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Establishment of Accuracy Limits and Standards for Comparative Thermal Conductivity Measurements[1]

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New techniques have been developed for reducing thermal conductivity data from thermal comparative measurements. The first of these techniques is based on making a Taylor-series expansion of the stack centerline temperature profile. The result is an expression giving the ratio of sample to reference conductivities at any temperature as a function of measured quantities, the stack thermocouple readings and stack element thicknesses. The conventional formula presently used to reduce comparative conductivity data is shown to be a special result of the general analysis. A second technique involves the use of linear least-squares (LS) techniques to derive both the sample and the reference conductivities from the measured data. The LS technique provides the coefficients for a polynomial temperature expansion of the reference and sample conductivities directly. Use of the new techniques is illustrated in a reduction of some comparative data on the conductivities of Pyrex 7740 and Pyroceram 9606. It is shown that a highly self-consistent pair of conductivity functions can be derived for these two commonly used reference materials if the conductivity vs temperature relation for Pyrex is modified slightly from its recommended value. The Pyroceram conductivity results from the comparative measurements are in good agreement with a conductivity derived from pulse diffusivity and differential scanning calorimetry measurements and also in good agreement with the recommended Pyroceram conductivity function.

KEY WORDS: comparative technique; least squares; Pyrex; Pyroceram; reference materials; standards; thermal conductivity.

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1. INTRODUCTION

The thermal comparative or cut-bar technique is frequently used to make steady-state thermal conductivity measurements on solid samples because it is easy to employ and is also relatively accurate. In this technique, the sample to be measured is sandwiched between two reference elements of known conductivity which act as heat flux gages and an axial heat flux is established in the three-element stack. The conductivity of the sample is calculated from the measured temperature drops across and thicknesses of the stack elements. The accuracy of the technique has been a subject of interest since its earliest use [1–3]. Critics of the method have questioned the reported precision of approximately 3% and reported accuracy of about 5% [4, 5]. The purpose of this paper is to reexamine the method by which data are reduced and to apply newer data reduction methods to an experimental determination of the conductivities of two commonly used reference materials, Pyrex 7740, a glass, and Pyroceram 9606, a glass ceramic.

The accuracy of the comparative technique depends on a number of factors. A schematic of the experimental setup is shown in Fig. 1. In a previous study, the question of errors produced by a nonuniform axial heat flux was addressed [6]. It was shown that, although the shunting of heat

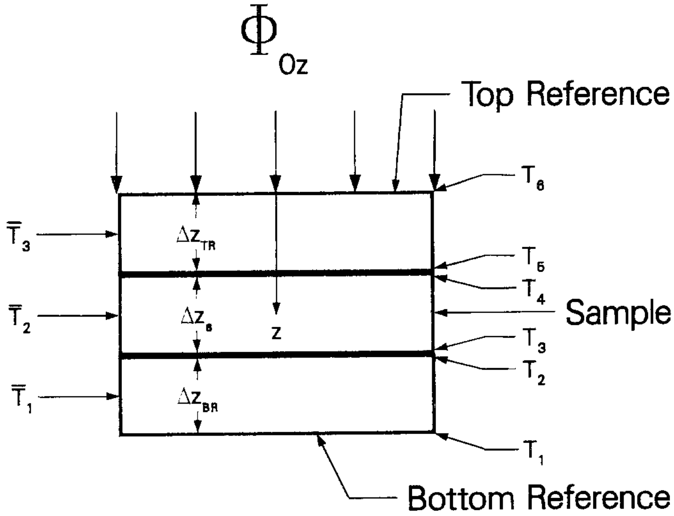

Fig. 1. Schematic of the reference–sample–reference stack used in comparative thermal conductivity measurements. T_1,..., T_6 designate the thermocouple locations and $\bar{T}_1$, $\bar{T}_2$, and $\bar{T}_3$ represent the average temperatures in the designated regions. The uniform axial heat flux in the stack is Φ_{0z}.

flux through the insulation surrounding the stack was not negligible, it did not produce a significant effect on the stack centerline temperatures for either Pyrex or Pyroceram references when the sample conductivity was larger than $\approx 1 W \cdot m^{-1} \cdot K^{-1}$. The same numerical techniques have been used to show that the presence of thermal contact resistance at the two reference–sample interfaces does not produce significant errors if the resistances are as small as normally observed. The remaining sources of potential error are those associated with measurement of stack element thicknesses, thermocouple locations, and temperatures.

