniques appeared to be suitably reliable and one of these was used for further measurements by two more of the participating laboratories (FIW and IFT).

Whilst this work was in progress, however, PTB announced the completion of a new apparatus; a 100 mm single-sided guarded hot-plate, designed specifically for high precision thermal conductivity measurements on materials such as glass. Using this and an earlier apparatus of similar concept PTB have carried out extremely precise measurements on two of the glass samples over the temperature range - 75 °C to 195 °C - a far wider range than could be covered by any of the other participants. Further, the uncertainties associated with these measurements were some 2 to 3 times smaller than those with the conventional guarded hot-plates. Consequently, it was decided that the certification of the material should be in terms of the PTB results alone with other results included as a check, or back-up, for the PTB values. (Results obtained prior to the NPL investigation are not included in the discussion but are summarised in Appendix 1).

With the certification based wholly on the PTB results, it was considered appropriate to describe their apparatus, procedures and error

analysis in detail alongside the discussion of their experimental results. In contrast, the apparatuses used by the other participants are described more briefly and likewise only those aspects of their procedures which bear significantly on their measurement uncertainties are described. The evaluation of these uncertainties is treated reasonably fully, however, since the majority of the potential users of the reference material will themselves operate conventional guarded hot plates.

2 PARTICIPANTS

Five laboratories participated in the project. These and the main personnel involved were:

Forschungsinstitut fur Warmeschutz E V Munchen (FIW)
Lochhamer Schlag 4
D-8032 Graefelfing
FR Germany
(M Zeitler)

Istituto di Fisica Tecnica (IFT)
Facolta di Ingegneria dell' Universita di Padova
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Italy
(F De Ponte)

Laboratoire National D'Essais (LNE)
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75015 Paris
France
(G Venuti)

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Teddington
Middlesex TW11 OLW
Great Britain
(I Williams)

Physikalisch-Technische Bundesanstalt (PTB)
Bundesalle 100
D-3300 Braunschweig
FR Germany
(W Hemminger)

3 DESCRIPTION OF THE MATERIAL

The material consisted of a specially prepared melt of Dow Corning 7740 glass cast into plates prepared by le Societe Corning France (Sovirel) for use as reference specimens for thermal conductivity using a guarded hot-plate technique.

The entire stock comprised 81 plates with the following nominal dimensions

Length	Breadth	Thicknesses
500 mm	500 mm	50, 30, 20 mm
300 mm	300 mm	50, 30, 20 mm

The precise dimensions, particularly the flatness and parallelism, of the plate surfaces were individually determined by the Laboratoire National D'Essais, Paris (Report no LNE 19 907 05; 10/80).

Density determinations were also carried out on 49 of the plates by LNE (Report no LNE 19 402 16; 7/85) and the results were found to lie within three narrow bands in the range 2222 to 2226 kg/m^3 as follows:

2222 kg/m^3; σ = 0.2 kg/m^3	13 plates of nominal thickness 30 mm
	11 plates of nominal thickness 20 mm
2224 kg/m^3; σ = 0.2 kg/m^3	8 plates of nominal thickness 30 mm
	4 plates of nominal thickness 20 mm
2226 kg/m^3; σ = 0.1 kg/m^3	13 plates of nominal thickness 50 mm

A histogram of the distribution is shown in Figure 1. The uncertainty in the measured density values was 0.6 kg/m^3.

The thermal conductivity of the glass was not expected to change significantly with density over the range 2222 to 2226 kg/m^3 but in the present studies measurements were made on specimens with densities extending virtually over the full range as follows:

2222 kg/m^3; 20 mm nominal thickness - PTB

2225 kg/m^3; 50 mm nominal thickness} - NPL
2222 kg/m^3; 30 mm nominal thickness}

2224 kg/m^3; 30 mm nominal thickness - FIW

2222 kg/m^3; 30 mm nominal thickness - IFT

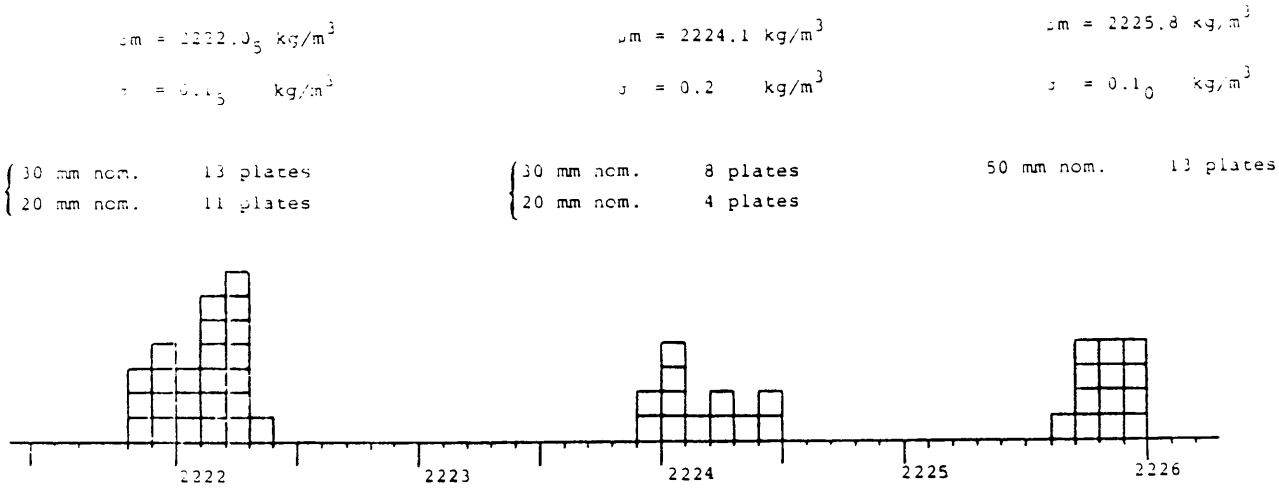


Figure 1: Histogram of density distribution

4 CERTIFICATION PROCEDURE

Measurements on the chosen reference material were conducted under contract with the Commission of the European Communities (Programme of the Community Bureau of Reference - BCR) at the laboratories previously listed in section 2 of this report.

The initial measurements were made using conventional guarded hot-plates having basic designs similar to those used by commercial testing laboratories. The measurements were not straightforward and involved significant prior development of the methodology. Later, these were reinforced by more accurate measurements conducted by one laboratory (PTB) using two compact guarded hot-plates designed specifically for high precision measurements on dense materials such as glass.

The principles of the various measurement techniques were considered and a detailed evaluation was made of the estimated maximum overall uncertainty of the measured thermal conductivity values based on an assessment of the individual uncertainties associated with the measurement of temperature, power, dimensions etc. Two uncertainty values were obtained by adding the individual uncertainties, ϵ, in quadrature, $(\Sigma\epsilon^2)^{\frac{1}{2}}$, and arithmetically, $\Sigma\epsilon$, the former being considered applicable to groups of measured values and the latter to individual results.

Because of their greater accuracy and much wider temperature range, the certified thermal conductivity values were based on the PTB results alone, with the results obtained with the more conventional equipment backing them up, serving both as a check and a guide in the assessment of the final uncertainty to be assigned to the certified values.

Power series of order 3 were fitted to the two sets of PTB results on two specimens both individually and collectively. The quality of the fit was examined in each case; the standard deviation was evaluated and the individual residuals noted. The 95% confidence uncertainty levels were also determined. All the curve fitting and statistical data were compared with the estimated uncertainty values referred to above; a close correlation would normally be expected between them, which was taken as an independent indicator of confidence.

The certified values were based on the polynomial fit through all the PTB results (two specimens, two apparatuses). The remaining six sets of results obtained by the other laboratories were then checked against the polynomial values; the deviation of the individual points and the root mean square values again being compared with their estimated uncertainty values.

The variation of the thermal conductivity value with density over the limited range of interest appeared to be small. An attempt was made to estimate an upper limit for this and an additional increment was added to the uncertainty of measurement to allow for it. This overall uncertainty assigned to the batch was finally compared with the deviation of all the data points from the certified values.

5 MEASUREMENTS WITH SPECIAL GUARDED HOT PLATES

5.1 PTB measurements

The PTB measurements were made on two 100 mm diameter disc shaped specimens over the temperature range - 75 °C to 195 °C. The specimens were machined from two 300 mm x 300 mm x 19 mm plates (Nos 42 and 43) taken from the BCR stock.

5.1.1 Apparatus and measurement procedures

Two guarded hot plates of basically similar concept and design were used for the measurements, the newer of the two, on which most of the measurements were made (Figure 2) [2], covering the temperature range - 75 °C to 195 °C and the other the range 10 °C to 100 °C. Both hot-plates were of the single specimen type and both had been specially designed to perform measurements of high accuracy on 100 mm diameter, hard, non-absorbent, insulating materials. In particular, considerable attention had been paid to achieving uniform thermal contact between the specimen and plate surfaces and to ensuring that, as far as possible, the heat flux generated electrically in the central metering section passed linearly through the specimen to the cold plate without loss or gain via the edges or the guards.

The principle of the method can be readily understood by reference to Figure 2. The specimen A is clamped between the heater plate B and the cold plate C, a thin layer of fluid of known thickness (silicone oil or helium) providing uniform thermal contact between them. A guard plate D and guard ring E, both independently maintained at the same temperature as B, serve to ensure that the heat generated in B is constrained to flow downwards through the specimen to C with minimum lateral flow. This is aided by the presence of the passive guard ring F in which the same temperature gradient as in the specimen is established through contact with plates E and C. The whole assembly is mounted in a steel casing J which, to further reduce lateral heat flow through the specimen edges, is immersed in a fluid bath controlled at the cold plate temperature. The ducts I provide access for measurement leads and supply lines whilst the central duct and push rod H hold the component parts together by

adjustable spring pressure.

To achieve good temperature uniformity coupled with stable, abrasion-resistant surfaces, the active components of the apparatus, the guards, metering section and cold plates, are made of nickel-plated copper. Ten 0.2 mm diameter copper-constantan thermocouples, calibrated against a precision platinum resistance thermometer, are installed in the apparatus (locations 1 to 10), which, in the present work, were further calibrated after installation to correct for any small voltages generated in the thermocouples wire segments that pass through temperature gradients (i.e. voltages associated with the local inhomogeneities in the thermocouple wires).

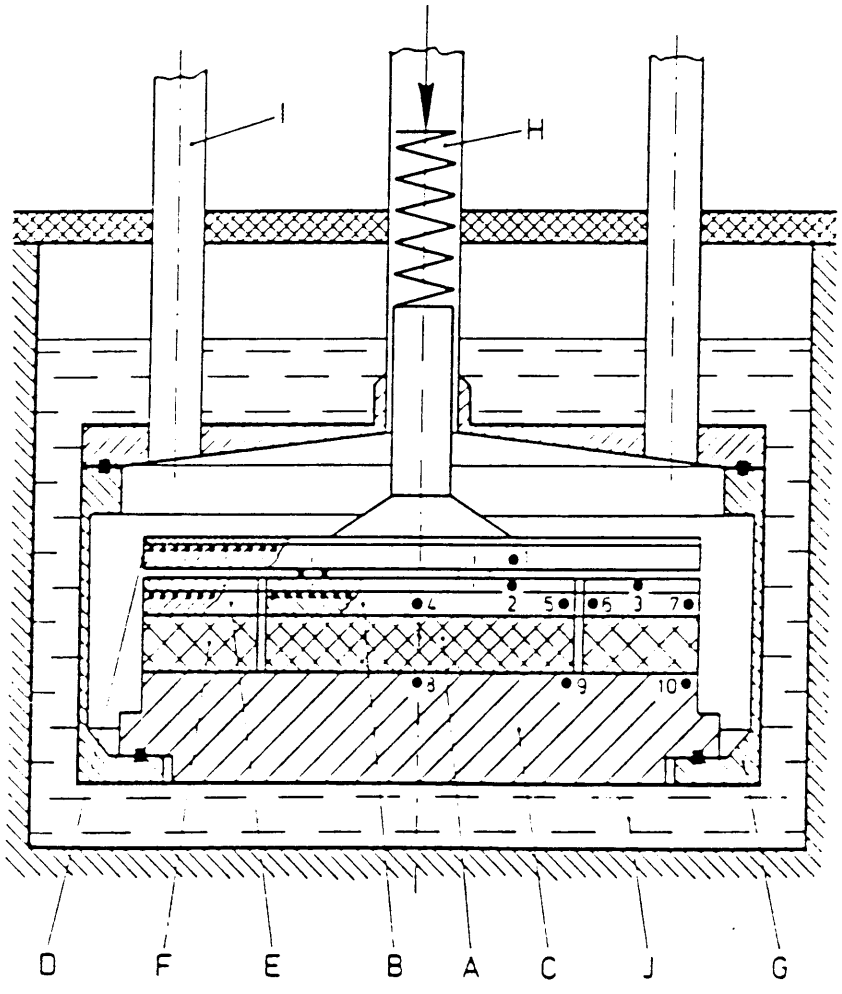


Figure 2. Guarded hot-plate for the temperature range -75 °C to 200 °C. (A specimen; B hotplate; C cold plate; D guard plate; E guard ring; F specimen guard ring; G casing; H push-rod; I ducts; J liquid bath)

The surfaces of the hot and cold plates of the apparatus (and those of the specimens) were machined flat to better than 1.25 μm (by surface grinding and lapping) in order that the fluid layers introduced at the interfaces should be both very thin and of uniform thickness. The small temperature drop through such layers can be readily evaluated if their thickness is known and the method, thus, permits the temperature drop through the specimen to be determined very conveniently from the temperatures registered by the plate-mounted thermocouples. This circumvents the drawback incumbent in other methods, of having to measure the specimen surface temperatures directly.

In the present work silicone oil (DC200; viscosity 12500 $mm^2 s^{-1}$ at 20 °C) was used as the contact medium for measurements down to - 45 °C. Helium gas was used at lower temperatures, although some check measurements were also made with nitrogen gas. The thickness of the silicone oil layers was determined by a weighing technique, whilst that of the gaseous layers was defined by the thickness of spacers coupled with a small correction for the remaining deviation from planeness of the surfaces.

5.1.2 Correction factors

When linear heat flow conditions, at steady-state, have been established in the assembly the thermal conductivity of the specimen is given by the relationship

$$\lambda = P_o d / A \Delta T_o$$

where P_o is the heat flux through the specimen, d is the specimen thickness, A its cross-sectional area and ΔT_o the temperature difference between its faces.

In the present method ΔT_o is not measured directly but is evaluated from the temperature difference ΔT registered by the thermocouples mounted in the hot and cold plates ($\Delta T = T_4 + T_5)/2 - (T_8 + T_9)/2$), corrected for the small temperature drop in the metal plates (between the thermocouple location points and the surface), ΔT_m, and the temperature drop through the thermal contact layers, ΔT_c. Thus

$$\Delta T_o = \Delta T - (\Delta T_m + \Delta T_c)$$

With ΔT_o chosen to be about 5 K, ΔT_m and ΔT_c were typically around 0.007 K and 0.040 K, respectively, in the present measurements.

Although edge losses are rendered negligibly small in the apparatus, unbalance losses due to slight temperature differences between the hot plate and guards could be significant and must therefore be allowed for. The heat flux P_o passing through the specimen can be represented by

$$P_o = P + P_x - \Sigma P_v$$

where P is the power supplied to the heater plate (B), P_x is a correction relating to slight differences in the thermoelectric power of individual thermocouples arising from the effects of thermal gradients and ΣP_v is the sum of the losses associated with

i) temperature imbalance between the hot plate (B) and the guard plate (D), which can be represented by

$$P_{v1} = C_1 \Delta T_1 = C_1 (T_2 - T_1)$$

ii) temperature imbalance between the hot plate (B) and the guard ring (E), which can be represented by

$$P_{v2} = C_2 \Delta T_2 = C_2 ((T_2 + T_5)/2 - (T_3 + T_6)/2)$$

iii) heat flow from the hot plate (B) to the cold plate (C) via the 2 mm gap between the specimen and the passive guard ring (F), which can be represented by

$$P_{v3} = (\lambda_{gap} . A_{gap}/2) \Delta T/d$$

The proportionality factors C_1 and C_2 are determined experimentally by the well known 'mismatch' method. Their magnitude depends on the design and constructional details of the apparatus and on the gaseous environment employed (air, helium or nitrogen). They also vary with temperature and must, therefore, be evaluated at several different temperatures.

The evaluation of P_{v3} is straightforward using known and measured quantities.

The correction P_x (or equivalently an alternative correction ΔT_x to ΔT) arises from small errors in the values of ΔT, ΔT_1 and ΔT_2 caused by the small differences in the thermoelectric power of individual thermocouples. Its magnitude can be determined experimentally by a procedure developed at PTB [2], preferably at two widely different temperatures to allow for any variation with temperature.

5.1.3 Assessment of uncertainties

5.1.3.1 Area and thickness

The diameters of the specimens were measured to ± 0.05 mm and their thickness to ± 0.005 mm. The uncertainties in the values of the area, A, and the thickness, d, were, therefore, 0.1% and 0.025% of the mean values, respectively.

5.1.3.2 Temperature differences

i) Temperature difference ΔT. All thermocouple voltages were read sequentially 10 times after reaching steady state. Typical standard deviations were 1 mK, representing an uncertainty due to random errors of 2 mK in ΔT. A further uncertainty was associated with the differences in temperature (averaging 10mK) between the centre and edges of the hot and cold plates (ie between T_4 and T_5 and between T_8 and T_9). A maximum uncertainty of 5 mK was assumed in the mean temperature of each face giving a further uncertainty of 10 mK in ΔT. The total uncertainty in ΔT was therefore estimated to be 12 mK.

ii) Temperature difference T_m. The distance between the centres of the thermocouple bores and the surfaces of the hot and cold plates included (3.3 ± 0.5) mm of copper and 0.04 mm of nickel. Using these values and the thermal conductivity of the metals, ΔT_m was calculated to be 7 mK with an uncertainty of 1.5 mK.

iii) Temperature difference ΔT_c.

Measurements down to - 45 °C: The combined thickness of both contact layers of silicone oil was typically (15 ± 2.3) x 10^{-6}m, which, using the thermal conductivity of the oil (uncertainty 1%) yields a maximum value for ΔT_c of 40 mK with an uncertainty of 6 mK.

Measurements below - 45 °C: The combined thickness of the two gas layers between the specimen and plate surfaces, allowing for the spacers and an additional 1.25 µm per surface for deviations from planeness, was 21 x 10^{-6}m. With helium as the contact medium, the maximum calculated value for ΔT_c was 46 mK with an uncertainty of 9 mK. The corresponding values during check measurements using nitrogen, which is a much poorer conductor, were 292 mK and 58 mK, respectively.

5.1.3.3 Power

i) Power P. The dc power supplied to the heater plate (≈ 2.5 W) was determined from voltage and current measurements with a maximum uncertainty of 0.04%.

ii) Correction P_x. The value of this correction was determined for both specimens at the two extremes of the temperature range, a linear interpolation being employed for intermediate temperatures. As the reference junctions of the thermocouples were at 0 °C, a change in the sign of the temperature dependence occurred above and below this temperature. The maximum value of P_x was found to be 0.0106 W (≈ 0.4% of P_o) with an uncertainty based on repeat measurements of 0.0015 W, equivalent to 0.05 to 0.08% of P_o (2 to 2.8 W).

iii) Corrections P_{v1} and P_{v2}. The proportionality factors C_1 and C_2 were determined at - 75 °C, 15 °C and 165 °C to better than 5%. The resulting values of P_{v1} and P_{vs} were less than 0.1% of P_o and the uncertainty associated with these values was consequently negligibly small.

iv) Correction P_{v3}. The expression used to determine this correction embodies the assumption that the heat flux passing down the gap between the heater and guard is provided in equal proportion by the heater and the guard ring. This is a reasonable assumption but is the main source of uncertainty in the value of this correction. In the present measurements P_{v3} was calculated to be approximately 0.0025 W when the atmosphere was air or nitrogen and about 0.0125 W when it was helium. A total uncertainty of 20% was assigned to these values, ie 0.0005 W and 0.0025 W, respectively in air and helium, equivalent to an uncertainty of 0.02% and 0.10% in P_o.