2. COMPARATOR DATA ANALYSES METHODS

2.1. Taylor-Series Method

In this method, the sample conductivity at the average sample temperature, $\bar{T}_s = (\bar{T}_3 + \bar{T}_4)/2$, is related to the reference conductivities at the average reference temperatures by expanding the reference conductivities in a Taylor series about their average temperatures (see Fig. 1). The uniform heat flux assumption is approximated by the statement that the product of the conductivity of each stack element at its average temperature and the average thermal gradient across the element is a constant. This assumption leads to Eqs. (1) and (2), which relate the conductivities of adjacent stack elements to each other:

$$k_r(\bar{T}_3) \cdot \frac{(T_6 - T_5)}{\Delta z_{\mathrm{TR}}} = k_s(\bar{T}_2) \cdot \frac{(T_4 - T_3)}{\Delta z_s} \qquad (1)$$

$$k_r(\bar{T}_1) \cdot \frac{(T_2 - T_1)}{\Delta z_{\mathrm{BR}}} = k_s(\bar{T}_2) \cdot \frac{(T_4 - T_3)}{\Delta z_s} \qquad (2)$$

In Eqs. (1) and (2), Δz_{TR} and Δz_{BR} are the top and bottom reference thicknesses and Δz_s is the sample thickness, while $\bar{T}_3$, $\bar{T}_2$, and $\bar{T}_1$ are the average temperatures of the upper reference, sample, and lower reference, respectively. If Eq. (1) and Eq. (2) are added and the resultant equation is solved for $k_s(\bar{T}_2)$, we obtain the conventional comparator data reduction formula,

$$k_s(\bar{T}_2) = \Phi_z / \{(T_4 - T_3)/\Delta z_s\} \qquad (3a)$$

where the axial flux, Φ_z, is given by the relation,

$$\Phi_z = \frac{1}{2}\left[k_r(\bar{T}_3) \cdot \frac{(T_6 - T_5)}{\Delta z_{\mathrm{TR}}} + k_r(\bar{T}_1) \cdot \frac{(T_2 - T_1)}{\Delta z_{\mathrm{BR}}} \right] \qquad (3b)$$

Equations (3a) and (3b) represent only one possible method of finding k_s from the experimental thermocouple data, $\{T_1, ..., T_6\}$. To see this in more detail, we expand the reference conductivities in Eqs. (1) and (2) in Taylor series about the sample average temperature, $\bar{T}_2$, retaining only the first two terms, and then solve the resulting equations for $k_s(\bar{T}_2)$. The results can be expressed as

$$k_s(\bar{T}_2) = \left[k_r(\bar{T}_2) + \left(\frac{dk_r}{dT}\right)_{\bar{T}_2} \cdot (\bar{T}_3 - \bar{T}_2) \right] \frac{G_{65}}{G_{43}} \tag{4a}$$

$$k_s(\bar{T}_2) = \left[k_r(\bar{T}_2) + \left(\frac{dk_r}{dT}\right)_{\bar{T}_2} \cdot (\bar{T}_1 - \bar{T}_2) \right] \frac{G_{21}}{G_{43}} \tag{4b}$$

In Eqs. (4a) and (4b), the gradient functions, G_{ij}, are defined by $G_{65} = (T_6 - T_5)/\Delta z_{\mathrm{TR}}$, $G_{43} = (T_4 - T_3)/\Delta z_{\mathrm{s}}$, and $G_{21} = (T_2 - T_1)/\Delta z_{\mathrm{BR}}$. If we further define the coefficients of $k_r(\bar{T}_2)$ and $(dk_r/dT)_{\bar{T}_2}$ in Eqs. (4a) and (4b) by the relations $a_{11} = G_{65}/G_{43}$, $a_{12} = (G_{65}/G_{43})(\bar{T}_3 - \bar{T}_2)$, $a_{21} = G_{21}/G_{43}$, and $a_{22} = (G_{21}/G_{43})(\bar{T}_1 - \bar{T}_2)$, then Eqs. (4a) and (4b) can be written

$$k_s(\bar{T}_2) = a_{11} k_r(\bar{T}_2) + a_{12} \left(\frac{dk_r}{dT}\right)_{\bar{T}_2} \tag{5a}$$

$$k_s(\bar{T}_2) = a_{21} k_r(\bar{T}_2) + a_{22} \left(\frac{dk_r}{dT}\right)_{\bar{T}_2} \tag{5b}$$

If the coefficients, a_{ij}, are thought of as being functions of the average sample temperature, $\bar{T}_2$, then Eq. (5a) and Eq. (5b) can be treated as a pair of equations, valid at all temperatures in the range of interest, which relate $k_r(T)$ and $k_s(T)$. The comparator experiment can then be viewed as an experiment to determine the $a_{ij}(T)$ functions.