5.1.3.4 Summary of estimated uncertainties

Parameter		Measured Value & Uncertainty	Uncertainty (ϵ) in λ (%)
Area A		$\approx$ (7.8 $\pm$ 0.008) x 10^{-3} m^2	0.10
Thickness d		$\approx$ (18.5 $\pm$ 0.005) mm	0.025
Temperature difference $\Delta T_o = \Delta T - (\Delta T_m + \Delta T_c)$			
ΔT		$\approx$ (5 $\pm$ 0.012) K	0.24
ΔT_m		$\approx$ (0.007 $\pm$ 0.0015) K	0.03
ΔT_c	oil	$\approx$ (0.040 $\pm$ 0.006) K	0.12
	He	$\approx$ (0.046 $\pm$ 0.009) K	0.18
	N_2	$\approx$ (0.292 $\pm$ 0.058) K	1.16
Energy flow P_o; $P_o = P + P_x - (P_{v1} + P_{v2} + P_{v3})$			
P		$\approx$ (2.5 $\pm$ 0.001) W	0.04
P_x		$\approx$ (0.0106 $\pm$ 0.0015) W	0.08
P_{v1}		$\approx$ (0.0025 $\pm$ 0.0001) W	negligible
P_{v2}		$\approx$ (0.0025 $\pm$ 0.0001) W	negligible
P_{v3}	air, N_2	$\approx$ (0.0025 $\pm$ 0.0005) W	0.02
	He	$\approx$ (0.0125 $\pm$ 0.0025) W	0.10

	Interface medium	oil	He	N_2
Total Uncertainty	$(\Sigma\epsilon)$	0.655	0.795	2.695
	$((\Sigma\epsilon^2)^{\frac{1}{2}})$	0.33	0.39	1.17

These uncertainy levels are exceptionally low reflecting the special precautions taken in the design of the apparatus, and the fact that P_o was so large (due to the high thermal conductivity of the glass) that the corrections for power and their uncertainties were relatively very small. The greatest uncertainty can be seen to be associated with the measurement of temperature and the evaluation of the temperature drop through the interfacial fluid layers. In any individual measurement there is of course, a significant probability that the larger uncertainties will add together.

5.1.4 Results and discussion

The thermal conductivity measurements on both specimens, Nos 42 and 43, were made over the temperature range - 75 °C to 195 °C using the two apparatuses and the measurement procedures described in the preceding sections.

The relevant dimensions of the specimens were as follows:

Specimen No	42	43
Diameter / mm	99.73	99.73
Thickness / mm	18.625	18.524

5.1.4.1 Specimen 42

The results obtained with this specimen (PTB1) are shown in Table 1; the values at 10 °C, 30 °C, 50 °C, 70 °C and 90 °C (numbers 6, 8, 10, 11 and 13) relating to PTB's older apparatus and the remainder to their new apparatus which covers the full temperature range.

Using the NPL curve fitting package, a third order power series was fitted to these values to yield the following expression for the thermal conductivity versus temperature relationship:

$$\lambda = (1.1003 + 1.654 \times 10^{-3}\theta - 3.970 \times 10^{-6}\theta^2 + 6.817 \times 10^{-9}\theta^3)\ \text{W/m.K}$$

where the temperature θ is in degrees Celsius.

Table 1: Results on specimen number 42 (PTB1)

Index No	Interface	Temperature (θ) °C	Thermal Conductivity (λ) W/m.K
1	He	-75.00	0.951
2	He	-60.00	0.985
3	Oil	-45.00	1.018
4	..	-30.00	1.047
5	..	-15.00	1.074
6	..	10.00	1.117
7	..	15.00	1.123
8	..	30.00	1.147
9	..	45.00	1.166
10	..	50.00	1.175
11	..	70.00	1.199
12	..	75.00	1.204
13	..	90.00	1.226
14	..	105.00	1.236
15	..	135.00	1.268
16	..	165.00	1.295
17	..	195.00	1.323

The measured and calculated (power series) values, λ and λ_{fitted}, respectively are compared in Table 2, where in addition to the residuals, $r = (\lambda_{fitted} - \lambda)$, values of the ratio r/λ percent have been tabulated to permit direct comparison with the values of the total estimated uncertainty given in the previous section. The 'sum of the squares of the residuals' at the bottom of the table has the usual meaning, ie Σr^2, whilst the 'root mean squared residual', $r_{rms} = [\Sigma r^2/(n - 1 - m)]^{\frac{1}{2}}$ where n is the number of data points and m is the order of the fit. The residuals are also illustrated graphically in Figure 3.

The fit is clearly extremely good over the whole temperature range. Thus the standard deviation, is only 0.00147 W/m.K (0.11% to 0.16%) and the maximum positive and negative residuals only 0.00214 W/m.K (0.17%) and 0.00399 W/m.K (0.33%), respectively (the values in brackets refer to r/λ% which are single valued for the two maxima but extend over a range for r_{rms} due to the temperature dependence of λ).

Table 2: Polynomial fit to PTB1

No	Interface	θ °C	λ W/m.K	λ_{fitted} W/m.K	Residuals W/m.K
1	He	-75.00	0.951	0.951	0.0000 (0.00%)
2	He	-60.00	0.985	0.985	0.0003 (0.03%)
3	Oil	-45.00	1.018	1.017	-0.0008 (0.08%)
4	..	-30.00	1.047	1.047	-0.0001 (0.01%)
5	..	-15.00	1.074	1.075	0.0006 (0.05%)
6	..	10.00	1.117	1.116	-0.0005 (0.05%)
7	..	15.00	1.123	1.124	0.0013 (0.11%)
8	..	30.00	1.147	1.147	-0.0004 (0.04%)
9	..	45.00	1.166	1.167	0.0013 (0.11%)
10	..	50.00	1.175	1.174	-0.0010 (0.09%)
11	..	70.00	1.199	1.199	0.0000 (0.00%)
12	..	75.00	1.204	1.205	0.0009 (0.08%)
13	..	90.00	1.226	1.222	-0.0040 (0.33%)
14	..	105.00	1.236	1.238	0.0021 (0.17%)
15	..	135.00	1.268	1.268	0.0001 (0.01%)
16	..	165.00	1.295	1.296	0.0008 (0.06%)
17	..	195.00	1.323	1.322	-0.0005 (0.04%)

Sum of squares of residuals 0.0000282581 $(W/m.K)^2$
Root mean squared residual 0.0014743480 W/m.K
Maximum positive residual 0.0021394938 W/m.K (0.17%) at 14
Maximum negative residual -0.0039851755 W/m.K (0.33%) at 13

Coefficients of polynomial fit:

i	c_i
0	1.100307882942 W/m.K
1	0.001654424906 $W/m.K^2$
2	-0.000003970489 $W/m.K^3$
3	0.000000006817 $W/m.K^4$

where c_i are the coefficients of: $\lambda_{fitted} = c_0 + c_1\theta + c_2\theta^2 + c_3{}^3$.

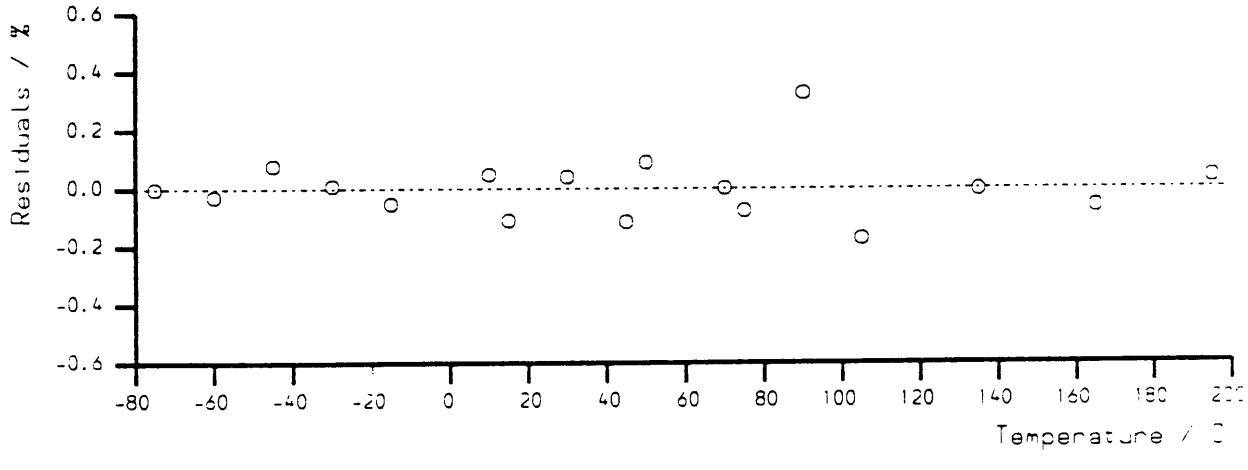


Figure 3: Residuals derived from polynomial fit to PTB1

The standard deviation is well below the total uncertainty (added in quadrature) for the measurements, 0.33%, and the largest deviation from the fit of any point is just equal to this value. This is in excellent accord with the estimated uncertainties and it has to be concluded that this is a very good set of results.

5.1.4.2 Comparison of the two sets of results

Inspection of the residuals columns of Table 2 shows no perceptible systematic difference between the results obtained with either apparatus except for the value at 90 °C with the older apparatus, which appears to be slightly less accurate than its counterparts at lower temperatures (r/λ = 0.33% compared with an average value of 0.05% for the other four results). A similar effect is seen in the results obtained with the second specimen but with the deviation in the opposite direction. Thus at 90 °C, which is close to the upper end of its range, this apparatus appears to be losing some accuracy, but the effect is altogether very small. It can be concluded therefore that as far as the present certification measurements are concerned these two apparatuses have virtually equal validity.

5.1.4.3 Specimen 43

The results for this specimen (PTB2) are given in Table 3 and, as before, the values at 10 °C, 30 °C, 50 °C, 70 °C and 90 °C (numbers 21, 23, 25, 26 and 28) relate to the first apparatus. The fit through these points yielded the following expression for the thermal conductivity

$$\lambda = (1.1076 + 1.649 \times 10^{-3}\theta - 3.960 \times 10^{-6}\theta^2 + 6.883 \times 10^{-9}\theta^3)\ \text{W/m.K}$$

which shows that these values are 0.7% or so higher than those obtained with specimen 42.

Table 3: Results on specimen number 43 (PTB2)

Index No	Interface	Temperature (θ) °C	Thermal Conductivity (λ) W/m.K
18	He	-75.00	(0.958) *
19	Oil	-45.00	1.026
20	..	-15.00	1.082
21	..	10.00	1.124
22	..	15.00	1.132
23	..	30.00	1.153
24	..	45.00	1.175
25	..	50.00	1.180
26	..	70.00	1.206
27	..	75.00	1.212
28	..	90.00	1.226
29	..	105.00	1.247
30	..	135.00	1.276
31	..	165.00	1.303
32	..	195.00	1.329

* point derived from PTB set 1

The quality of the fit through these data is equally good, however, as can be seen by inspection of Table 4 and Figure 4. Thus the standard deviation is only 0.00129 W/m.K (0.10% to 0.14%) and the maximum positive and negative residuals 0.00290 W/m.K (0.24%) and 0.00197 W/m.K (0.16%), respectively, well within the estimated uncertainty levels for the method as in the previous set of data. The results with the two apparatuses are again in excellent agreement, the slightly greater deviation at 90 °C having already been commented upon.

Although the results for the two specimens are on average ± 0.33% about the fit through all the points (see next section), which happens also to be the estimated accuracy of the data, the quality of the fits to the two sets clearly suggests that the difference between them is significant. For such a difference to show reproducibly in two apparatuses, the reason for it must relate directly to the characteristics of the two specimens, their composition, their dimensions or their detailed surface profiles or roughness.

Table 4: Polynomial fit to PTB2

No	Interface	θ °C	λ W/m.K	λ_{fitted} W/m.K	Residuals W/m.K
18	He	-75.00	0.958	0.959	0.0008 (0.08%)
19	Oil	-45.00	1.026	1.025	-0.0012 (0.12%)
20	..	-15.00	1.082	1.082	0.0000 (0.00%)
21	..	10.00	1.124	1.124	-0.0003 (0.02%)
22	..	15.00	1.132	1.131	-0.0005 (0.05%)
23	..	30.00	1.153	1.154	0.0007 (0.06%)
24	..	45.00	1.175	1.174	-0.0006 (0.05%)
25	..	50.00	1.180	1.181	0.0010 (0.09%)
26	..	70.00	1.206	1.206	0.0000 (0.00%)
27	..	75.00	1.212	1.212	-0.0001 (0.01%)
28	..	90.00	1.226	1.229	0.0029 (0.24%)
29	..	105.00	1.247	1.245	-0.0020 (0.16%)
30	..	135.00	1.276	1.275	-0.0011 (0.08%)
31	..	165.00	1.303	1.303	-0.0003 (0.02%)
32	..	195.00	1.329	1.330	0.0005 (0.04%)

Sum of squares of residuals 0.0000182964 $(W/m.K)^2$
Root mean squared residual 0.0012896943 W/m.K
Maximum positive residual 0.0029363601 W/m.K (0.24%) at 28
Maximum negative residual -0.0019680933 W/m.K (0.16%) at 29

Coefficients of polynomial fit:

i	c_i
0	1.107624483265 W/m.K
1	0.001648557240 $W/m.K^2$
2	-0.000003959974 $W/m.K^3$
3	0.000000006883 $W/m.K^4$

where c_i are the coefficients of: $\lambda_{fitted} = c_0 + c_1\theta + c_2\theta^2 + c_3{}^3$.

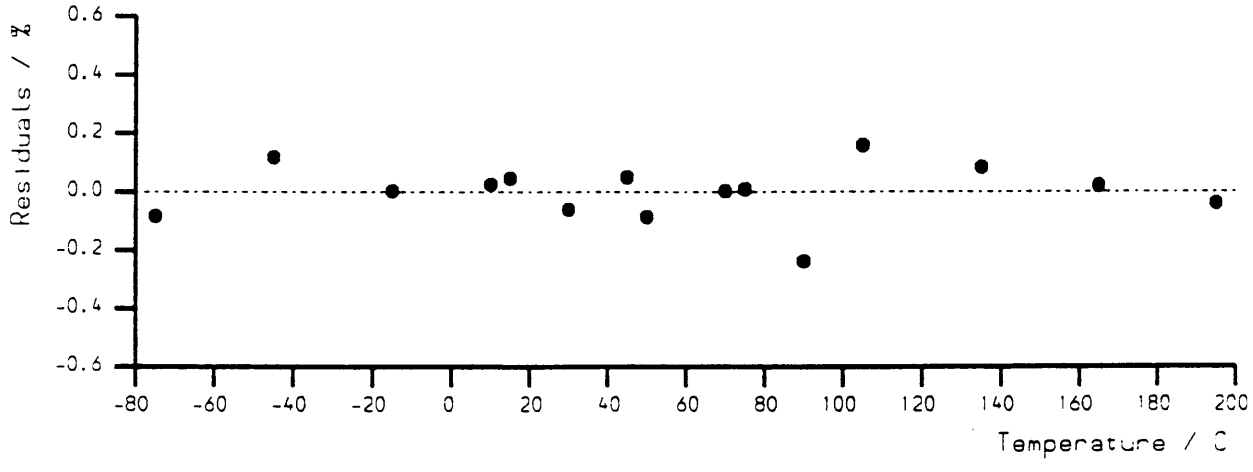


Figure 4: Residuals derived from polynomial fit to PTB2

When the densities of the two specimens were measured at PTB they found the values to be 2222 kg/m^3 and 2224 kg/m^3, respectively but with a 0.1% uncertainty. Nevertheless, it appeared possible that the difference in the thermal conductivity values could be correlated with the variation in density. However, more recent values provided by LNE, (2222.1 ± 0.6) kg/m^3 and (2222.0 ± 0.6) kg/m^3, respectively, have made any correlation with density quite indeterminate. Attempts to resolve a thermal conductivity difference in the 2222 kg/m^3 and 2225 kg/m^3 specimens measured by NPL were also indeterminate as will be explained later.

The alternative possibility that the difference arose from an undetected difference in the dimensions or surface profile of the specimens is rather speculative but worth considering. The uncertainty in the measurement of the area and thickness of the specimens, if they acted in opposite directions (ie additively) for the two specimens, would lead directly to a difference of 0.25% in their thermal conductivity. This would leave another 0.4% to be accounted for. A slight curvature of the specimen and plate surfaces (or some more complicated profile) remaining within the 1.25 μm deviation from flatness of each face, could go some way towards accounting for this. The interface layer thickness is only 7.5 μm thick and an uncertainty of 1.25 μm in its determination has already been allowed for. A further 1.5 μm per interface would be required to account for the remaining 0.4% difference in conductivity, which is probably too large, but it illustrates how really small and close to the limits of accuracy this difference in the two sets of results is.

To put it all into context, it has to be stressed that these PTB results are of unprecedented precision. An uncertainty of about 2% was the best previously achieved anywhere with this type of material and errors up to 10% are not uncommon (see Appendix 1). Most users of the reference material would probably be content with an uncertainty in its certified values of 2%. In view of this and the considerable effort required to produce results of this precision, it was decided that the certified values for the material should be based on the best fit to both sets of data.

5.1.4.4 Specimens 42 and 43

The fit through all the PTB results (PTB1 and 2) yielded the following expression for the thermal conductivity of the material:

$$\lambda = (1.1036 + 1.659 \times 10^{-3}\theta - 3.982 \times 10^{-6}\theta^2 + 6.764 \times 10^{-9}\theta^3)\ W/m.K$$

Table 5 compares the measured and calculated values, and the residuals are plotted as a function of temperature in Figure 5, in the same way as for the individual sets. The standard deviation is now 0.00402 W/m.K (0.30% to 0.42%) and the maximum positive and negative residuals 0.00572 W/m.K (0.46%) and 0.00580 W/m.K (0.57%), respectively, which remain very good.

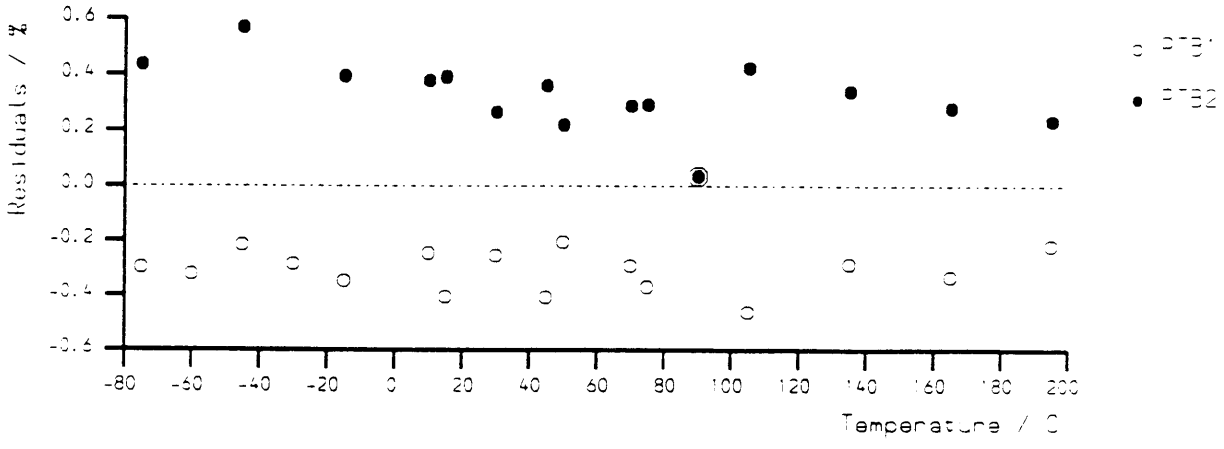


Figure 5: Residuals derived from polynomial fit PTB(1+2)

Subject to the results obtained by the other three laboratories substantially agreeing with the PTB values (which they do, as will be seen in the following sections), and allowing a small margin for possible variations with composition, it was concluded that the values given by the power series could be safely accepted as the certified values for the material. (The statistical evaluation of uncertaintities and the question of the margin to allow for material variability are dealt with later in the report).