Equations (5a) and (5b) can be analyzed in a number of different ways to yield information about $k_r(T)$, $k_s(T)$, and the ratio $\gamma_{sr}(T) = k_s(T)/k_r(T)$. The utility of different approaches is linked to how accurately the various $a_{ij}(T)$ functions can be derived from the experimental data. The most useful approach is to eliminate the derivative term, $(dk_r/dT)_{\bar{T}_2}$ from Eqs. (7) and (8), the resultant equation can be solved for the ratio function, $\gamma_{sr}(T)$,

$$\gamma_{sr}(T) = \frac{a_{21}(T) + a_{11}(T)}{2} + \frac{[a_{22}(T) + a_{12}(T)][a_{11}(T) - a_{21}(T)]}{2[a_{22}(T) - a_{12}(T)]} \tag{6}$$

The first term in Eq. (6) is very similar to the right-hand side of Eq. (3b), except that in Eq. (6) all functions are arguments of the same temperature.

The second term in Eq. (6) represents a correction which accounts for the temperature dependence of $k_r(T)$. Equation (6) shows that determination of the ratio function, $\gamma_{sr}(T)$, requires no prior knowledge of $k_r(T)$.

2.2. Least-Squares Regression Method

In the least-squares (LS) method, we start by assuming that the conductivity functions can be represented by a finite power series in the temperature, of the order $N_c - 1$, as suggested by Hust and Lankford in their discussion of the thermal conductivity integral method [9].

$$k_{r,s}(T) = \sum_{j=1}^{N_c} c_{j-1}(r, s)\, T^{(j-1)} \tag{7}$$

Using the formalism in Ref. 9, the following equation can be derived for the conductivity coefficients of any stack element:

$$\frac{\Phi_{0i}\, \Delta z_{ba}}{(T_{bi} - T_{ai})} = \sum_{j=1}^{N_c} X_{ij}(T_{bi}, T_{ai})\, c_{j-1} \tag{8}$$

$T_b - T_a$ is the temperature drop across the element of thickness Δz_{ba}. Φ_{0i} is the heat flux when the ith set of data is recorded, and the index i runs over NDAT data points or sets of values $\{T_{1i}, \ldots, T_{6i}\}$. Equation (8) relates the left-hand side response term at the ith data point to the coefficients in Eq. (7) through the X or sensitivity matrix, defined by

$$X_{ij}(T_{bi}, T_{ai}) = \frac{(T_{bi}^{j} - T_{ai}^{j})}{j(T_{bi} - T_{ai})} \tag{9}$$

Equation (8) may be analyzed by linear regression techniques [7]. In the case of the materials we have studied, the temperature dependence of the conductivity is not too strong, and hence the LS method yields results very close to those obtained by the conventional method if a least-squares fit is made to the results computed from Eqs. (3a) and (3b).

3. EXPERIMENTAL MEASUREMENTS

The conductivity measurements on Pyrex 7740 and Pyroceram 9606 were made as part of a recent round-robin study devoted to the development of thermal conductivity standards in the range of 1–5 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ [10]. The system used for measurements was a Dynatech Model TCFCM [11]. The geometry and operation of this system have been discussed in detail in previous work [6, 12]. In the measurements described in this report, a stack temperature drop, $T_6 - T_1 \sim 50°C$, was maintained and several sets of stack temperatures were measured at approximately 50°C, changes in average sample temperature. A calculation of the net experimental uncertainty caused by errors in measuring thermocouple locations, thermocouple temperatures, and stack element thicknesses indicates that our measurements should have an overall one sigma uncertainty of $\approx \pm 3\,\%$.

A series of six experimental runs was conducted as outlined in Table I. There was no a priori reason to suppose that corresponding Dynatech and Sandia specimens were identical materials. One of the purposes of our test matrix design was to determine experimentally whether or not the specimens of each type from different sources behaved similarly from a thermal standpoint.

The experimental matrix shown in Table I was chosen to yield as much information as possible from a limited number of runs. Runs 5 and 6 were repeated to give some information about the experimental precision. The a and b parts for runs 5 and 6 were separated in time by ~3 months and involved remounting but not rewiring the stack elements. In the case of Pyroceram 9606, which is opaque, pulse diffusivity and specific heat measurements were also made on a sample of Dynatech-supplied material to provide an independent check on its conductivity.