A plot of the thermal conductivity versus temperature curve given by the power series, with the PTB data points superimposed, is shown in Figure 6.

Table 5: Polynomial fit to PTB sets 1 and 2

No	Interface	θ °C	λ W/m.K	λ_{fitted} W/m.K	Residuals W/m.K
1	He	-75.00	0.951	0.954	0.0028 (0.30%)
2	He	-60.00	0.985	0.988	0.0032 (0.32%)
3	Oil	-45.00	1.018	1.020	0.0022 (0.22%)
4	..	-30.00	1.047	1.050	0.0030 (0.29%)
5	..	-15.00	1.074	1.078	0.0037 (0.35%)
6	..	10.00	1.117	1.120	0.0028 (0.25%)
7	..	15.00	1.123	1.128	0.0046 (0.41%)
8	..	30.00	1.147	1.150	0.0029 (0.26%)
9	..	45.00	1.166	1.171	0.0048 (0.41%)
10	..	50.00	1.175	1.177	0.0024 (0.21%)
11	..	70.00	1.199	1.203	0.0035 (0.29%)
12	..	75.00	1.204	1.208	0.0045 (0.37%)
13	..	90.00	1.226	1.226	-0.0004 (0.03%)
14	..	105.00	1.236	1.242	0.0057 (0.46%)
15	..	135.00	1.268	1.272	0.0036 (0.29%)
16	..	165.00	1.295	1.299	0.0043 (0.33%)
17	..	195.00	1.323	1.326	0.0029 (0.22%)
18	He	-75.00	0.958	0.954	-0.0042 (0.44%)
19	Oil	-45.00	1.026	1.020	-0.0058 (0.57%)
20	..	-15.00	1.082	1.078	-0.0043 (0.39%)
21	..	10.00	1.124	1.120	-0.0042 (0.38%)
22	..	15.00	1.132	1.128	-0.0044 (0.39%)
23	..	30.00	1.153	1.150	-0.0031 (0.27%)
24	..	45.00	1.175	1.171	-0.0042 (0.36%)
25	..	50.00	1.180	1.177	-0.0026 (0.22%)
26	..	70.00	1.206	1.203	-0.0035 (0.29%)
27	..	75.00	1.212	1.208	-0.0035 (0.29%)
28	..	90.00	1.226	1.226	-0.0004 (0.03%)
29	..	105.00	1.247	1.242	-0.0053 (0.43%)
30	..	135.00	1.276	1.272	-0.0044 (0.34%)
31	..	165.00	1.303	1.299	-0.0037 (0.28%)
32	..	195.00	1.329	1.326	-0.0031 (0.24%)

Sum of squares of residuals 0.0004528746 $(W/m.K)^2$
Root mean squared residual 0.0040217029 W/m.K
Maximum positive residual 0.0057221390 W/m.K (0.46%) at 14
Maximum negative residual -0.0057998906 W/m.K (0.57%) at 19

Coefficients of polynomial fit:

i	c_i
0	1.103553539779 W/m.K
1	0.001659415180 $W/m.K^2$
2-	-0.000003981903 $W/m.K^3$
3	0.000000006764 $W/m.K^4$

where c_i are the coefficients of: $\lambda_{fitted} = c_0 + c_1\theta + c_2\theta^2 + c_3{}^3$.

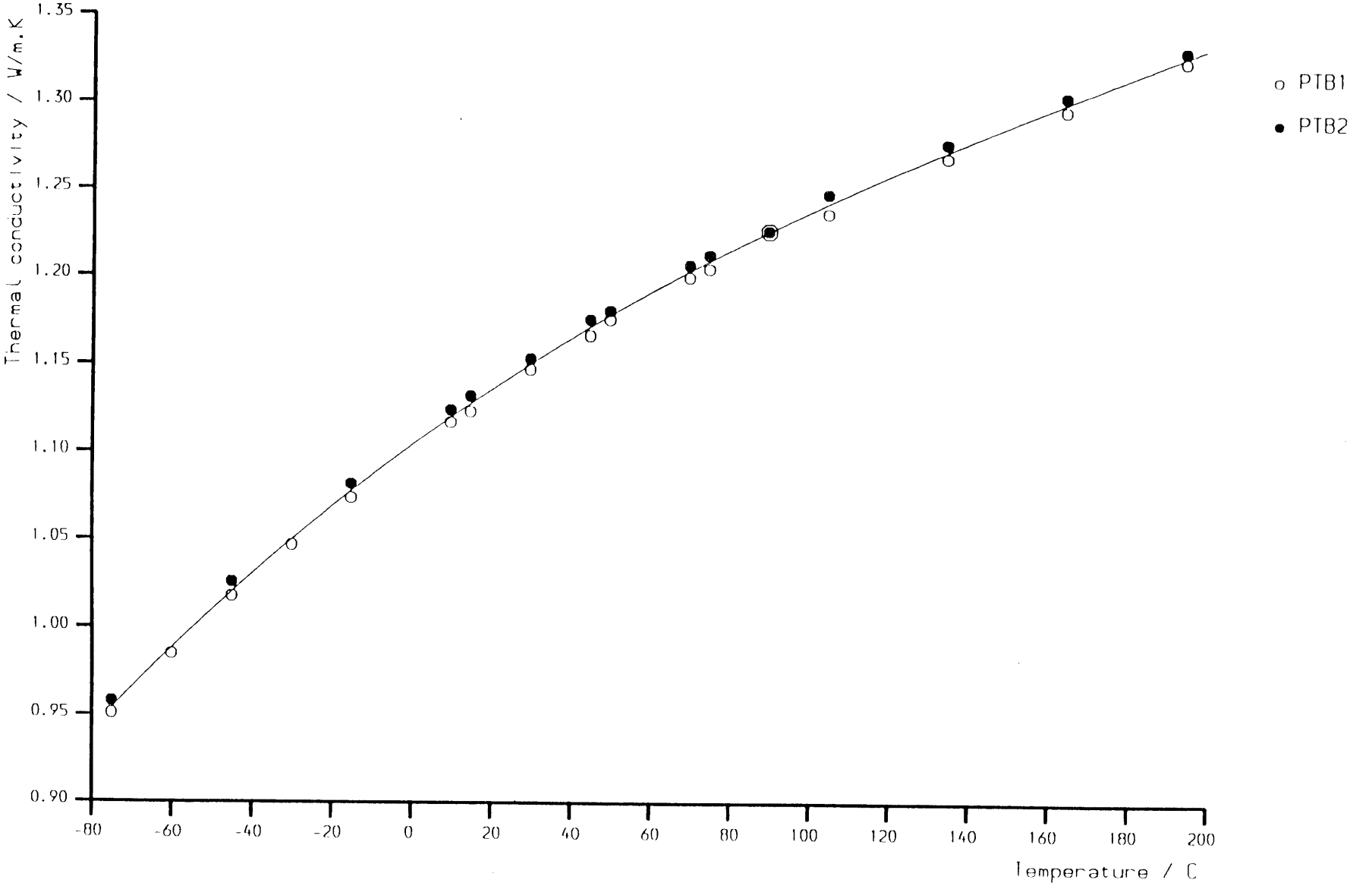


Figure 6: Comparison of experimental results with the correlation equation PTB(1+2)

6 MEASUREMENTS WITH CONVENTIONAL GUARDED HOT PLATES

The remaining participants in the measurement programme (NPL, FIW and IFT) used more conventional 300 mm and 500 mm double-sided guarded hot-plates for the measurements [3] relying on compressible rubber sheets for good interfacial thermal contact and the use of surface-mounted thermocouples for the measurement of the temperature difference between the specimen faces (Figure 7). Exceptional care has to be taken to maintain good accuracy using this technique and it has already been pointed out that the first results (obtained by LNE, NPL, FIW, and IFT, Appendix 1) were excessively divergent. This led to the postponement of further certification measurements until a subsidiary investigation of the critical experimental parameters, carried out by NPL, had resulted in the definition of improved procedures suitable for use by all three laboratories. Detailed consideration is given in this part of the report to the several sets of measurements made by NPL during the course of this investigation and to those made subsequently by FIW and IFT using the recommended methodology (previous results are not considered).

The guarded hot-plate method relies on the establishment of linear heat flow conditions in the specimens. When the latter are rigid solids extraneous thermal resistances in the heat flow path become progressively more disruptive as the thermal resistance of the specimens being tested decreases. Such resistances must therefore be eliminated, as far as this is possible, especially contact resistances associated with air films at the interfaces. This can be achieved very satisfactorily by tightly clamping a compressible material such as soft rubber between the specimen and plate surfaces. However, for the best accuracy, the contact sheet itself must have uniform resistance and, hence, uniform composition and thickness, which, in turn, calls for the surfaces of the specimens and the apparatus to be as flat as possible. In addition, it now becomes necessary to measure the temperature difference between the specimen faces directly, using thermocouples pressed firmly onto their surfaces beneath the thermal contact sheets. Unfortunately, their presence causes a small perturbation of the heat flow pattern in their immediate vicinity leading to a small error in the measured temperature difference, the magnitude of which increases as the

thickness of the thermocouples (or their mounting pads when applicable) increases and also as the thermal resistivity of the contact material increases.

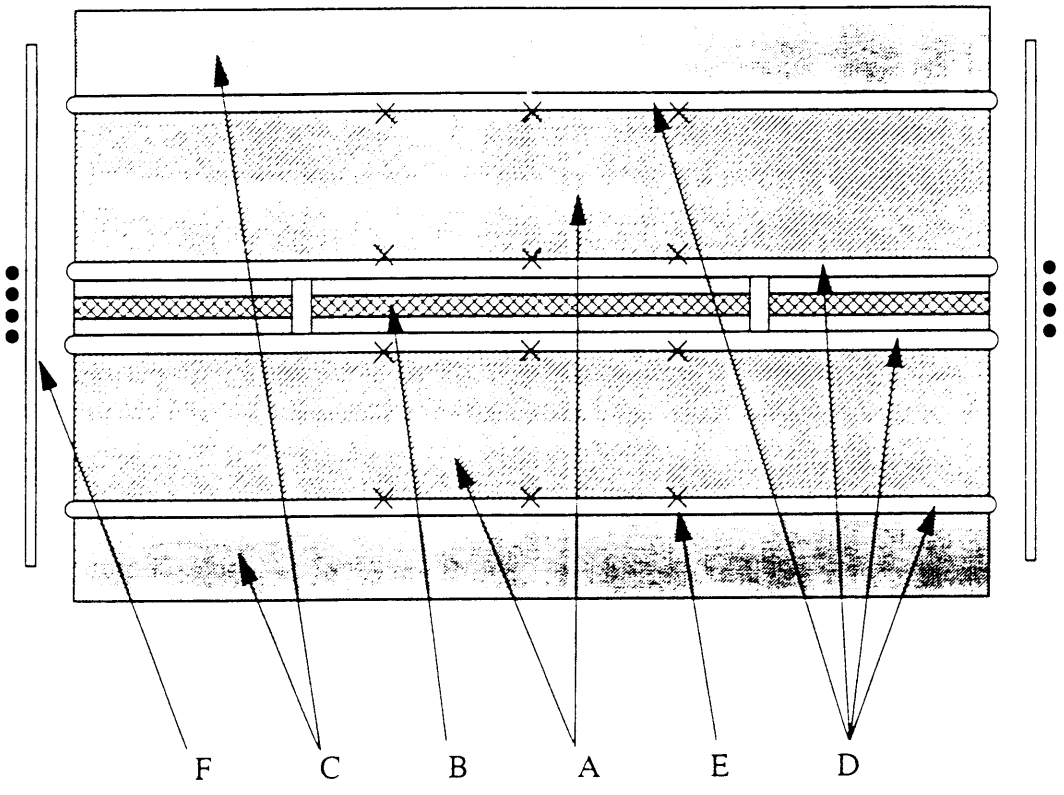


Figure 7. Guarded hot-plate for rigid specimens.
(A specimen; B heater plate; C cold plates;
D thermal contact sheets; E thermocouples; F edge guard)

This would suggest that a compressible material having the highest possible conductivity should be used for thermal contact (a conflicting requirement which has to be met in practice by a compromise solution) and the finest possible foil-type thermocouples for surface temperature measurements. Additionally, it would appear possible to derive analytical corrections for the remaining errors in the measured temperature values.

These considerations were taken fully into account in the NPL investigation and tested by systematically changing some of the critical parameters. Thus in the first series of NPL measurements (method 1) three different contact materials were used, two specimen thicknesses and thin copper pads of various dimensions as thermocouple mounts on the specimen surfaces. The next set of measurements (method 2) involved the use of the same contact materials but with the thermocouples (very thin foil types) now clamped directly onto the specimen surfaces. A final set involved the use of a technique in which foil-thin thermocouples were embedded in 1 mm deep grooves accurately machined in the specimen surfaces (method 3). This rather elaborate technique was intended to provide the most accurate measurements possible with large guarded hot-plates of this type, against which the accuracy of more practical alternative techniques could be gauged.

The FIW and IFT measurements were made over different, though partially overlapping, temperature ranges using procedures based on the second technique above, ie involving the use of fine, foil-type thermocouples mounted directly on the specimen surfaces.

6.1 NPL measurements

The NPL measurements were made on two pairs of specimens 45 mm and 33 mm thick (numbers 68, 69 and 44, 45, respectively) over the temperature range 10 °C to 80 °C.

6.1.1 Apparatus

The apparatus used was a 305 mm square double-sided guarded hot-plate designed to conform with the British Standard BS 874 and fitted with appropriate loading bars and extra terminals to cater for measurements on hard materials using the above techniques. The heater plate of the apparatus was a symmetrical double-sided unit incorporating a 202 mm square metering section with a 50 mm wide guard separated from it by a 1.5 mm gap. The surface of the heater plate was flat to better than ± 0.03 mm and those of the cold plates to better than ± 0.015 mm. 16 thermocouples made from calibrated wire stock were permanently installed in the heater plate on either side of the guard/centre gap and 3 each in

the faces of the cold plates. A 20-element thermopile was used to control the energy supply to the guard heater. During measurements, the apparatus was sealed with a 100 mm layer of insulation about its edges; voltages were logged using a low noise scanner and fed to a high quality digital voltmeter linked to a micro-computer. All the electrical measuring instruments were calibrated against NPL standards.

6.1.1.1 Thermocouples for surface temperature measurements

Experimental procedures involving three different methods of mounting thermocouples on the specimen surfaces were evaluated. In all of these the thermocouples themselves were fabricated from a stock of 0.075 mm diameter Nichrome-Constantan wire, the thermo-junction ends of which had been reduced to a thickness of about 0.03 mm by rolling. In the first and second set of measurements the flattened wires were soft-soldered, side by side, onto thin copper mounting pads (Figure 8), whilst in the remaining measurements the thermocouples were used un-mounted and made by soft-soldering the flattened wires together and rolling again over a length of about 20 mm from the junction tips to a thickness of about 0.04 mm (see Appendix 3).

Six sample thermocouples prepared from the un-rolled and heavily rolled wire were carefully calibrated under identical conditions against NPL standards. The effect of heavy rolling was very small and consistent, changing the calibration curve over the temperature range of interest by a mere 0.1%. Calibration and consistency checks were also made on the thermocouples actually used for the measurements both before and after mounting on the specimen surfaces. For example, under isothermal conditions up to 65 °C the maximum scatter observed in the individual voltages of a full set of 20 mounted thermocouples was ± 1 μV (±0.025K).

6.1.1.2 Interface material

The following three materials, available in the form of 3 mm thick sheets and having the required compressibility and homogeneity, were used:

i) 415 kg/m^3 foamed silicone rubber (F4), λ = 0.08 W/m.K

ii) 620 kg/m^3 foamed silicone rubber (F6), λ = 0.11 W/m.K

iii) A10 urethane elastomer (A1), λ = 0.18 W/m.K

Their thermal conductivities were measured as a function of temperature up to 80 °C using a 76 mm guarded hot-plate and, in the case of the foamed rubbers (pore size ≈ 0.3 mm), also as a function of compressive deformation. The values given above apply to the materials as used in the apparatus under a clamping pressure of about 20 kPa (compressed about 10%) at 20 °C.

6.1.1.3 Measurement procedure

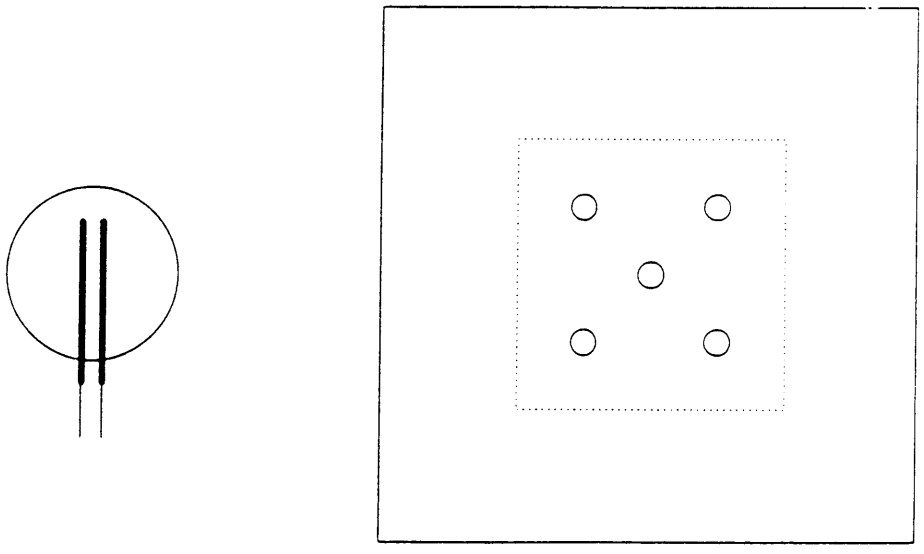
The specimens with the thermocouples firmly attached to their surfaces and overlaid with the chosen thermal contact sheets were inserted in the apparatus and the appropriate clamping force applied. When using the elastomer it was necessary to place an additional layer of aluminium foil on the cold plates to facilitate dis-assembly. The mean thickness of the contact sheets was determined using a micrometer depth-gauge technique, then, with the external insulation applied about the specimen edges, the power to the heater plate was set to produce a temperature drop of about 17 °C across the specimens. Voltages were read every two hours until equilibrium was established. Two sets of final readings, separated by at least two hours, were then taken and the mean of the two values, usually differing by no more than 0.1%, was taken.

6.1.2 Method 1: Thermocouples mounted on thin copper discs

A series of measurements was carried out on the 45 mm thick specimens using each of the previously named contact materials (F4, F6 and A1) and copper discs of the following sizes for mounting the thermocouples

i) 12 mm dia x 0.05 mm thick (12/05)
ii) 12 mm dia x 0.15 mm thick (12/15)
iii) 30 mm dia x 0.05 mm thick (30/05)
iv) 30 mm dia x 0.15 mm thick (30/15)

The discs were spark-machined from copper sheets of the appropriate thickness to avoid burring or distorting their edges and the flattened thermocouple wires were soft soldered onto their surfaces as described previously. Twenty such thermocouples, mounted on discs of a given size were required for each measurement, five per specimen face. These were carefully glued to the surface in a symmetrical pattern within the central measuring area (Figure 8). The sets on the opposite faces of each specimen were displaced one from the other by a 45° rotation about the centre, such that only the central thermocouple pad was directly above, or below, a similar pad on the other face.



(a) (b)

Figure 8. Thermocouple mounting pads
a) construction
b) locations on the specimen surface within the central metering area

Similar measurements were made using the 33mm specimen but only the contact material A1, which requires the smallest correction to be applied to the measured temperature differences, was used in this case.