Table I. Round–Robin Experimental Matrix for Pyrex 7740 and Pyroceram 9606 Measurements Reported in this Paper[a]

		Sample	
Run No.	Ref. type (SNL)	Sample type	Supplier
1	Pyrex	Pyrex	Dynatech
2	Pyroceram	Pyrex	Dynatech
3	Pyrex	Pyroceram	Dynatech
4	Pyroceram	Pyroceram	Dynatech
5(a)	Pyroceram	Pyrex	Sandia
5(b)	Pyroceram	Pyrex	Sandia
6(a)	Pyrex	Pyroceram	Sandia
6(b)	Pyrex	Pyroceram	Sandia
*	None–pulse diff.	Pyroceram	Dynatech

[a] The samples used were supplied either by Dynatech R/D Co. or by Sandia (SNL). The references were materials used for routine conductivity measurements in our laboratory.

4. DATA ANALYSIS

The major result from this study is a determination of the conductivity ratio function, $\gamma = k_{\text{Pyroc.}}/k_{\text{Pyrex}}$, from Eq. (6). The curve-fit results from each run in which the sample and reference materials were different are shown in Fig. 2 along with a curve calculated from the NBS/Dynatech recommended values for the two materials [12, 13]. It is evident that our data clearly indicate a discrepancy between the measurements and the NBS/Dynatech curve at low temperature but reasonably good agreement above ~300°C. At 0°C, our data indicate that $\gamma = 3.50 \pm 0.12$, where the ± limits represent one standard deviation. In the case of run 1 with a Pyrex sample and Pyrex references, the ratio was in the range 0.979–0.981 between 0 and 400°C, while the ratio for the corresponding Pyroceram run (run 4) was in the range 0.998–1.002. Hence our data support the conclusion that the Pyrex and Pyroceram samples from both sources are identical in their thermal response.

The experimental data from all of the runs in Table I were also analyzed by the LS method. If the flux function is taken from the conventional comparator data reduction formula, as specified by Eq. (3b), then

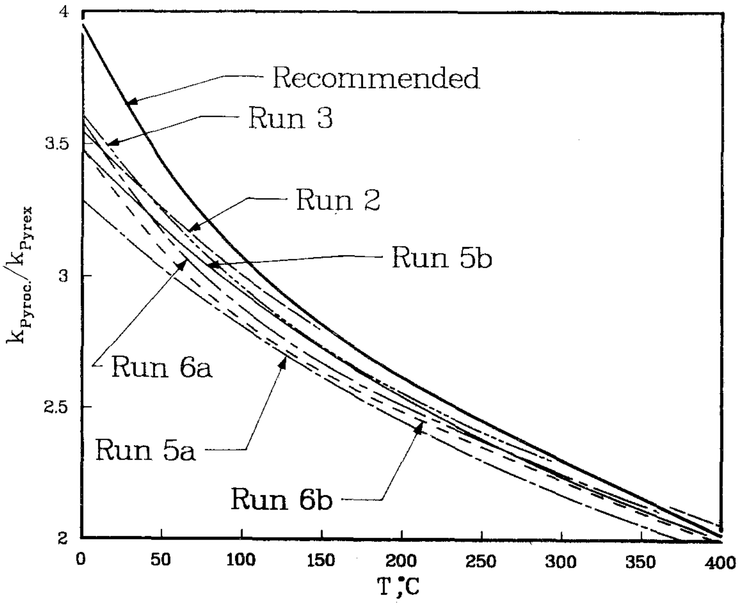

Fig. 2. Experimental results for the ratio, $\gamma = k_{\text{Pyroceram}}/k_{\text{Pyrex}}$ as derived from runs 2, 3, 5, and 6. The ratio derived from the recommended conductivities is the upper heavy solid curve.

the LS technique will yield $k(T)$ for each stack element directly. The agreement of the least-squares $k_r(T)$ functions for the top and bottom references with the assumed reference conductivity function used to calculate the heat flux gives some indication of both the accuracy of the assumed conductivity function and the agreement of assumed and actual experimental conditions. Ideally, the measured $k_r(T)$ functions should agree with each other and with the assumed conductivity function.