As explained earlier, the local changes in thermal resistance in the heat flow path introduced by the thermocouples and their mountings would be expected to cause the thermocouples to register temperatures which are slightly different from those of the unperturbed areas of the surfaces, leading to too large a value for the temperature drop through the specimens and, hence, to too low a value for the thermal conductivity. On the basis of a simple network analysis [4] (see also Appendix 2) it was expected that the as-measured results using this method would be consistently too low by an amount that increased as the thickness and diameter of the thermocouple mounting pads increased and as the thermal conductivity of the thermal contact material decreased. The aim of this series of measurements, therefore, was to test the model by systematically varying all the critical parameters and, further, to investigate whether by applying individual corrections to the results their accuracy could be enhanced to a level that would render them suitable for the certification of the material.

The correction required to the measured temperature difference between the top and bottom faces of each specimen was calculated using the expression (see Appendix 2)

$$2e = \frac{2\Delta r_1}{r_2 + r_2(2r_1 + \Delta r_1)/r_5 + (r_1 + \Delta r_1)[1 + r_1 r_5/r_2(2r_1 + r_5)]^{-1}}$$

where

r_1 is the thermal resistance of the thermal contact material as used under compression in the apparatus,

Δr_1 is the change in that resistance above (or below) a thermocouple pad,

r_2 is the thermal resistance of each specimen and

r_5 is given by $r_5 = 2xr_2/d_2$, where 2x can be taken to be the diameter of the thermocouple mounting pad (to a very close approximation) and d_2 is the specimen thickness.

6.1.2.1 Assessment of uncertainties

Under linear heat flow conditions at steady state, the mean value of the thermal conductivity of the specimens is given by

$$\lambda = P_o d/2A\Delta T_o$$

where P_o is the heat flux through the specimen, d is the specimen thickness, A is the effective area of the heater plate metering section and ΔT_o is the temperature difference between the specimen faces.

6.1.2.1.1 Area and thickness

The edges of the metering area, defined by the centre lines of the centre-guard gap, were nominally 202 mm x 202 mm and could be measured to 0.1 mm. Thus the uncertainty in the area, A, was 0.1%.

The thickness of the specimens could be measured to 0.02%, but the slight departure from planeness of their surfaces (about ± 35 μm in the 45 mm thick specimens and ± 70 μm in the 33 mm pair) could introduce a further small uncertainty to the measured mean values. It was estimated, therefore, that uncertainties up to 0.1% and 0.15%, respectively, could be associated with the thickness of the 45 mm and 33 mm specimens.

6.1.2.1.2 Temperature differences: $\Delta T_o = \Delta T_s - \Delta T_z$

Sample thermocouples were calibrated to an accuracy estimated to be better than 0.3% (resolution 0.05%), but the uncertainty in the measurement of temperature differences should be much less than this. The calibration curves of sample thermocouples, disc-mounted and flattened types, were consistent to 0.05% (2 μV in 4000 μV).

The outputs of 20 of the disc-mounted thermocouples were compared, in-situ in the apparatus by replacing the heater plate with a 12 mm thick copper plate housing a calibrated platinum resistance thermometer. The temperature of the stack was controlled by the cold plates and an edge guard system. At equilibrium at the three test temperatures chosen, nominally 30 °C, 45 °C and 65 °C, the thermocouple voltages were found to be very consistent, the root mean square deviation from the mean on

each face being less than 0.5 μV. This would contribute an uncertainty of 0.15% to the temperature difference. A further similar amount could arise from a possible 0.5 μV thermal noise on the switching channels and, finally a small uncertainty could also be associated with the unevenness of the temperature on the faces due to slight variations in the thermal resistance through the stack. Taking all these factors into account, an overall uncertainty of 0.6% was assigned to ΔT_s.

The correction ΔT_z was evaluated using the expression for 2e previously given and allowing also for a contribution due to the layer of glue beneath the copper pads. Evaluated as a percentage of ΔT_s, it ranged from 1.12% for the pad/contact sheet combination 12/05/A1 to 4.3% for the combination 30/15/F4. Unfortunately, although the layer of glue was on average only 0.026 mm thick, it represented a significant portion of the overall correction (see example in Appendix 2). The estimated uncertainty in the average thickness of the glue was about 0.017 mm leading to an uncertainty of around 0.56% in ΔT_s. The uncertainty in 2e depends principally on the uncertainty in the overall pad thickness (including glue) and in the thermal conductivity of the contact material. The uncertainty in the pad thickness could be as much as 12% (making allowance for the small area occupied by the thermojunctions). The uncertainty in the measured thermal conductivity values of the thermal contact sheets was estimated to be 3% but another 5% was associated with the temperature dependence of the values, which was not allowed for. (The 20 °C values were used for all the corrections whilst at 75 °C the values would have been 8%, 6% and 2% different for F4, F6 and A1 respectively).

Combining the uncertainty of 0.56% in ΔT_s associated with the thickness of the glue with a further contribution due to an uncertainty of about 20% in the value of the correction 2e leads to a total uncertainty given by (0.56 + 2e/5) % in the measured conductivity values (for the examples above this amounted to 0.62% and 1.26%, respectively).

6.1.2.1.3 Energy flow: P_o

The heat flux P_o was given by the electrical power P supplied to the metering section of the guarded hot plate. This was determined by measuring the voltages across the heater and a standard resistor with a

total estimated uncertainty of 0.07%. A small uncertainty estimated to be no more than 0.05% was associated with a possible residual temperature mis-match across the gap. The edge heat losses or gains were negligibly small.

6.1.2.1.4 Summary of estimated uncertainties

Parameter	Measured Value & Uncertainty	Uncertainty(ϵ) in λ(%)
Area A	$\approx 0.04\ m^2 \pm 4 \times 10^{-5} m^2$	0.10
Thickness d	$\approx$ 45 mm $\pm$ 0.045 mm	0.10
	$\approx$ 3 mm $\pm$ 0.045 mm	0.15

Temperature difference ΔT_o: $\Delta T_o = \Delta T_s - \Delta T_z$

Parameter	Measured Value & Uncertainty	Uncertainty(ϵ) in λ(%)
ΔT_s	$\approx$ 17 K $\pm$ 0.10 K	0.60

Parameter		Uncertainty(ϵ) in λ(%) for different pad-interface combinations			
		12/05	30/05	12/15	30/15
ΔT_z					
45 mm Specimens	F4	0.70	0.86	0.93	1.26
	F6	0.69	0.79	0.91	1.21
	A1	0.62	0.66	0.75	0.88
33 mm Specimens	A1		0.70		

Energy flow P_o: $P_o = P - P_{v1}$

Parameter	Measured Value & Uncertainty	Uncertainty(ϵ) in λ(%)
P	$\approx$ 35 W $\pm$ 0.025 W	0.07
P_{v1}	$\pm$ 0.0165 W	0.05

Total uncertainty in measured λ(%)

45 mm Specimens		12/05	30/05	12/15	30/15
F4	$\Sigma\epsilon$	1.72	1.78	1.85	2.18
	$(\Sigma\epsilon^2)^{\frac{1}{2}}$	0.94	1.07	1.12	1.41
F6	$\Sigma\epsilon$	1.71	1.71	1.83	2.13
	$(\Sigma\epsilon^2)^{\frac{1}{2}}$	0.93	1.01	1.11	1.36
A1	$\Sigma\epsilon$	1.54	1.58	1.67	1.80
	$(\Sigma\epsilon^2)^{\frac{1}{2}}$	0.88	0.91	0.98	1.08
33 mm Specimens					
A1	$\Sigma\epsilon$		1.77		
	$(\Sigma\epsilon^2)^{\frac{1}{2}}$		0.96		

6.1.2.2 Results and discussion

The dimensions of the specimens and their densities were as follows:

Specimen No.	Dimensions mm	Density kg/m^3
68	308 x 308 x 45.22	2225
69	307 x 308 x 45.08	2225
44	308 x 308 x 32.77	2223
45	307 x 306 x 32.89	2221

The measurements were made on both pairs of specimens over the temperature range 10 °C to 80 °C using the apparatus and procedures described in the preceding sections and a variety of pad/interface combinations. The results are given in Table 6.

It will be recalled that the original aims of this series of measurements were to evaluate the new correction procedures and ascertain whether the overall accuracy of the technique (method 1) had now been raised to a level suitable for the continuation of the certification programme.

Table 6: NPL results using disc-mounted thermocouple technique

Index No	Pad/Interface	Temperature (θ) °C	Thermal Conductivity (λ) W/m.K
45mm Specimens			
33	12/05/F4	19.80	1.112
34	12/05/F4	47.39	1.157
35	12/05/F4	66.49	1.189
36	12/05/F6	21.04	1.125
37	12/05/F6	69.58	1.202
38	12/05/A1	19.60	1.129
39	12/05/A1	35.54	1.153
40	12/05/A1	67.79	1.202
41	12/15/F4	21.37	1.122
42	12/15/F4	66.21	1.193
43	12/15/F6	22.56	1.130
44	12/15/F6	66.97	1.197
45	12/15/A1	19.06	1.131
46	12/15/A1	50.39	1.184
47	12/15/A1	67.56	1.214
48	30/05/A1	19.96	1.134
49	30/05/A1	42.52	1.172
50	30/05/A1	72.51	1.214
51	30/05/F4	18.78	1.116
52	30/05/F4	28.20	1.132
53	30/05/F4	47.70	1.167
54	30/05/F4	68.20	1.197
55	30/05/F6	24.12	1.135
56	30/05/F6	48.97	1.174
57	30/05/F6	72.14	1.211
58	30/15/F4	20.64	1.129
59	30/15/F4	28.02	1.140
60	30/15/F4	41.30	1.160
61	30/15/F4	58.96	1.193
62	30/15/F4	61.68	1.197
63	30/15/A1	19.98	1.130
64	30/15/A1	41.63	1.170
65	30/15/A1	62.56	1.204
33mm Specimens			
66	30/05/A1	17.03	1.111
67	30/05/A1	67.52	1.196
68	30/05/A1	15.73	1.115
69	30/05/A1	48.02	1.167
70	30/05/A1	68.46	1.202

The application of the correction was indeed successful in bringing the measured thermal conductivity values much closer to the true values and also in considerably reducing the previous scatter in the results. However, it is a somewhat laborious technique and its relatively large uncertainty levels made it less than ideal for certification purposes and the search for a suitable technique was continued.

Nevertheless, it was felt that the results of these rather carefully executed and evaluated measurements could usefully be included in the comparison with the proposed certified values based on the PTB work. Thus in Table 7 the NPL results (λ) are compared with the PTB(1 + 2) polynomial values (λ_c) and the residuals $r = \lambda - \lambda_c$ and the ratio $(r/\lambda)\%$ are compared with the corresponding values of the uncertainties $(\Sigma\epsilon^2)^{\frac{1}{2}}$ and $\Sigma\epsilon$. The uncertainties of the measurements are quite strongly linked to the value of the correction factor, as explained in the previous section, and they, therefore, change in value with every change in the pad/interface combination, as can be seen from the table. Inspection of the tabulated data for the complete set of 38 measurements (45 mm and 33 mm specimens), shows that 29(77%) of the results deviate from the calculated values by less than their $(\Sigma\epsilon^2)^{\frac{1}{2}}$ values; 36(95%) by less than their $\Sigma\epsilon$ values and only 2(5%) are outside this limit. The deviation from the PTB values is also shown graphically in Figure 9, the error bars corresponding to the value of $\Sigma\epsilon$ in each case. Overall the agreement between the results appears to be entirely satisfactory.

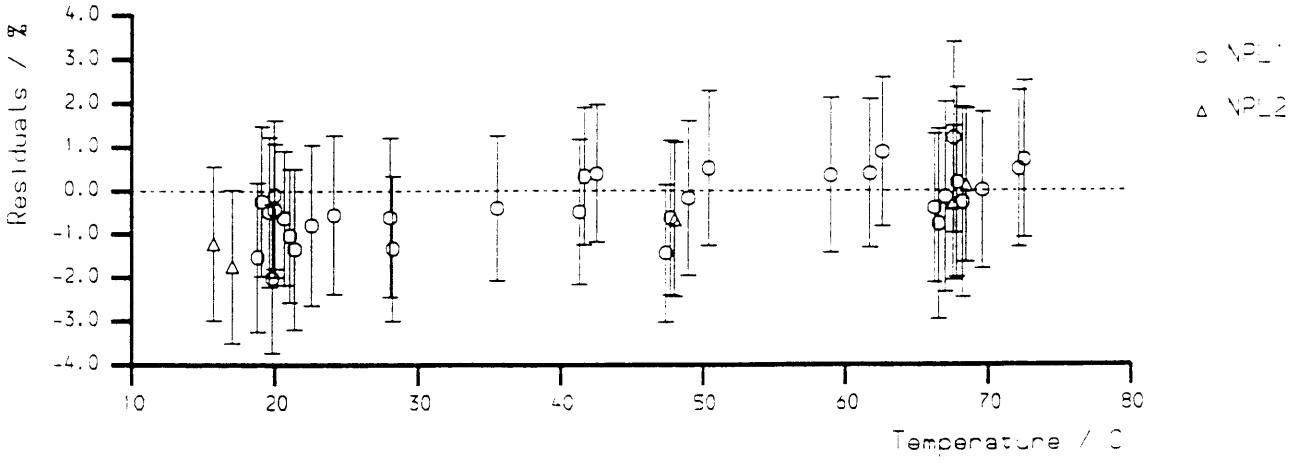


Figure 9: Deviation of NPL Method 1 results from PTB(1+2) polynomial values

Table 7: Comparision of NPL method 1 results with PTB(1+2) polynomial values

No	Pad/Interface	θ °C	λ W/m.K	λ_c W/m.K	Residuals W/m.K	$(\Sigma \epsilon^2)^{\frac{1}{2}}$ %	$\Sigma \epsilon$ %
45mm Specimens							
33	12/05/F4	19.80	1.112	1.135	-0.0229 (2.02%)	0.94	1.72
34	12/05/F4	47.39	1.157	1.174	-0.0170 (1.45%)	0.94	1.72
35	12/05/F4	66.49	1.189	1.198	-0.0093 (0.77%)	0.94	1.72
36	12/05/F6	21.04	1.125	1.137	-0.0118 (1.04%)	0.93	1.71
37	12/05/F6	69.58	1.202	1.202	0.0000 (0.00%)	0.93	1.71
38	12/05/A1	19.60	1.129	1.135	-0.0056 (0.49%)	0.88	1.54
39	12/05/A1	35.54	1.153	1.158	-0.0048 (0.41%)	0.88	1.54
40	12/05/A1	67.79	1.202	1.200	0.0021 (0.18%)	0.88	1.54
41	12/15/F4	21.37	1.122	1.137	-0.0153 (1.34%)	1.12	1.85
42	12/15/F4	66.21	1.193	1.198	-0.0049 (0.41%)	1.12	1.85
43	12/15/F6	22.56	1.130	1.139	-0.0090 (0.79%)	1.11	1.83
44	12/15/F6	66.97	1.197	1.199	-0.0019 (0.15%)	1.11	1.83
45	12/15/A1	19.06	1.131	1.134	-0.0028 (0.25%)	0.98	1.67
46	12/15/A1	50.39	1.184	1.178	0.0061 (0.52%)	0.98	1.67
47	12/15/A1	67.56	1.214	1.200	0.0144 (1.20%)	0.98	1.67
48	30/05/A1	19.96	1.134	1.135	-0.0011 (0.10%)	0.91	1.58
49	30/05/A1	42.52	1.172	1.167	0.0046 (0.39%)	0.91	1.58
50	30/05/A1	72.51	1.214	1.206	0.0085 (0.70%)	0.91	1.58
51	30/05/F4	18.78	1.116	1.133	-0.0174 (1.53%)	1.07	1.78
52	30/05/F4	28.20	1.132	1.147	-0.0153 (1.34%)	1.07	1.78
53	30/05/F4	47.70	1.167	1.174	-0.0074 (0.63%)	1.07	1.78
54	30/05/F4	68.20	1.197	1.200	-0.0034 (0.28%)	1.07	1.78
55	30/05/F6	24.12	1.135	1.141	-0.0064 (0.56%)	1.01	1.71
56	30/05/F6	48.97	1.174	1.176	-0.0021 (0.18%)	1.01	1.71
57	30/05/F6	72.14	1.211	1.205	0.0059 (0.49%)	1.01	1.71
58	30/15/F4	20.64	1.129	1.136	-0.0072 (0.63%)	1.41	2.18
59	30/15/F4	28.02	1.140	1.147	-0.0071 (0.62%)	1.41	2.18
60	30/15/F4	41.30	1.160	1.166	-0.0058 (0.50%)	1.41	2.18
61	30/15/F4	58.96	1.193	1.189	0.0041 (0.34%)	1.41	2.18
62	30/15/F4	61.68	1.197	1.192	0.0047 (0.39%)	1.41	2.18
63	30/15/A1	19.98	1.130	1.135	-0.0052 (0.46%)	1.08	1.80
64	30/15/A1	41.63	1.170	1.166	0.0038 (0.32%)	1.08	1.80
65	30/15/A1	62.56	1.204	1.193	0.0106 (0.88%)	1.08	1.80
33mm Specimens							
66	30/05/A1	17.03	1.111	1.131	-0.0197 (1.74%)	0.96	1.77
67	30/05/A1	67.52	1.196	1.200	-0.0035 (0.29%)	0.96	1.77
68	30/05/A1	15.73	1.115	1.129	-0.0137 (1.21%)	0.96	1.77
69	30/05/A1	48.02	1.167	1.175	-0.0078 (0.66%)	0.96	1.77
70	30/05/A1	68.46	1.202	1.201	0.0013 (0.11%)	0.96	1.77

6.1.3 Method 2: Foil-type thermocouples placed on specimen surfaces

This method was investigated because the redistribution of heat flow by foil-type thermocouples should be much smaller than the disc-mounted thermocouples of the previous method. Therefore, using the same measurement procedure as before, three sets of thermal conductivity versus temperature measurements were carried out on the 45 mm glass specimens using a different thermal contact material for each set.

The thermocouples were prepared from 0.075 mm diameter Nichrome Constantan wire as outlined previously (see also Appendix 2) and were on average 0.03 mm thick over a length of 20 mm from their junctions. Calibration tests on a set of twenty such thermocouples showed that their outputs were exceptionally reproducible.

For the reasons outlined in the previous section, it was decided not to glue the thermocouples to the specimen surfaces, but instead to use a thin layer of a ZnO-loaded thermo-conductive compound to establish good thermal contact between them. This medium has the advantage of having a much higher thermal conductivity than the glue and it can be relied on to assume the minimum thickness possible under the compressive load applied to the apparatus during the measurements.

Five such thermocouples per specimen face were used in the measurements, positioned symmetrically as in Method 1, and held on the specimen surfaces by means of narrow strips of Kapton tape. The latter were used very sparingly and transverse to the wire near the junction ends of the thermocouples to avoid any unnecessary distortion of the thermal field in this region.

As the change in the surface temperature directly beneath the thermocouples, caused by the local redistribution of heat flow, are greatly attenuated in this case on account of the small surface area covered by the thermocouples and the relatively large conductivity of the glass, the thermocouples become more influenced by the steep temperature gradient in the thermal contact material pressing against them. If it is assumed that the contact resistances between the thermocouples and the two media (glass and contact material) are similar and relatively small then the recorded temperature difference would be expected to lie close to half way between the true value through the glass (away from any disturbance) and the slightly larger value betwen the isothermal planes in the thermal contact material at a distance of one thermocouple thickness from the surfaces. On the basis of this

assumption a simple correction amounting to the temperature drop through a layer of the contact material of thickness equivalent to that of one of the foil thermocouples was applied to the measured temperature difference between the specimen faces.

6.1.3.1 Assessment of uncertainties

The thermal conductivity of the specimens is given by

$$\lambda = P_o d/2A\Delta T_o$$

6.1.3.1.1 Area and thickness

The estimated uncertainties in A and d were both 0.1% (see method 1).

6.1.3.1.2 Temperature differences: $\Delta T_o = \Delta T_s - \Delta T_z$

The estimated uncertainty in the correction term ΔT_s was the same as in method 1, namely 0.6%.

The uncertainty in the correction term ΔT_z is determined primarily by the uncertainties in the mean thickness of the thermocouples and in the temperature gradient in the thermal contact material. In the set of 20 thermocouples used for the measurements the mean thickness was 0.03 mm with a spread of ± 0.01 mm. An uncertainty of half the spread, that is 0.005 mm, or 15%, was considered to be appropriate for the thermocouple thickness. Adding to this the previously explained uncertainty of 8% in the thermal conductivity of the contact layers and a further tentative 15% for the intrinsic inaccuracy in the method of deriving the correction, a total uncertainty of 40% was assigned to ΔT_z. However, as ΔT_z is small relative to ΔT_o in this method, this leads to an uncertainty of only 0.3%, 0.4% and 0.5% in ΔT_o, respectively, when using the contact materials A1, F6 and F4.

6.1.3.1.3 Energy flow: P_o: $P_o = P - P_{v1}$

The uncertainty in P was 0.07% with a further 0.05% associated with centre-guard unbalance (as in method 1).

6.1.3.1.4 Summary of estimated uncertainties

Parameter	Measured Value & Uncertainty		Uncertainty(ϵ) in λ(%)
Area A	= 0.04 m^2	± 4 x 10^{-5} m^2	0.10
Thickness d	= 45 mm	± 0.045 mm	0.10
Temperature difference ΔT_o: $\Delta T_o = \Delta T_s - \Delta T_z$			
ΔT_s	= 17 K	± 0.10 K	0.60
ΔT_z			F4 0.50
			F6 0.40
			A1 0.30
Energy flow P_o: $P_o = P - P_{v1}$			
P	= 35 W	± 0.025 W	0.07
P_{v1}		± 0.0165 W	0.05

Total uncertainty (%)

F4	$\Sigma\epsilon$	1.42
	$(\Sigma\epsilon^2)^{\frac{1}{2}}$	0.80
F6	$\Sigma\epsilon$	1.32
	$(\Sigma\epsilon^2)^{\frac{1}{2}}$	0.75
A1	$\Sigma\epsilon$	1.22
	$(\Sigma\epsilon^2)^{\frac{1}{2}}$	0.70

6.1.3.2 Results and discussion

The measurements were made on the 45 mm specimens only, using each of the interface materials F4, F6 and A1 in turn. The temperature range covered was 10 °C to 80 °C.

The results are shown in Table 8 and are compared with the PTB (1+2) polynomial values in Table 9. The data are tabulated in the same format as in the corresponding table for method 1, to permit easy comparison of the residuals and the estimated uncertainty values. The deviation from the PTB values is also illustrated graphically in Figure 10, the error bars representing the estimated uncertainty $\Sigma\epsilon$ of each measurement.

The corrections applied to the measured temperature differences was much smaller in these measurements than in the disc-mounted thermocouple method and this is reflected in the lower uncertainties associated with the measurements and the smaller difference between their values when the different thermal contact materials are used. It was very re-assuring, therefore, to find that the results obtained with the different materials were in very close agreement over this restricted temperature range.

The reproducibility of the method and its relative simplicity (at room temperature and above, at least) represented a considerable advance over previously tried procedures and this led to its being adopted for a small series of measurements over different temperature ranges by F1W and IFT. These measurements are described later in the report. (The method is also described in the Guidance Note for Users of the Reference Material in Appendix 3).

With regard to the comparison with the PTB values, there is a tendency for the NPL values near to room temperature to be slightly lower, but overall the agreement between the results is clearly very good. Thus the rms deviation of the nine experimental values from the polynominal values is less than 0.5% and eight of the nine residuals, expressed as r/λ%, are seen to be smaller than the estimated uncertainty of measurement $(\Sigma\epsilon^2)^{\frac{1}{2}}$, while the ninth is less than $\Sigma\epsilon$.

Table 8: NPL results using surface mounted foil thermocouple technique

Index No	Interface	Temperature (θ) °C	Thermal Conductivity (λ) W/m.K
71	F4	19.47	1.127
72	F4	64.99	1.197
73	F6	21.08	1.126
74	F6	66.14	1.200
75	A1	12.49	1.121
76	A1	20.00	1.128
77	A1	42.34	1.166
78	A1	65.81	1.203
79	A1	79.14	1.218

Table 9: Comparison of NPL Method 2 results with PTB(1+2) polynomial values

Method 2: 45mm Specimens

No	Interface	θ °C	λ W/m.K	λ_c W/m.K	Residuals W/m.K	$(\Sigma \epsilon^2)^{\frac{1}{2}}$ %	$\Sigma \epsilon$ %
71	F4	19.47	1.127	1.134	-0.0074 (0.65%)	0.80	1.42
72	F4	64.99	1.197	1.196	0.0006 (0.05%)	0.80	1.42
73	F6	21.08	1.126	1.137	-0.0108 (0.95%)	0.75	1.32
74	F6	66.14	1.200	1.198	0.0022 (0.18%)	0.75	1.32
75	A1	12.49	1.121	1.124	-0.0027 (0.24%)	0.70	1.22
76	A1	20.00	1.128	1.135	-0.0072 (0.63%)	0.70	1.22
77	A1	42.34	1.166	1.167	-0.0012 (0.10%)	0.70	1.22
78	A1	65.81	1.203	1.197	0.0056 (0.46%)	0.70	1.22
79	A1	79.14	1.218	1.213	0.0047 (0.39%)	0.70	1.22

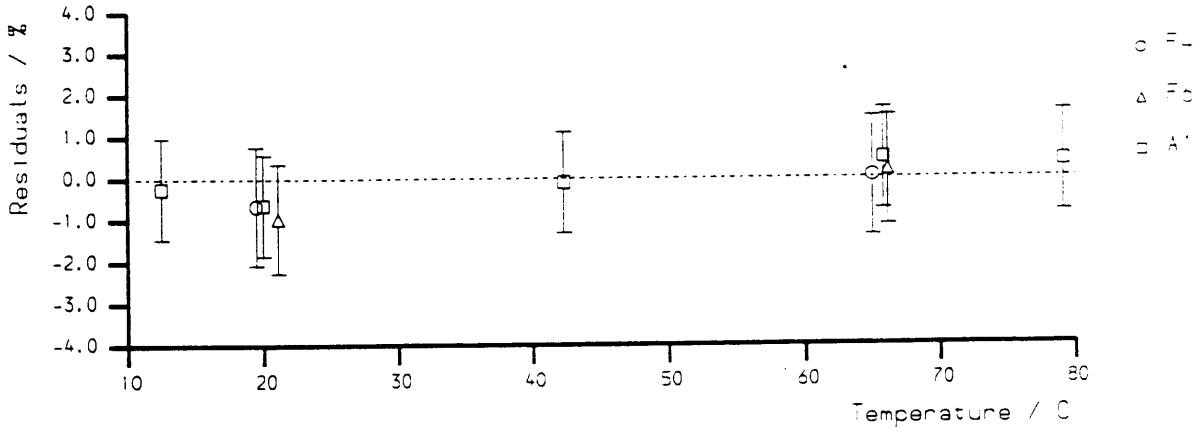


Figure 10: Deviation of NPL Method 2 results from PTB(1+2) polynomial values

6.1.4 Method 3: Foil-type thermocouples embedded in slots

This method was adopted for the final set of measurements in an attempt to obtain the most accurate thermal conductivity values possible with the present apparatus, over a limited range of temperature (10 to 75 °C), so as to be able to check the validity of the practically much simpler surface-mounted thermocouple method (method 2). The measurements were made on the 45 mm specimens only using the foamed silicone rubber F6 for thermal contact.

The method involved machining slots of accurately known depth in the specimen surfaces, placing foil type thermocouples similar to those used in method 2, on the bottom of the slots, using ZnO-loaded heat sink compound to promote good thermal contact between the thermocouples and the specimen surfaces and filling the remaining slot space with an electrically insulating medium of conductivity roughly matching that of the glass. In this way the redistribution of heat flow about the temperature sensors would be very small and the previous uncertainty associated with the temperature gradient in the thermal contact sheets would be eliminated. In principle, therefore, the experimental results obtained would be expected to be very close to the correct values.

Using a precision diamond grinding technique, three parallel slots (having smooth, flat bottoms) exactly 1 mm deep and 1.5 mm wide were cut across the full width of each specimen face. One slot was positioned centrally and the others were approximately 55 mm on either side. It proved difficult to find an electrically insulating filler material having a thermal conductivity closely matching that of the glass and the most suitable material found was plasticine, which has a conductivity of 0.89 W/m.K at 15 °C reducing to 0.78 W/m.K at 70 °C. Five foil-type thermocouples 0.03 mm thick, prepared from the 0.075 mm diameter Nichrome-Constantan wire, as in method 2, were placed on a thin layer of ZnO-loaded heat sink compound at the bottom of the slots in each specimen face and positioned symmetrically within the central metering area. The slots were then filled with pasticine taking great care to ensure a) that the foil-tipped thermocouples remained seated at the bottom of the slots, b) that the thermocouple wires were electrically isolated one from the other and c) that the filled slots were exactly level with the specimen surfaces. Thermal conductivity measurements were then carried out using the previously described procedures.

Owing to the differences in the conductivities of the plasticine and the glass a small correction was again needed to compensate for the slight distortion of the heat flow pattern around the slots. The correction factor was (1-2e) in this case, and found on the basis of a finite element analysis to be 0.997 over the range of temperature covered.

6.1.4.1 Assessment of uncertainties

The thermal conductivity of the specimens is given by

$$\lambda = P_o d/2A\Delta T_o$$

6.1.4.1.1 Area and thickness

The estimated uncertainty in A was the same as in methods 1 and 2, but the uncertainty in d, which now referred to the distance between the base of the slots, was increased to 0.2%.

6.1.4.1.2 Temperature differences: $\Delta T_o = \Delta T_s - \Delta T_z$

The estimated uncertainty in ΔT_s was the same as in method 1, namely 0.6%.

The uncertainty in ΔT_z was considered to be no greater than 15%, equivalent to an uncertainty of 0.05% in ΔT_o.

6.1.4.1.3 Energy flow: P_o, $P_o = P - P_{v1}$

The uncertainty in P was 0.07% with a further 0.05% associated with centre-guard imbalance (as in methods 1 and 2).

6.1.4.1.4 Summary of estimated uncertainties

Parameter	Measured Value & Uncertainty	Uncertainty(ϵ) in λ(%)
Area A	$\approx 0.04\ m^2 \pm 4 \times 10^{-5} m^2$	0.10
Thickness d	$\approx$ 45 mm $\pm$ 0.045 mm	0.20
Temperature difference ΔT_o: $\Delta T_o = \Delta T_s - \Delta T_z$		
ΔT_s	$\approx$ 17 K $\pm$ 0.10 K	0.60
ΔT_z		0.05
Energy flow P_o: $P_o = P - P_{v1}$		
P	$\approx$ 35 W $\pm$ 0.025 W	0.07
P_{v1}	$\pm$ 0.0165 W	0.05
	Total uncertainty (%)	
	$\Sigma\epsilon$	1.07
	$(\Sigma\epsilon^2)^{\frac{1}{2}}$	0.65

6.1.4.2 Results and discussion

The results of these measurements are given in Table 10, and are compared with the PTB (1+2) polynomial values in Table 11. The deviation of the measured values from the PTB results is shown graphically in Figure 11; the error bars representing $\Sigma\epsilon$ as before.

These measurements were intended to be about the most accurate that could be produced using the existing guarded hot-plates at NPL and, significantly, the results appear to be in very good agreement with the PTB values. Thus the rms deviation of the experimental results from the proposed certified values is only 0.34%. There is however a tendency for the deviation to increase at the higher temperatures.

The results obtained with this method were, in fact, in very good

agreement with the previous results using method 2; both showing a linear dependence on temperature between 10 °C and 80 °C which could be represented by the expression

$$\lambda = (1.101 + 1.53 \times 10^{-3}\theta)\ W/m.K$$

The standard deviation of the fit to the combined results (methods 1 and 2) was 0.0035 W/m.K and the maximum positive and negative deviations were 0.32% and 0.63%, respectively. The rather steeper slope of this line than would be expected from the PTB results cannot be explained, but it is a relatively small effect compared with the uncertainties associated with these measurements.

Table 10: NPL results using thermocouples embedded in the specimen surface

Index No	Interface	Temperature (θ) °C	Thermal Conductivity (λ) W/m.K
80	F6	15.83	1.128
81	F6	21.90	1.138
82	F6	30.73	1.151
83	F6	40.53	1.166
84	F6	51.65	1.183
85	F6	62.44	1.198
86	F6	72.21	1.214

Table 11: Comparison of NPL Method 3 results with PTB(1+2) polynomial values

Method 3: 45mm Specimens

No	Interface	θ °C	λ W/m.K	λ_c W/m.K	Residuals W/m.K	$(\Sigma \epsilon^2)^{\frac{1}{2}}$ %	$\Sigma \epsilon$ %
80	F6	15.83	1.128	1.129	-0.0009 (0.08%)	0.65	1.07
81	F6	21.90	1.138	1.138	-0.0001 (0.00%)	0.65	1.07
82	F6	30.73	1.151	1.151	0.0000 (0.00%)	0.65	1.07
83	F6	40.53	1.166	1.165	0.0013 (0.11%)	0.65	1.07
84	F6	51.65	1.183	1.180	0.0034 (0.29%)	0.65	1.07
85	F6	62.44	1.198	1.193	0.0047 (0.39%)	0.65	1.07
86	F6	72.21	1.214	1.205	0.0088 (0.73%)	0.65	1.07

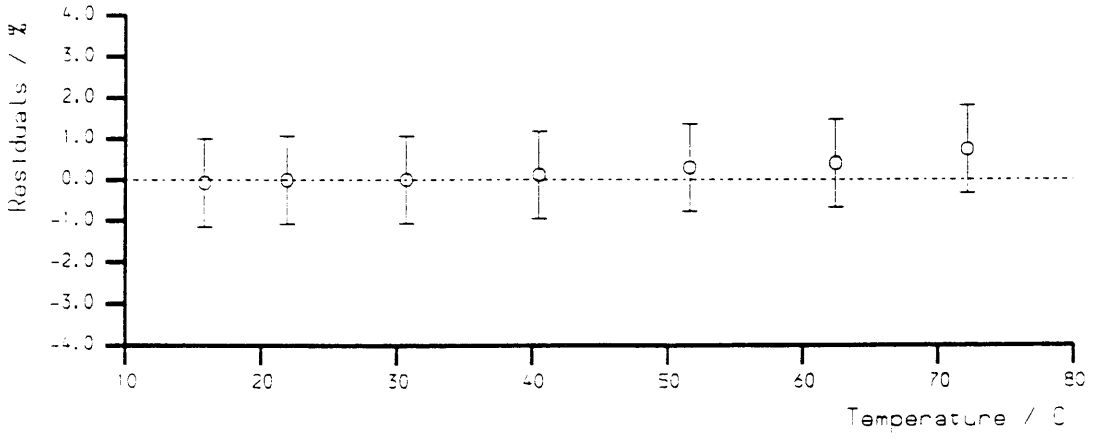


Figure 11: Deviation of NPL Method 3 results from PTB(1+2) polynomial values

6.2 FIW measurements

The FIW measurements were made on a pair glass plates (Nos 19 and 20) measuring approximately 500 mm x 500 mm x 33 mm over the temperature range - 30 °C to 50 °C.

6.2.1 Apparatus

The apparatus was a double-sided guarded hot-plate comprising two fluid-cooled cold plates and a heater plate surrounded by two separately heated guard rings both maintained at the metering section temperature. The central metering section measured 298.5 mm x 298.5 mm and the gap between it and the guard was 1.5 mm. The hot and cold plates were made of copper for good temperature uniformity and their surfaces were flat within 0.1 mm and 0.05 mm, respectively. Five calibrated 0.1 mm diameter copper/constantan thermocouples were installed in each of the hot and cold plate surfaces and thermopiles having 20 and 40 junctions, respectively, were used to control the inner and outer guard heaters. A third electrically heated guard, also held at the heater plate temperature, was mounted on the inner surface of the thermally insulated box housing the apparatus. All power and voltage terminals were mounted on this guard to eliminate heat losses or gains along the leads. Power and thermocouple voltages were measured using standard resistors and a good quality digital voltmeter; a computer-based system was used for data logging and the evaluation of the results.

6.2.1.1 Thermocouples for surface temperature measurement

The experimental procedure was based on the use of thin, foil-type thermocouples mounted directly on the specimen surfaces, as described in Appendix 3. The thermocouples were fabricated from 0.1 mm copper/constantan wire stock, the respective ends being rolled to a thickness of 0.05 mm before tinning and soft soldering them together and then rolling again over a length of about 20 mm from the junctions to a thickness of 0.1 mm. The thermocouples were calibrated against a standard platinum resistance thermometer prior to mounting on the specimen surfaces.

6.2.1.2 Interface material

Sheets of foamed silicone rubber 3 mm thick were used to achieve uniform thermal contact between the specimen and plate surfaces. The material had a density of 800 kg/m^3 and thermal conductivity in the temperature range - 50 °C to + 50 °C given by $\lambda = (0.140 + 0.00035\theta)$ W/m.K, where θ is the temperature in degrees Celsius. Compression tests showed that a pressure of about 20 kP was required to reduce the sheet thickness by 0.1 mm, and this was applied by means of a clamping device attached to the apparatus.

6.2.1.3 Measurement procedure

The specimens were inserted in the apparatus between two 3 mm thick silicone rubber sheets. An additional layer of very thin aluminium foil was placed between the rubber and the cold plates to prevent sticking. Five foil-type thermocouples were attached in a symmetrical pattern to each specimen face within the metering area using small strips of 0.05 mm thick self-adhesive Teflon foil. The latter measured approximately 2 mm x 4 mm and were attached near the thermojunctions. A thin layer of ZnO-based thermoconductive paste was used to ensure good thermal contact with the specimen surfaces. The appropriate clamping pressure was applied to the assembly and the thickness of the interface material under load was measured using vernier calipers.

The power supplied to the heater plate was set to produce a temperature drop of 10 K across the specimens and the determination of the thermal conductivity at each temperature was commenced five hours after the attainment of steady state conditions. Measurements were repeated every 30 minutes for the following three hours. The arithmetic mean of all these values was taken as the value at the particular mean temperature. A small correction evaluated analytically was then applied to compensate for the effects of thermal field distortions around the thermocouples.

6.2.2 Assessment of uncertainties

At steady state and under linear heat flow conditions the mean value of the thermal conductivity of the two specimens is given by

$$\lambda = P_o d/2A\Delta T_o$$

6.2.2.1 Area and thickness

The edges of the metering area, which included the half width of the air gap between the centre and guard sections, were approximately 300 mm and were measured to ± 0.1 mm. The specimen thickness was approximately 33 mm and was measured to 0.05 mm. The uncertainty in the values of A and d were therefore 0.07% and 0.15%, respectively.

6.2.2.2 Temperature difference

The temperature difference between the specimen faces is given by

$$\Delta T_o = \Delta T_s - \Delta T_z$$

where, as before, ΔT_s is the mean temperature difference indicated by the thermocouples on the specimen faces and ΔT_z is a small correction associated with the steep temperature gradient in the thermal contact layer and the local redistribution of heat flow in the neighbourhood of the thermocouples.

The thermocouples were calibrated over the temperature range - 40 °C to 60 °C by mounting them on a 300 mm x 300 mm copper plate housing a standard platinum resistance thermometer. The plate, sandwiched between 3 mm thick silicone rubber sheets, to protect and electrically insulate the thermocouples, was clamped between the cold plates of the apparatus which could be set and controlled at any temperature in the above range. Calibration measurements were made at 15 different temperatures, 12 hours being allowed to reach equilibrium in each case before taking 10 sets of emf readings and evaluating the arithmetic mean. All the individual thermocouple emfs were found to be within ± 2 μV of the mean values and the overall uncertainty of the calibration was estimated to be within 0.03 K. Allowing for further random errors in the measurement

of the thermocouple voltages averaged over 5 thermocouples per face, the estimated maximum uncertainty in the measurement of ΔT_s was 0.075 K (0.75%).