Since our experiment was designed to measure the conductivity of reference materials against each other, we performed the analysis in a slightly different way. The flux function was taken as the usual flux function, Eq. (3b), within a multiplicative constant and the value of the constant was determined by fixing $k_r(0°C)$ for the top reference at a preassigned value. Since all the conductivity polynomial coefficients, c_j, in Eq. (7) are proportional to the flux function, through Eq. (8), fixing the conductivity of any one stack element at any one temperature uniquely determines the value of the multiplicative constant. In the calculations discussed below, the conductivity of the upper reference was fixed at the value $k = 1.17\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$ for Pyrex and $k = 4.10\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$ for Pyroceram. The ratio of these two conductivities is $k_{\mathrm{Pyroc.}}/k_{\mathrm{Pyrex}}(0°C) = \gamma(0°C) = 3.5$, in agreement with the prediction of $\gamma(0°C)$ from Fig. 2. The $k(T)$ coefficients, Eq. (7) were then calculated for each stack element in each experimental run. The IMSL library subroutine RLSEP was used to perform the least-squares analysis [14, 15]. The maximum order for the fit was fixed at three and the criterion for inclusion or deletion of a coefficient was an F test performed at the 5% level of significance [7, 15].

Results from the polynomial fit for Pyrex sample runs 1, 2, 5(a), and 5(b) are shown in Fig. 3. The bottom heavy solid curve is the recommended Pyrex conductivity. The experimental curve for run 1 in which Pyrex references were used has the same general shape as the reference curve but is displaced upward because of the assumption that $k_{\mathrm{Pyrex}}(0°C) = 1.17\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$ instead of the recommended value, $1.06\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$. If it is assumed that $k_{\mathrm{Pyrex}}(0°C) = 1.06\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$ for reduction of the run 1 data, then the calculated and recommended curves agree quite closely although not exactly, with a maximum fractional difference of about 5% at $T = 400°C$ and an rms difference of $\sim 2.5\%$. Results for runs 2, 5(a), and 5(b) in which Pyroceram references were utilized agree well with each other but deviate significantly from the run 1 results.

If the conductivity for Pyrex is then adjusted to that measured with Pyroceram references, run 1 can be recalculated using a flux function derived from the adjusted Pyrex reference conductivity. The result is shown by the curve marked run 1 (recalc.) in Fig. 3. It can be seen that the agreement of the run 1 results with the other results is now quite close.

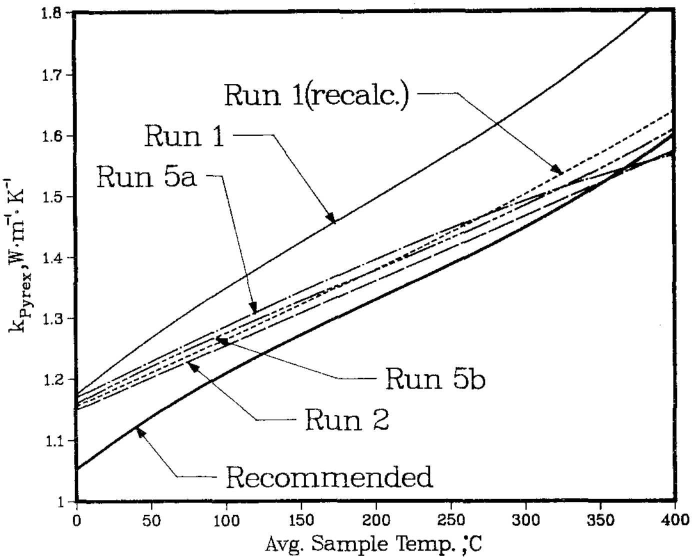

Fig. 3. Results from Pyrex conductivity measurements. The lower heavy curve is the recommended conductivity. The curve marked run 1 (recalc.) was recalculated using a flux function based on the run 5b result.

The results for the runs with Pyroceram samples are shown in Fig. 4. The experimental points shown in Fig. 4 are conductivities derived from pulse diffusivity data, with the error bars indicating the estimated measurement error associated with the conductivity determination from the diffusivity, density, and specific heat measured data. It can be seen that the conductivity derived from diffusivity data agrees well with the assumed reference conductivity [11, 12] (heavy dot–dash curve) and with the conductivity measured in run 4 where Pyroceram references were used. The three comparator runs with Pyrex references and a Pyroceram sample [runs 3, 6(a), and 6(b)] produced results which were consistent among themselves but predicted higher conductivities with a generally flatter temperature dependence than either the diffusivity-derived or the run 4 conductivities. In the LS calculation for these runs, the magnitude of the flux function at $T = 0°\mathrm{C}$ was again fixed by requiring that $k = 1.17\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$ for the upper Pyrex reference at that temperature.