The correction factor ΔT_z was evaluated by a three dimensional finite difference method and found to range from 2.8 to 3.1% of ΔT_s. Its magnitude depends strongly on the thickness of the thermocouples (0.1 mm) and on the thermal conductivity and thickness of the thermal contact layer (≈ 0.14 W/m.K and 2 to 2.5 mm, respectively). It also varies with the thermal resistance of the specimens. The uncertainty in ΔT_o (or λ) arising from the uncertainty in the thermocouple thickness was estimated to be 0.2% and from the uncertainty in the properties of the thermal contact material 0.15%. Adding to these a contribution due to possible variations in the contact resistance between thermocouple and specimen, a maximum uncertainty of 0.5% was estimated to arise from the correction factor ΔT_z.

6.2.2.3 Energy flow P_o

As the edge heat losses or gains were negligibly small, the heat flux P_o was given simply by the electrical power P supplied to the metering section. This was determined with a maximum uncertainty of 0.11% by measuring the voltage across the heater and a standard resistance. However, a small uncertainty, P_{v1}, associated with a temperature mismatch across the gap has to be added to this; the maximum estimated uncertainty in P_o then becoming 0.21%.

6.2.2.4 Summary of estimated uncertainties

Parameter	Measured Value & Uncertainty	Uncertainty(ϵ) in λ(%)
Area A	$\approx$ 0.09 m^2 $\pm$ 2 x 10^{-4} m^2	0.07
Thickness d	$\approx$ 33 mm $\pm$ 0.05 mm	0.15
Temperature difference ΔT_o: $\Delta T_o = \Delta T_s - \Delta T_z$		
ΔT_s	$\approx$ 10 K $\pm$ 0.075 K	0.75
ΔT_z	$\pm$ 0.05 K	0.50
Energy flow P_o: $P_o = P - P_{v1}$		
P	$\approx$ 60 W $\pm$ 0.068 W	0.11
P_{v1}	$\pm$ 0.06 W	0.10
	Total uncertainty (%)	
	$\Sigma\epsilon$	1.68
	$(\Sigma\epsilon^2)^{\frac{1}{2}}$	0.93

6.2.3 Results and discussion

The measurements were made on plate Numbers 19 and 20 which had the following dimensions and mean density:

Specimen No.	Dimensions
19	502 mm x 504 mm x 32.82 mm
20	502 mm x 501 mm x 33.15 mm

Density 2224 kg/m^3

The results at seven temperatures in the range - 30 °C to 51 °C are shown in Table 12. A second order polynomial fit through these experimental values gives

$$\lambda = (1.0894 + 1.7632 \times 10^{-3}\theta - 2.3399 \times 10^{-6}\theta^2)\ W/m.K$$

The results are compared with the PTB values in Table 13 and the deviations between them are shown graphically in Figure 12, with the same $\Sigma\epsilon$ error bars as in previous similar graphs.

The results are observed to be systematically some 1.1% (rms) lower than the PTB values, which could be explained by a small residual thermal contact problem at the interfaces. However, within the uncertainty levels involved, these results again are in quite close agreement with the PTB values.

Table 12: FIW results

Index No	Interface	Temperature (θ) °C	Thermal Conductivity (λ) W/m.K
87	F.S. rubber	-29.38	1.036
88	..	-11.46	1.068
89	..	0.15	1.090
90	..	10.18	1.107
91	..	20.79	1.125
92	..	30.08	1.141
93	..	51.03	1.173

Table 13: Comparision of FIW results with PTB(1+2) polynomial values

No	Interface	θ °C	λ W/m.K	λ_c W/m.K	Residuals W/m.K	$(\Sigma \epsilon^2)^{\frac{1}{2}}$ %	$\Sigma \epsilon$ %
87	F.S.rubber	-29.38	1.036	1.051	-0.0152 (1.45%)	0.93	1.68
88	..	-11.46	1.068	1.084	-0.0160 (1.48%)	0.93	1.68
89	..	0.15	1.090	1.104	-0.0138 (1.25%)	0.93	1.68
90	..	10.18	1.107	1.120	-0.0130 (1.16%)	0.93	1.68
91	..	20.79	1.125	1.136	-0.0114 (1.00%)	0.93	1.68
92	..	30.08	1.141	1.150	-0.0090 (0.79%)	0.93	1.68
93	..	51.03	1.173	1.179	-0.0058 (0.49%)	0.93	1.68

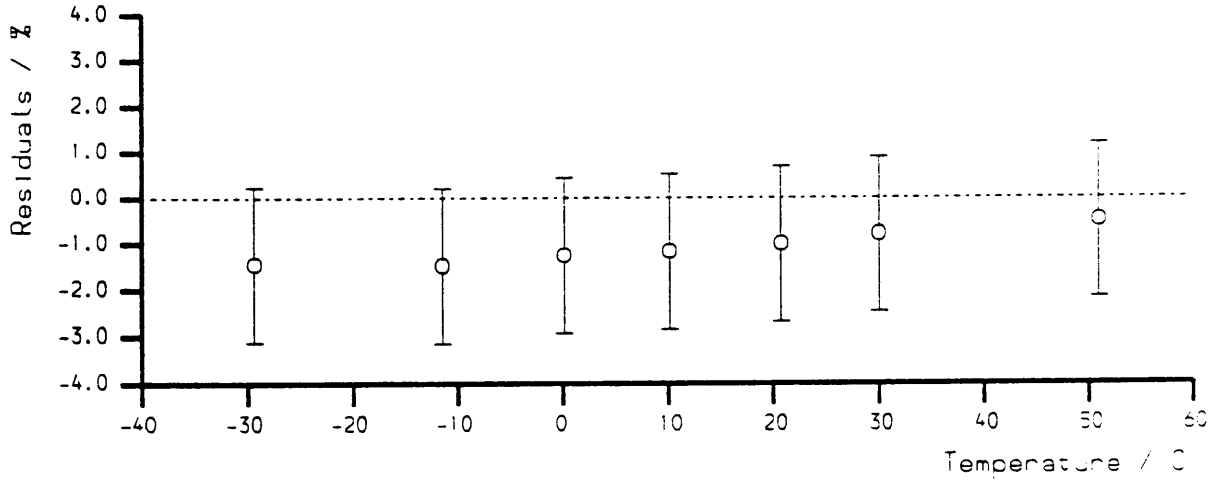


Figure 12: Deviation of FIW results from PTB(1+2) polynomial values

6.3 IFT measurements

The IFT measurements were made over the temperature range - 125 °C to 42 °C on a pair of glass plates (Nos 29 and 30) measuring approximately 300 mm x 300 mm x 33 mm. Measurements at lower temperatures were also attempted but were unsuccessful due to excessive uncertainty arising from the embrittlement of the thermal contact material.

6.3.1 Apparatus

The apparatus used for the measurements was a 300 mm x 300 mm, double-sided guarded hot-plate built to conform with UNI-CTI standards. The guarded heater plate was fabricated from high conductivity copper and the cold plates from aluminium alloy. Their surfaces were machined flat to conform to a true plane within 0.05 mm. The guarded heater plate had a 146 mm x 146 mm metering section surrounded by a 75 mm wide guard separated from it by a 2 mm gap. The guard heater power was controlled using the output of an 18 element thermopile evenly distributed about the centre/guard gap. An edge guard system, held at the heater plate temperature, surrounded the specimen edges and this was also used to mount all the power and voltage terminals so as to eliminate heat flow along the leads. The assembly was further insulated about its edges by a 100 mm thickness of low density insulation. The plate temperatures were measured by means of an array of copper/constantan thermocouples referenced to two precision platinum resistance thermometers permanently installed in the cold plates. The thermocouple voltages were read using a low noise scanning system connected to a nanovolt amplifier. A good quality digital voltmeter was used for the measurement of dc power.

6.3.1.1 Thermocouples for surface temperature measurements

The temperature drop through the specimens was measured by means of supplementary foil-type thermocouples mounted directly on the specimen surfaces in the manner described in Appendix 3. The thermocouples were fabricated from a stock of 0.07 mm diameter Teflon-coated, copper-constantan thermocouple wire; the wires, after removal of the Teflon, being tinned over a length of at least 10 mm, rolled to 0.02 mm - 0.03 mm, then overlapped, soldered and finally rolled again to 0.04 mm - 0.06 mm.

6.3.1.2 Interface material

Sheets of soft polyurethane rubber 3 mm thick having a thermal conductivity of 0.21 W/m.K at room temperature were used to facilitate good thermal contact between the specimen and plate surfaces. The material had the advantage of being extremely soft and of homogeneous composition but the disadvantages of requiring a special mounting technique to avoid air entrapment and of presenting considerable difficulties during disassembly.

6.3.1.3 Measurement procedure

A total of eight of the foil-type thermocouples were mounted on the specimen surfaces, two per face, positioned some 5 mm and 50 mm from the centre; a thin layer of a silicon-based thermoconductive paste being applied beneath their thermojunctions to facilitate good thermal contact. Care was taken to apply the rubber sheets firmly over the instrumented specimen surfaces before inserting in the apparatus under an appropriate clamping pressure. Power was then supplied to the various heater plates and the establishment of equilibrium was carefully monitored before commencing final readings. As a result of differences in the thickness of the thermal contact sheets the temperature distribution in the apparatus could be slightly asymmetric such that the mean temperature of the specimens could be slightly different from the mean temperature indicated by the plate thermocouples. A 1 K difference would lead to a 0.1% error in the thermal conductivity value and, therefore, to ensure that it was considerably less, the power was adjusted to produce a temperature drop of no more than 2 K across the specimens. The latter was measured with the necessary accuracy by connecting the thermojunctions in series to form a sensitive thermopile reading the mean temperature drop across both specimens. A small correction was applied to this value, calculated, as proposed in Appendix 3, from the thickness of the thermojunctions and the temperature gradient in the interface material, the latter being determined during the course of each measurement from the temperatures of the hot and cold plates.

6.3.2 Assessment of uncertainties

Under linear heat flow conditions at steady state the mean value of the thermal conductivity of the specimens is given by

$$\lambda = P_o d/2A\Delta T_o$$

where the symbols have the same meaning as in previous sections of this report.

6.3.2.1 Area and thickness

The boundary edges of the metering area, which include the half width of the centre-guard gap, were nominally 148 mm x 148 mm and were measured to ± 0.1 mm. The uncertainty in the measurement of the area, A, was therefore 0.14%.

The uncertainty in the measurement of the thickness of the specimens at LNE was less than 0.02%. A further uncertainty was associated with the slight departure from planeness of each surface. If the sum of these for a pair of faces were added to the uncertainty of the measurement then the maximum overall uncertainty in the thickness, d, would be 0.09%.

6.3.2.2 Temperature difference

The temperature difference between the specimen faces is given by

$$\Delta T_o = \Delta T_s - \Delta T_z$$

where ΔT_s is the mean temperature difference indicated by the series-connected thermocouples mounted on the specimen surfaces and ΔT_z is a two-part correction, one associated with the temperature gradient in the thermal contact material embedding the thermojunctions and the other the departure from parallelism of the thermal contact sheets.

The measuring system had ample sensitivity and stability (better than 0.05 μV) to enable the thermocouple voltages to be measured with high precision, However, allowing for the fact that the copper/constantan wire used was uncalibrated and not of premium grade, it was estimated

that a total uncertainty of 0.55% could apply to the value of ΔT_s near ambient temperatures which would increase to about 0.75% at low temperatures.

The correction associated with the thermal gradient in the contact material amounted to no more than 1% in these measurements. The uncertainty in the combined mean thickness of the thermocouples and mounting compound (0.06 mm ± 0.01 mm), coupled with the uncertainty in the thickness and conductivity of the thermal contact sheets could introduce an uncertainty of up to 30% in the above 1% correction, ie 0.3% in λ. An additional uncertainty of 0.2% was associated with the non-parallelism of the thermal contact sheets, leading to an overall uncertainty of 0.5% in ΔT_z near ambient temperatures. At lower temperatures effects arising from the thermal contraction and hardening of the thermal contact material suggested that the overall uncertainty should be increased to 0.8%.

6.3.2.3 Energy flow P_o

The heat flux P_o through the metering area is given by

$$P_o = P \pm P_{v1}$$

where P is the power supplied to the heater plate and P_{v1} is the heat lost or gained due to imbalance error across the centre-guard gap. P was determined through voltage measurements across the plate heater and a standard series resistor. The estimated uncertainty in P was 0.03%. The maximum uncertainty due to temperature imbalance across the gap was estimated to be 0.03% at ambient temperatures, rising to 0.15% at the lower temperatures. Edge losses were negligibly small.

6.3.2.4 Summary of estimated uncertainties

Parameter	Measured Value & Uncertainty	Uncertainty(ϵ) in λ(%)
Area A	$\approx$ 0.02 m^2 $\pm$ 2.7 x 10^{-5} m^2	0.14
Thickness d	$\approx$ 33 mm $\pm$ 0.03 mm	0.09
Temperature difference ΔT_o: $\Delta T_o = \Delta T_s - \Delta T_z$		
ΔT_s	$\approx$ 2 K $\pm$ 0.011 K	0.55 ($\theta > 0$ °C)
	$\pm$ 0.015 K	0.75 ($\theta < 0$ °C)
ΔT_z	$\approx$ 2 K $\pm$ 0.01 K	0.50 ($\theta > 0$ °C)
	$\pm$ 0.015 K	0.80 ($\theta < 0$ °C)
Energy flow P_o: $P_o = P - P_{v1}$		
P	$\approx$ 3 W $\pm$ 0.0009 W	0.07
P_{v1}	$\pm$ 0.0009 W	0.03 ($\theta > 0$ °C)
	$\pm$ 0.0045 W	0.15 ($\theta < 0$ °C)
Total uncertainty (%)		
	$\Sigma\epsilon$	1.34 ($\theta > 0$ °C)
		1.94 ($\theta < 0$ °C)
	$(\Sigma\epsilon^2)^{\frac{1}{2}}$	0.77 ($\theta > 0$ °C)
		1.18 ($\theta < 0$ °C)

6.3.3 Results and discussion

The measurements at IFT were made over the temperature range - 125 °C to 45 °C using soft polyurethane rubber sheets for thermal contact. The latter was not ideal for the lowest temperatures and some difficulties (such as thermocouple breakages) were encountered as a result of the large thermal contraction and embrittlement of the material.

The dimensions of the specimen, Nos 29 and 30, were as follows:

Specimen No.	Dimensions
29	308 x 308 x 32.73 mm
30	308 x 309 x 32.91 mm

The density was not measured but the specimens came from a series in which all the other plates had a density of 2222 kg/m^3.

The results are given in Table 14 and were found to be well represented by the following regression curve

$$\lambda = (1.105 + 1.553 \times 10^{-3}\theta - 4.173 \times 10^{-6}\theta^2 + 3.394 \times 10^{-8}\theta^3)\ W/m.K$$

Comparison of the results with those of the PTB (1 + 2) polynomial values is made in Table 15 and the residuals are plotted in Figure 13 with the appropriate $\Sigma\epsilon$ values as error bars. Within the range covered by PTB (1 + 2) (lower limit - 75 °C) there is excellent agreement between the data. Thus the deviation of each result from PTB values, expressed as r/λ%, is well below the uncertainty of measurement $(\Sigma\epsilon^2)^{\frac{1}{2}}$ (0.77%) and the rms deviation is only 0.26%.

Table 14: IFT results

Index No	Interface	Temperature (θ) °C	Thermal Conductivity (λ) W/m.K
94	pu rubber	-125.45	0.779
95	..	-95.96	0.881
96	..	-93.65	0.898
97	..	-65.47	0.979
98	..	-33.75	1.046
99	..	-33.71	1.047
100	..	-0.42	1.106
101	..	25.30	1.140
102	..	25.64	1.141
103	..	42.21	1.166
104	..	42.30	1.168

Table 15: Comparison of IFT results with PTB(1+2) polynomial values

No	Interface	θ °C	λ W/m.K	λ_c W/m.K	Residuals W/m.K	$(\Sigma \epsilon^2)^{\frac{1}{2}}$ %	$\Sigma \epsilon$ %
94	pu rubber	-125.45	0.779	*		1.18	1.94
95	..	-95.96	0.881	*		1.18	1.94
96	..	-93.65	0.898	*		1.18	1.94
97	..	-65.47	0.979	0.976	0.0031 (0.31%)	1.18	1.94
98	..	-33.75	1.046	1.043	0.0032 (0.31%)	1.18	1.94
99	..	-33.71	1.047	1.043	0.0042 (0.40%)	1.18	1.94
100	..	-0.42	1.106	1.103	0.0031 (0.29%)	0.77	1.34
101	..	25.30	1.140	1.143	-0.0031 (0.27%)	0.77	1.34
102	..	25.64	1.141	1.144	-0.0026 (0.23%)	0.77	1.34
103	..	42.21	1.166	1.167	-0.0010 (0.09%)	0.77	1.34
104	..	42.30	1.168	1.167	0.0009 (0.07%)	0.77	1.34

* these points are outside the range of PTB(1+2)

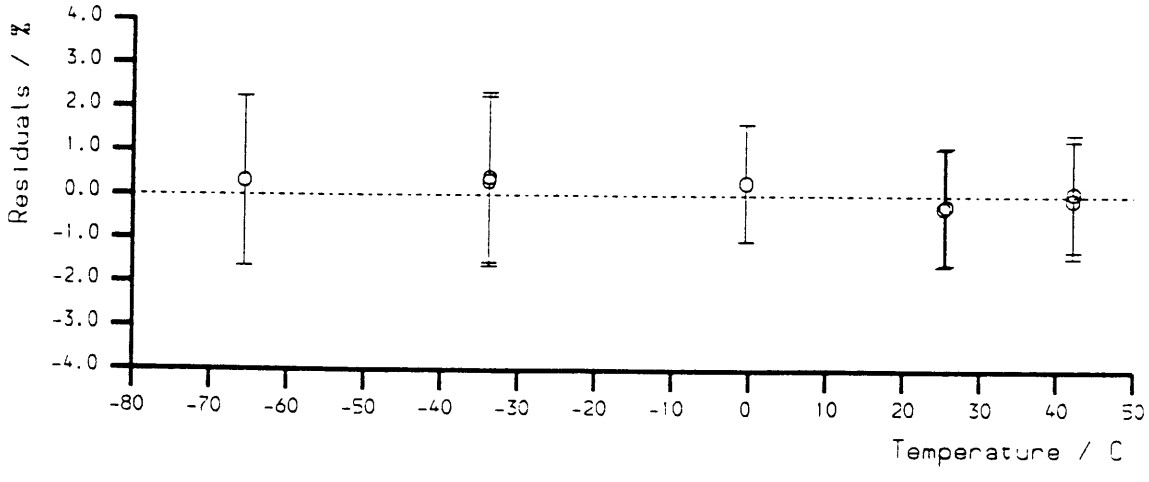


Figure 13: Deviation of IFT results from PTB(1+2) polynomial values

7 EVALUATION OF RESULTS AND UNCERTAINTIES

It was concluded in section 5 that the certified thermal conductivity values for the material should be those given by the third order polynomial fit to all the PTB results, PTB(1+2), but the uncertainty level to be assigned to them, to cover both the measurement uncertainty and the material variability, was left open until all the support data obtained with the conventional guarded hot-plates had been examined.

Dealing first with the uncertainty associated with the PTB measurements, it will be recalled that the PTB results were derived from four sets of independent measurements using two specimens, Nos 42 and 43, and two different apparatuses. Over their common temperature range, no systematic differences of any significance could be detected between the results obtained with the two apparatuses and the four sets of results were therefore grouped into two, one for each specimen.

Power series of third order fitted through the individual sets of results and through the combined set yielded the following expressions for the thermal conductivity of the samples as a function of temperature/°C (θ):

PTB 1/42: $\lambda = (1.1003 + 1.654\times10^{-3}\theta - 3.970\times10^{-6}\theta^2 + 6.817\times10^{-9}\theta^3)$ W/m.K

PTB 2/43: $\lambda = (1.1076 + 1.649\times10^{-3}\theta - 3.960\times10^{-6}\theta^2 + 6.883\times10^{-9}\theta^3)$ W/m.K

PTB(1+2): $\lambda = (1.1036 + 1.659\times10^{-3}\theta - 3.982\times10^{-6}\theta^2 + 6.764\times10^{-9}\theta^3)$ W/m.K

The standard deviation, $r_{rms} = [\Sigma(\lambda_f - \lambda)^2/(n-1-m)]^{\frac{1}{2}}$, and the maximum positive and negative residuals, r_{max+} and r_{max-}, for the three fits were as follows:

	r_{rms} W/m.K		r_{max+} W/m.K		r_{max-} W/m.K	
PTB 1/42	0.00147	(0.11-0.16%)	0.00214	(0.17%)	-0.00399	(0.33%)
PTB 2/43	0.00129	(0.10-0.14%)	0.00290	(0.24%)	-0.00197	(0.16%)
PTB(1+2)	0.00402	(0.30-0.42%)	0.00572	(0.46%)	-0.00580	(0.57%)

These values are in excellent accord with the estimated maximum uncertainty of the measurements ($(\Sigma\epsilon^2)^{\frac{1}{2}}$ = 0.33% to 0.40% and $\Sigma\epsilon$ = 0.66% to 0.80%), indeed, they are better than might be expected.

The 95% confidence interval for the calculated λ values using the above equations can be determined from the expression $\pm t.S_y$, where t is the Student t-value for (n - 1 - m) degrees of freedom and S_y is given by

$$S_y = S_{yx}[1 + 1/n + (\theta - \theta_o)^2/\Sigma(\theta - \theta_o)^2]^{\frac{1}{2}} \text{ W/m.K.}$$

where S_{yx} is the standard deviation (r_{rms} above)

θ_o = 20 °C

n is the number of data points and

m is the order of the fit, 3.

Thus the uncertainty in the calculated values at the 95% confidence level ranges from 0.32 to 0.34% over the full temperature range for PTB 1 and 0.30 to 0.32% for PTB 2. On this basis some fraction of the difference of 0.66% between the values for the two specimens could be attributed to a compositional difference between them or alternatively to a minute difference in their dimensions or surface morphology (see discussion in 5.4.3).

An uncertainty of 0.7% imposed on the PTB(1+2) polynomial values would cover both these interpretations, 0.35% for the random errors and 0.35% for the compositional or geometrical effects. Whilst the random component is at the 95% confidence level, it is not so easy to evaluate a confidence factor for the second 0.35% without undertaking measurements on many more specimens, which would be quite impracticable. However, as far as the geometrical factors are concerned, uncertainties of greater magnitude than this are most unlikely. Had the distribution of the experimental points been normal about the PTB(1+2) values then a straightforward uncertainty of 0.8% at the 95% confidence limit would have been indicated. In view of the actual distribution, however, the previous approach, leading to the 0.7% uncertainty, is more soundly based.

The remaining question to be decided is the extent to which this uncertainty level should be increased to allow for any (further) effects due to variable composition of the batch as a whole. There is a small spread in the density of the material ranging from 2222 to 2226 kg/m^3 (0.2%) but it has proved very difficult to establish whether there is a significant change in the thermal conductivity over this narrow range. Thus with reference to the two sets of results obtained by NPL using the

disc-mounted thermocouple technique (6.1.2.2), the first set on the 45 mm specimens can be represented by the linear equation

$$\lambda = (1.094 + 1.61 \times 10^{-3}\theta)\ W/m.K$$

between 10 °C and 75 °C with a standard deviation of 0.006 W/m.K and maximum positive and negative residuals of about 1%.

The second set on the 33 mm specimens covering the same temperature range can be represented by

$$\lambda = (1.086 + 1.67 \times 10^{-3}\theta)\ W/m.K$$

with a standard deviation of 0.0032 W/m.K and maximum positive and negative residuals of 0.3%.

According to these fitted equations the thermal conductivity of the 33 mm specimens (mean density 2222 kg/m^3) is lower than that of the 45 mm specimens (mean density 2225 kg/m^3) by 0.0053 W/m.K (0.47%) at the mid-range temperature of 45 °C.

The significance of this difference between the mean values of the sets of results can be tested using the expression

$$n_1 n_2/(n_1 + n_2)[(\lambda_1 - \lambda_2)^2/s^2] \geq Z$$

where n_1 and n_2 are the number of data points in the first and second sets, 33 and 5, respectively, λ_1 and λ_2 are the values of λ at the same mean temperature given by the above equations, s^2 is given by $(\Sigma r_1^2 + \Sigma r_2^2)/(n_1 + n_2 - 2)$ and the value of Z is given in standard Significance Tables with $N_1 = 1$ and $N_2 = (n_1 + n_2 - 2)$.

Following this procedure one finds that $(\lambda_1 - \lambda_2)$ has to be $\geq$ 0.0063 W/m.K (0.57%) to be significant at the 0.05 level. Therefore, at the mid-range temperature the difference (0.47%) is not significant but at the lower end of the range (due to the different slopes of the two lines) it becomes so. Although the outcome is rather indeterminate, the difference between the thermal conductivity of the two specimens is so small as to suggest that an additional uncertainty of 1% would

provide ample cover for the spread in density of the material.

This can to some extent be tested by examining all the results obtained with the conventional apparatus. The average deviation $(\Sigma r^2/n)^{\frac{1}{2}}$, and the maximum positive and negative deviations (r_{max+} and r_{max-}), of these results from the PTB (1+2) values (which relate to specimens of density 2222 kg/m^3), together with their averaged estimated uncertainties ($(\Sigma\epsilon^2)^{\frac{1}{2}}$ and $\Sigma\epsilon$), are given below.

Density Results	n	$(\Sigma r^2/n)^{\frac{1}{2}}$ (%)	r_{max+} (%)	r_{max-} (%)	$(\Sigma\epsilon^2)^{\frac{1}{2}}$ (%)	$\Sigma\epsilon$ (%)
2222 kg/m^3:						
NPL 2	5	0.98	0.11	1.74	0.96	1.77
IFT	11	0.26	0.40	0.27	0.77	1.32
2224 kg/m^3:						
FIW	7	1.08	-	1.48	0.93	1.68
2225 kg/m^3:						
NPL 1	33	0.79	1.20	2.02	1.06	1.78
NPL 3	9	0.49	0.46	0.95	0.75	1.31
NPL 4	7	0.34	0.73	0.08	0.65	1.07

The figures in the $(\Sigma r^2/n)^{\frac{1}{2}}$ column show no systematic variation with the specimen density and appear to reflect only the estimated uncertainty of the measurements themselves. The proposed additional 1% uncertainty on the certified values, leading to an overall uncertainty of 1.7%, would on this basis appear to be more than adequate as a safeguard against any effects due to compositional variations. The same conclusion presents itself when all the experimental results obtained during the course of the project are compared with the certified values (Figure 14). It is observed that only 2 of the 104 points fall outside the 1.7% uncertainty band about the certified values, leaving a margin, or reserve, the size of the uncertainties associated with the measured values themselves.

Thus, as far as can be judged from the present results, the overall uncertainty of 1.7% assigned to the certified values is a generous one.

(Note: it is to some extent a matter of judgement and preference how the effects of composition/density should be accommodated. An alternative conservative approach, would have been to assign an uncertainty on the certified values of 1%, 1.5%, and 2%, for samples with densities near 2222 kg/m^3, 2224 kg/m^3 and 2226 kg/m^3 respectively.)

One final comment on the decision to take the values given by the PTB(1+2) polynomial as the certified values for the material: a polynomial based on all the results between - 75 °C to 195 °C, weighted in inverse ratio of their estimated uncertainties, would have yielded values very close to those of PTB(1+2), but in view of the much greater accuracy of the PTB apparatus this course was not adopted. However, to cater for users requiring data below - 75 °C, a weighted fit was made to all the data below - 30 °C to yield the following third order polynomial,

$$\lambda = (1.1046 + 1.520 \times 10^{-3}\theta - 3.311 \times 10^{-6}\theta^2 + 4.309 \times 10^{-8}\theta^3)\ \text{W/m.K}$$

which, it is proposed, could be taken to describe the thermal conductivity of the material over the temperature range - 125 °C to - 75 °C to an uncertainty of about 3%.

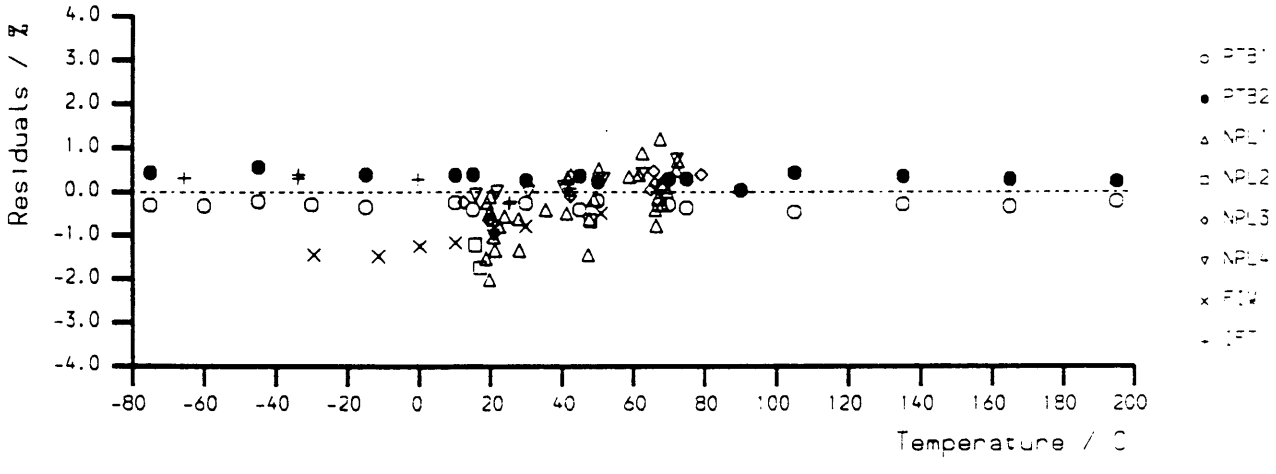


Figure 14: Deviation of all results from PTB(1+2) polynomial values

8 CERTIFIED VALUES AND AVAILABILITY OF THE MATERIAL

8.1 Certified values

The certified values from - 75 °C to 195 °C which are given by the equation

$$\lambda = (1.1036 + 1.659 \times 10^{-3}\theta - 3.982 \times 10^{-6}\theta^2 + 6.764 \times 10^{-9}\theta^3)\ W/m.K$$

are presented in Table 16.

8.2 Indicative values

A further set of values of lower accuracy (deriving from one laboratory) for the temperature range - 125 °C to - 75 °C and represented by

$$\lambda = (1.1046 + 1.520 \times 10^{-3}\theta - 3.311 \times 10^{-6}\theta^2 + 4.309 \times 10^{-8}\theta^3)\ W/m.K$$

is given in Table 17.

Both of the above expressions for λ are represented graphically in Figure 15.

8.3 Availability of the reference material

This reference material is available as approximately square plates either 500 mm x 500 mm or 300 mm x 300 mm in nominal thicknesess of 20, 30 and 50 mm. Only limited supplies of any one combination of dimensions may be available. The samples provided will meet the dimensional requirements (flatness and parallelism, see Appendix 3) for accurate measurements unless otherwise stated. Potential users of the material using conventional guarded hot-plates are advised to choose the 50 mm or 30 mm thick specimens as their own measurement uncertainty using this method will increase as the thickness of the specimen decreases. Guidance on measurement procedures and the sources of uncertainty is given in Appendix 3.

Table 16: Certified values for the thermal conductivity of the Pyrex glass reference material and their limit of uncertainty between -75°C and 195°C.

Temperature	Certified values of the Thermal Conductivity	Limit of uncertainty at 95% confidence
°C	W/m.K	%
-75.00	0.954	1.7
-70.00	0.966	...
-60.00	0.988	...
-50.00	1.010	...
-40.00	1.030	...
-30.00	1.050	...
-20.00	1.068	...
-10.00	1.087	...
0.00	1.104	...
10.00	1.120	...
20.00	1.135	...
30.00	1.150	...
40.00	1.164	...
50.00	1.177	...
60.00	1.190	...
70.00	1.202	...
80.00	1.214	...
90.00	1.226	...
100.00	1.236	...
110.00	1.247	...
120.00	1.257	...
130.00	1.267	...
140.00	1.276	...
150.00	1.286	...
160.00	1.295	...
170.00	1.304	...
180.00	1.313	...
190.00	1.322	...
195.00	1.326	...

Table 17: Indicative values for the thermal conductivity of the Pyrex glass reference material between -125°C and -75°C.

Temperature	Thermal Conductivity	Limit of uncertainty at 95% confidence
°C	W/m.K	%
-125.00	0.779	3.0
-120.00	0.800	...
-115.00	0.821	...
-110.00	0.840	...
-105.00	0.859	...
-100.00	0.876	...
-95.00	0.893	...
-90.00	0.910	...
-85.00	0.925	...
-80.00	0.940	...
-75.00	0.954	...

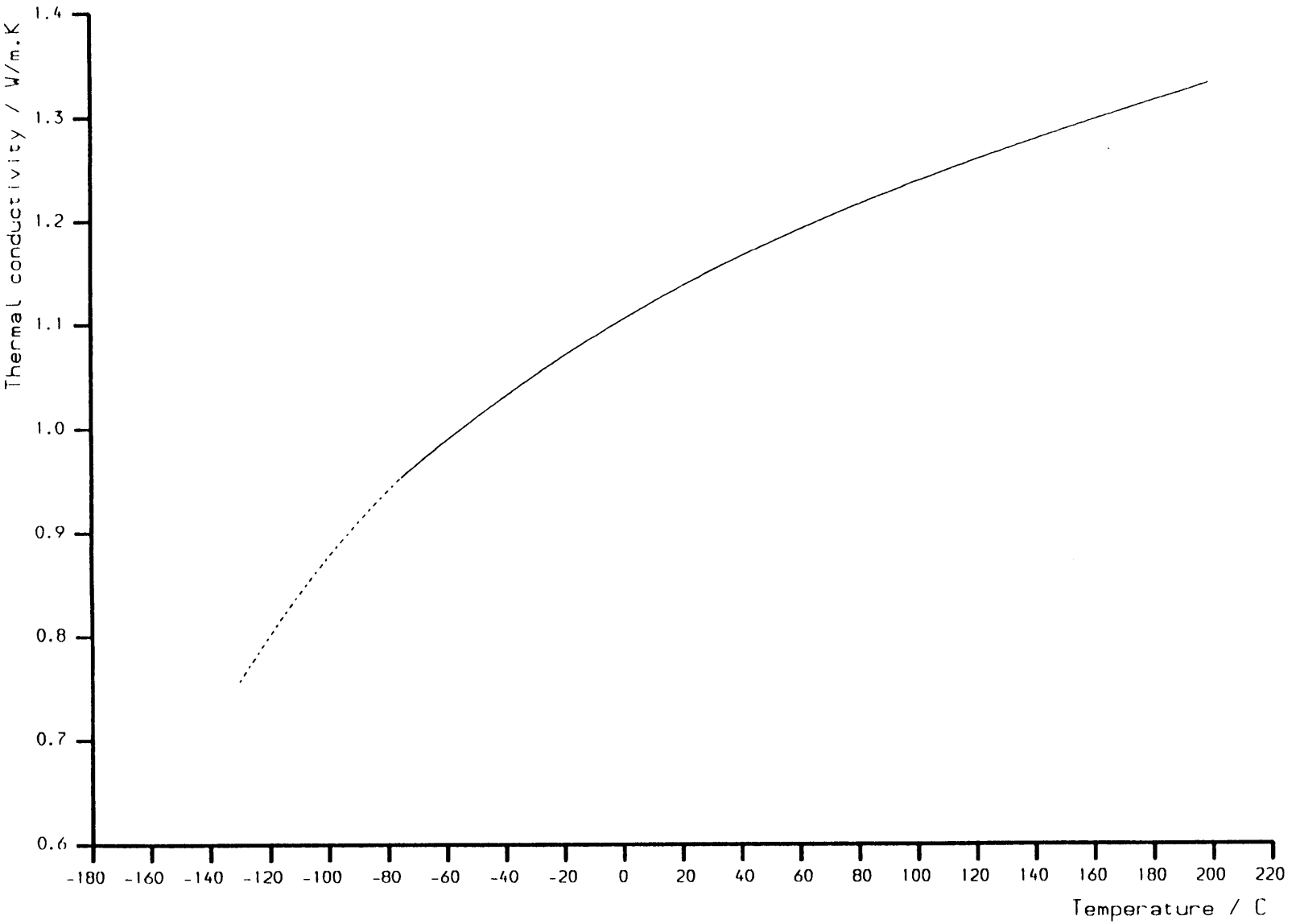


Figure 15: Certified values of the thermal conductivity from -75 C to +195 C (solid line), indicative values from -125 C to -75 C (dotted line).

9 REFERENCES

1. Ziebland, H; 'Certification Report on a Reference Material for Thermal Conductivity of Insulating Materials between 170 K and 370 K. Resin Bonded Glass Fibre Board (RM No. 64)'; Commission of the European Communities, BCR.

2. Hemminger, W and Jugel, R; 'A Guarded Hot-Plate Apparatus for Thermal Conductivity Measurements over the Temperature Range - 75 to 200 °C; Int. Journal of Thermophysics, Vol 6, No 5, Sept. 1985.

3. International Standard ISO 8302 Thermal Insulation: Determination of Steady State Thermal Resistance and Related Properties: Guarded Hot-Plate Apparatus.

4. Corsan, J M and Williams, I; 'Errors Associated with Imperfect Surfaces in Standard Hot-Plate Thermal Conductivity Measurements; NPL Report QU 57, Feb. 1980.

APPENDIX 1

RESULTS OF PRELIMINARY INTERCOMPARISONS

A series of comparative measurements on samples of the Pyrex glass was carried out and evaluted for the BCR before the work described in this report was started. These intercomparison measurements involved five European laboratories all using conventional guarded hot-plates designed to conform with the specifications laid down by their respective national standardising bodies. The five laboratories adopted individual techniques to overcome the thermal contact and temperature measurement problems associated with the method but, as already indicated, the results were disappointing. These are shown in Figure A1.1 and are clearly too divergent for certification purposes. They may be compared with the present results shown in Figure A1.2.

An analysis of these results by H Ziebland [1] involving the elimination of some results and the application of a weighting factor to others, led him to propose the following relationship for the thermal conductivity of the material as a function of temperature

$$\lambda = (1.090 + 1.64 \times 10^{-3}\theta - 4.78 \times 10^{-6}\theta^2 + 1.80 \times 10^{-8}\theta^3)\ W/m.K$$

This yields values within 2% of the present certified values over a wide temperature range and is a good approximation.

Reference:

1. Ziebland, H. Report for BCR, 'Comparative Measurements of the Thermal Conductivity of Dow Corning Glass 7740 (Pyrex)', December 1979.

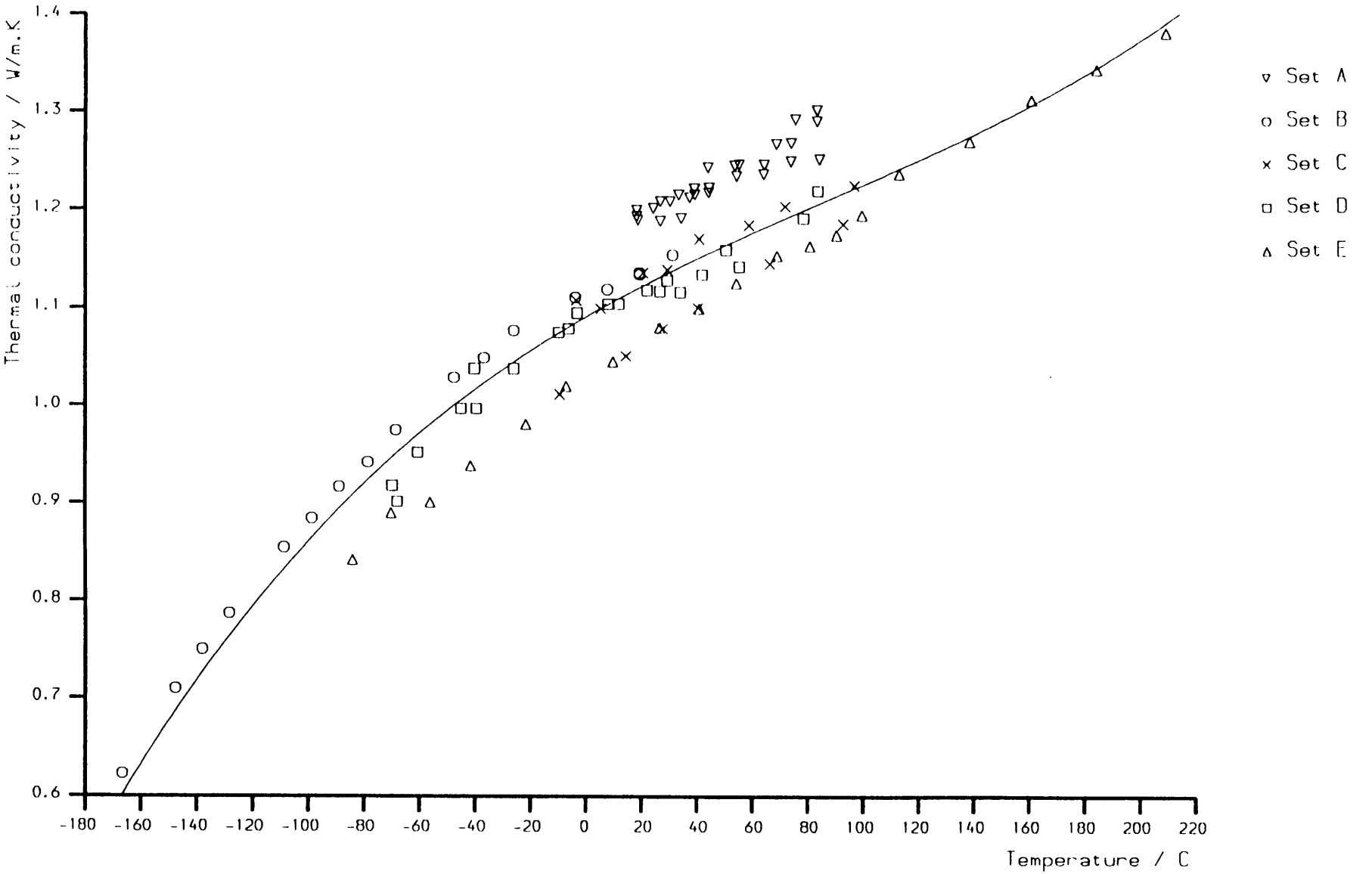


Figure A1.1: Early results using conventional guarded hot plates (Ziebland [1])

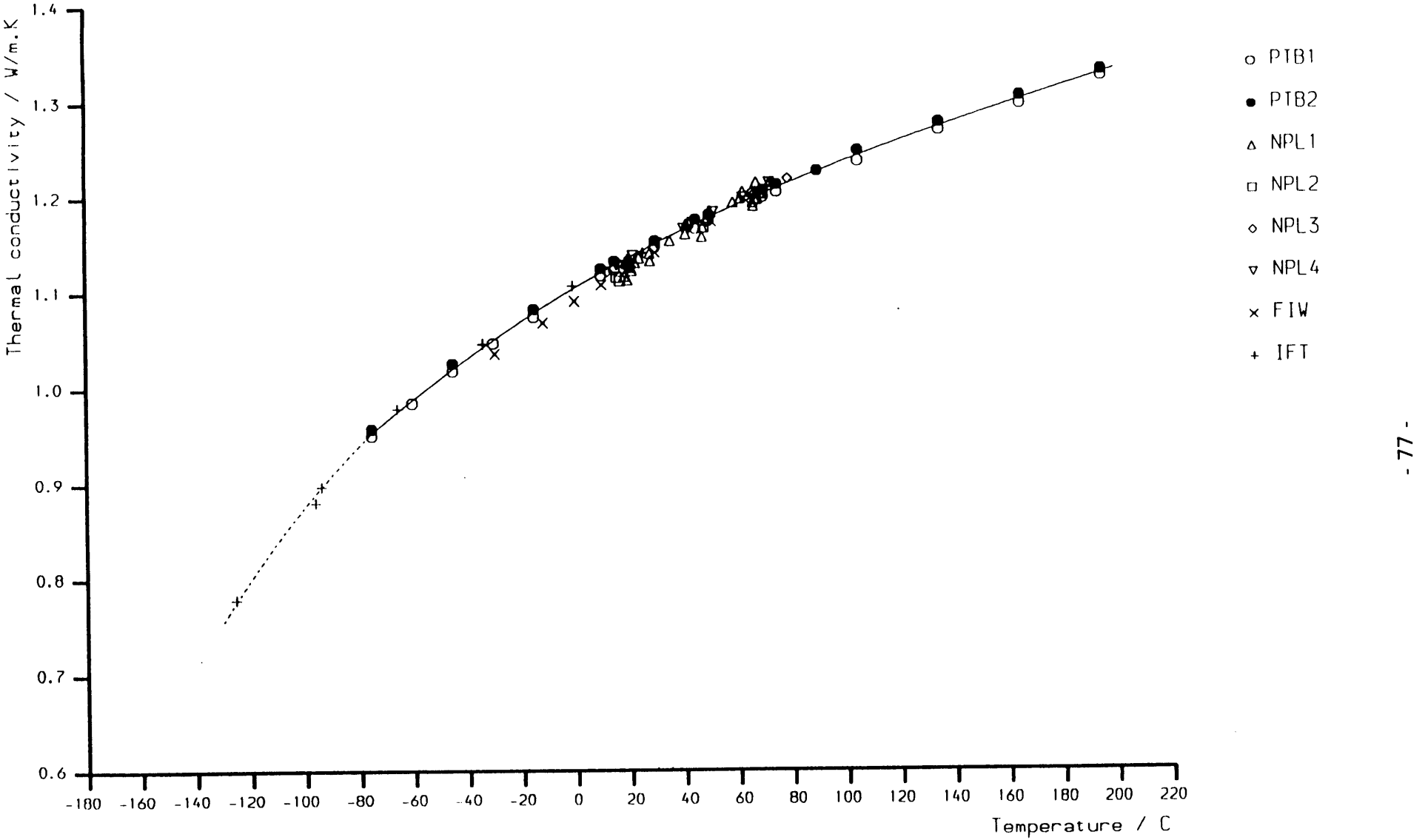


Figure A1.2: Present results with the certified (solid line) and indicative (dotted line) values.

APPENDIX 2

EVALUATION OF CORRECTION FACTORS FOR DISC-MOUNTED THERMOCOUPLES

The presence of temperature measuring probes betwen the specimen and the thermal contact layer in guarded hot-plate measurements on rigid materials inevitably introduces thermal field distortions in their vicinity which result in the temperature they were intended to measure being altered. The extent of this temperature error depends on a number of factors but a correction based on a simple network analysis can be applied provided the values of the relevant parameters are known and the probes on the surfaces are of circular, planar geometry (copper disc mounting pads).

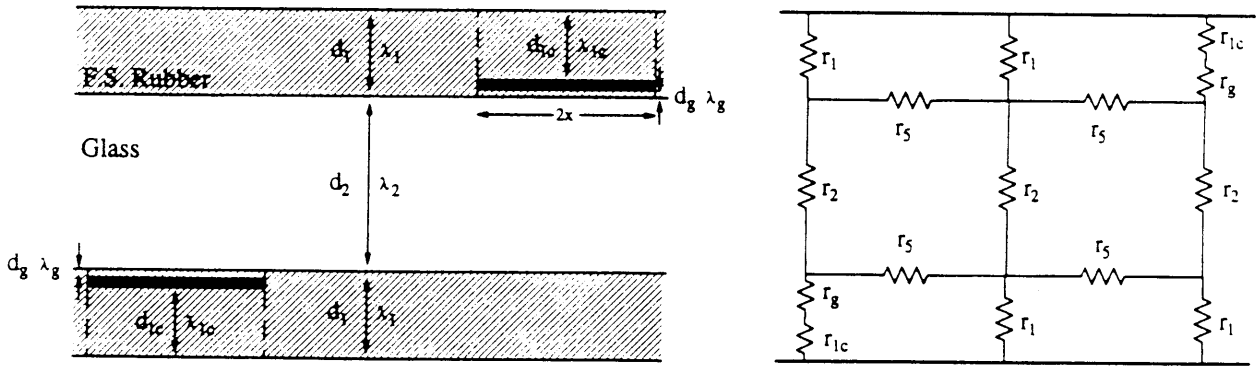


Figure A2.1 Thermal resistances associated with thermocouple mounting pads.

For the arrangement depicted in the diagram the correction which must be applied to the measured temperature difference between the top and bottom faces of the specimen is given by the expression

$$2e = \frac{2\Delta r_1}{r_2 + r_2(2r_1 + \Delta r_1)/r_5 + (r_1 + \Delta r_1)[1 + r_1 r_5/r_2(2r_1 + r_5)]^{-1}}$$

where

r_1 is the thermal resistance of the thermal contact material as used under compression in the appratus,

Δr_1 is the change in that resistance above (or below) a thermocouple pad,

r_2 is the thermal resistance of each specimen and

r_5 is given by $r_5 = 2xr_2/d_2$, where 2x can be taken to be the diameter of the thermocouple mounting pad (to a very close approximation) and d_2 is the specimen thickness.

To illustrate how this is evaluated an example is given below for an arrangement in which fine wire thermocouples are mounted on circular copper discs glued to the specimen (glass) surface and a porous, foamed rubber, whose thermal conductivity changes with compression, is used as the thermal contact medium between the specimen and the plates (the evaluation is less complicated when non-porous soft rubber are used and the use of a thermoconductive glue would be beneficial).

Example:

Specimens: Pyrex glass 45 mm thick

Mounting pads: 30 mm dia. x 0.05 mm copper discs
Interface material: 420 kg/m^3 foamed silicone rubber (F4)

Interface material	d_1	= 2.75 mm	λ_1	= 0.078	W/m.K
Interface material above pads	d_{1c}	= 2.676 mm	λ_{1c}	= 0.079	W/m.K
Glue beneath pads	d_g	= 0.025 mm	λ_g	= 0.15	W/m.K
Specimens (Pyrex)	d_2	= 45.16 mm	λ_2	= 1.13	W/m.K

$$-\Delta r_1 = [r_1 - (r_{1c} + r_g)] = [d_1/\lambda_1 - (d_{1c}/\lambda_{1c} + d_g/\lambda_g)]$$

$$= 1.23 \times 10^{-3}\ m^2K\ W^{-1}$$

$$r_1 = \frac{d_1}{\lambda_1} = 3.526 \times 10^{-2}\ m^2K\ W^{-1}$$

$$r_2 = \frac{d_2}{\lambda_2} = 3.996 \times 10^{-2}\ m^2K\ W^{-1}$$

$$r_5 = \frac{2xr_2}{d_2} = \frac{30}{45.16} r_2 = 2.65 \times 10^{-2} \ m^2K \ W^{-1}$$

$\therefore$ $2e = 0.0144$, (2 x e allows for the pads on both surfaces).

Thus the surface to surface temperature drop through the glass specimens beneath the thermocouple pads is too large by a factor of 1.0144.

But the thermocouples register the temperature of the upper surface of the layer of glue beneath the discs. Taking this into account, for both specimen surfaces, an additional factor of $2 \times r_g/r_2 = 1.0084$ is introducted.

Thus the measured temperature drop through the specimens is too large by a factor of 1.023.

APPENDIX 3

GUIDANCE NOTE FOR USERS OF THE REFERENCE MATERIAL:
A GUARDED HOT-PLATE METHOD FOR RIGID MATERIALS

Introduction

The measurement of the thermal conductivity of hard materials using conventional guarded hot-plate equipment is not straightforward and a number of precautions must be taken to minimise thermal field distortions and related temperature measurement uncertainties if serious errors are to be avoided.

Measurement techniques for such materials are not well documented in standards or in the literature and it was felt therefore, that a Guidance Note providing the details of a proven method, with some explanation of the problems involved, would be generally useful. The method is relatively uncomplicated and has been shown to be capable of yielding results accurate to better than ± 2% on Pyrex glass. It is therefore recommended to users of the Reference Material and indeed to any laboratory involved in the testing of hard materials (eg concretes) using the guarded hot-plate method.

Technique for Rigid Solids

The apparatus and general measurement procedure used should conform with the requirements specified in national and international standards.

The following further requirements should be met:

i) The surfaces of the plates of the apparatus (cold plates and heater) should be machined flat to a minimum tolerance of ± 0.05 mm over the full width ie, i.e. each of these surfaces should be contained within a region bounded by two parallel planes separated by a distance no greater than 0.1 mm.

ii) The surfaces of the specimens should also be flat to ± 0.05 mm and parallel to one another to the extent that the relative change in

the specimen thickness, $\Delta d/d$, per unit length over their full width, L, (i.e. $\Delta d/dL$) is less than 0.05 m^{-1}.

iii) Sheets of compressible, rubber-like material 2 to 3 mm thick should be clamped between the specimen and plate surfaces to facilitate uniform, low resistance, thermal contact between them.

The characteristics of the material chosen for this purpose are critically important. It is essential that the sheets should be homogeneous, uniform in thickness, have reasonably good surfaces, and, most important of all, have adequate compressibility. The material must be sufficiently compressible to ensure that under load it presses firmly over the entire working area of the specimen and plate surfaces, displacing all air pockets from the interfaces. (If the compressibility of the material is not known then it should be measured using platens large enough to avoid error due to sideways displacement of material).

If all other requirements are met, material of the highest thermal conductivity available should be chosen to minimise uncertainties associated with thermal field distortions and temperature gradients (see v).

iv) The clamping force required will depend on the characteristics of the thermal contact material chosen and the flatness of the bearing surfaces. It is likely to be fairly large, e.g. a pressure of the order of 25 kPa may be required. Steps should therefore be taken to ensure that the necessary force can be applied uniformly to the apparatus without distorting or damaging the plates.

v) The temperature drop through the specimens should be measured by means of thin, foil-type thermocouples placed directly on the specimen surfaces. Five such couples should be distributed symmetrically on each face, within the central guarded area and with one in the centre. Guard-centre balance should be monitored by means of the plate-mounted thermocouples, or thermopile, in the usual way.

Thermocouples suitable for this purpose can be b ought ready-made

or prepared from a stock of fine thermocouple wire (preferably of the order of 0.08 mm diameter) either by welding or soldering techniques. Their junctions, and about 20 mm of the adjoining wire, should be rolled or pressed flat to a thickness of 0.03 to 0.04 mm. A smear of ZnO-loaded heat sink compound should be placed beneath them on the specimen surfaces and to hold them in position on the surface only a narrow strip of sellotape (or similar) some 2 mm wide may be used near the tip. More generous amounts of tape may be used elsewhere especially in the guard area to protect the protruding ends of the wire. Compensation leads, if used, should be of the same material. Several thermocouples (having flattened ends) should be calibrated to establish that the material is homogeneous and that thermocouples with identical characteristics are being produced.

The temperature drop registered by thermocouples mounted on the specimen surfaces in this way will be slightly too large because of the influence of the temperature gradient in the thermal contact material in which they are partially embedded. This should be allowed for by reducing the observed temperature drop through the specimens by an amount equivalent to the temperature drop through a layer of the thermal contact material the thickness of one thermocouple.

The temperature gradient through the contact material should be determined in the course of the thermal conductivity measurement.

Thermal conductivity measurements carried out in accordance with the above requirements would be expected to be accurate within ± 2% and reproducible within ± ½%.

European Communities — Commission

EUR 13358 — Certification report for a pyrex glass reference material for thermal conductivity between -75°C and 195°C (CRM 039)

I. Williams, R.E. Shawyer

Luxembourg: Office for Official Publications of the European Communities

1991 — IV, 83 pp. — fig., tab. — 21.0 × 29.7 cm

BCR Information series

ISBN 92-826-2404-8

Catalogue number: CD-NA-13358-EN-C

Price (excluding VAT) in Luxembourg: ECU 7.50

This report describes the work done at the five laboratories which participated in the certification of this reference material for thermal conductivity.

The certified values are based on results obtained with special high-precision guarded hot-plates, backed up by further measurements using more conventional equipment. Details of the apparatus, procedures and the estimated uncertainties are given and the various results are discussed, intercompared and statistically analysed. Problems to be avoided with conventional guarded hot-plate techniques are fully considered.

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements

CERTIFIED REFERENCE MATERIAL
BCR® – 039

CERTIFICATE OF ANALYSIS

PYREX GLASS			
	Thermal conductivity coefficient λ		Number of accepted sets of data p
	Certified value [1] [W/m·K]	Uncertainty [2] [%]	
Thermal conductivity from -75 °C to 195 °C	$1.1036 + 1.659 \times 10^{-3}\theta - 3.982 \times 10^{-6}\theta^2 + 6.764 \times 10^{-9}\theta^3$	1.7	4

1) The certified value is based on the results of 4 sets of results. It can be calculated using the given formula in the temperature range -75 °C to 195 °C with θ = temperature [°C]. The certified value is traceable to the International System of Units (SI).

2) The uncertainty is taken as the half-width ot the 95 % confidence interval of the mean given in 1). It is expressed in relative percentage of the certified value and must be calculated at a given temperature θ. The uncertainty includes the possible effect of small density variations in the plates in the batch.

This certificate is valid for one year after purchase.

Sales date:

INTENDED USE

This material is intended for the calibration of guarded hot-plates for thermal conductivity measurements.

NOTE

This material has been certified by BCR (Community Bureau of Reference, the former reference materials programme of the European Commission). The certificate has been revised under the responsibility of IRMM.

Brussels, September 1990
Latest revision: May 2007

Signed:

Prof. Dr. Hendrik Emons
Unit for Reference Materials
EC-JRC-IRMM
Retieseweg 111
2440 Geel, Belgium

Indicative Values

	Thermal conductivity coefficient λ	
	Indicative value [1] [W/m·K]	Uncertainty [2] [%]
Thermal conductivity from -130 °C to -75 °C	$1.1046 + 1.520 \times 10^{-3}\theta - 3.311 \times 10^{-6}\theta^2 + 4.309 \times 10^{-8}\theta^3$	3

1) The certified value is based on the results of 1 laboratory. It can be calculated using the given formula in the temperature range -130 °C to -75 °C with θ = temperature [°C]. The certified value is traceable to the International System of Units (SI).

2) The uncertainty is taken as the half-width ot the 95 % confidence interval of the mean given in 1). It is expressed in relative percentage of the certified value and must be calculated at a given temperature θ.

DESCRIPTION OF THE SAMPLE

This certified RM is available in the form of plates with the following sizes:
BCR-039A: length 300 mm, width 300 mm, thickness 20 mm
BCR-039B: length 300 mm, width 300 mm, thickness 30 mm
BCR-039C: length 300 mm, width 300 mm, thickness 50 mm

ANALYTICAL METHOD USED FOR CERTIFICATION

Guarded hot plate.

PARTICIPANTS

- Forschungsinstitut für Wärmeschutz EV München (FIW), Gräfelfing (DE)
- Istituto di Fisica Tecnica (IFT), Università di Padova, Padova (IT)
- National Physical Laboratory (NPL), Teddington (GB)
- Physikalisch-Technische Bundesanstalt (PTB), Braunschweig (DE)

The certified value is based on the results obtained by PTB alone.

SAFETY INFORMATION

The usual laboratory safety precautions apply.

INSTRUCTIONS FOR USE

The user should consult the certification report.

STORAGE

No particular storage precautions.
The European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises.

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NOTE

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