If the Pyroceram conductivities for runs 3, 6(a), and 6(b) are recalculated using the adjusted Pyrex conductivity found in run 5(b), then the results from all four runs with Pyroceram samples are quite consistent and also agree with the pulse diffusivity and recommended Pyroceram conductivities. The results of this recalculation are shown in Fig. 5.

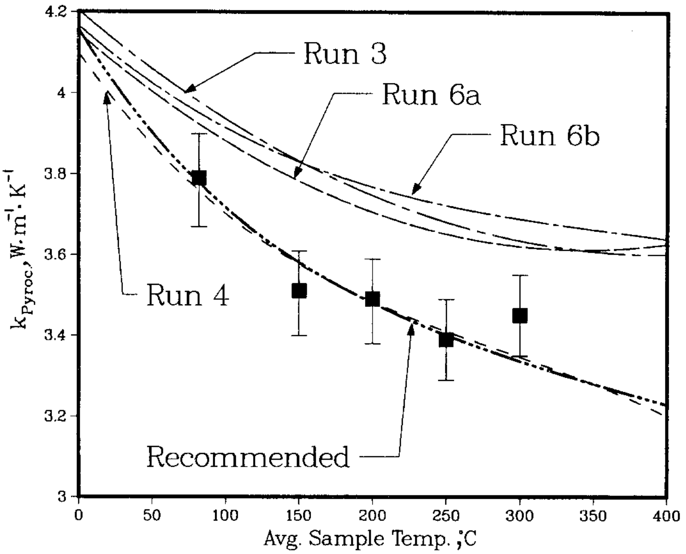

Fig. 4. Results from Pyroceram conductivity measurements. The experimental points with error bars are from pulse diffusivity measurements as described in the text. The heavy dot–dash curve is the recommended conductivity.

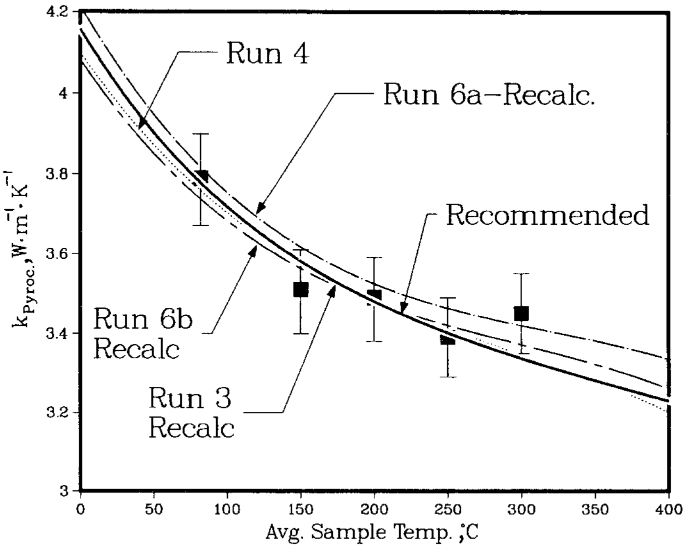

Fig. 5. Recalculated Pyroceram conductivities using the adjusted Pyrex conductivity from run 5b for calculation of the heat flux. The recalculated run 3 result is nearly coincident with the recommended curve and is not shown for clarity.

5. DISCUSSION

The results presented in Section 4 indicate that a highly self-consistent set of comparator results can be obtained by making a small but significant adjustment in the Pyrex conductivity function. This adjustment is not unique, as any adjustment of Pyrex and Pyroceram conductivities which is consistent with the measured conductivity ratio function, $\gamma(T)$, in Fig. 2 would in principle be feasible. However, the pulse diffusivity results strongly suggest that the Pyroceram conductivity is quite well specified by the recommended reference curve, and hence we conclude that most or all of the required correction should be in the Pyrex conductivity. This is consistent with a tentative conclusion stated in Ref. 6. That conclusion was based on both an examination of the primary data from which the suggested reference curves were derived and a large amount of comparative data obtained in our laboratory.

6. CONCLUSIONS

We have demonstrated that new data analysis methods can be highly useful in evaluating comparative thermal conductivity data. These methods provide more information than the conventional technique and can also be used to check for proper operation of the experimental equipment during a run.

Analysis of data from recent measurements of Pyrex and Pyroceram samples indicates that the recommended conductivities for these materials are not consistent with our experimental comparative data. A small but significant shift in the Pyrex conductivity function brings all of our conductivity data into self-consistent agreement, and in the case of Pyroceram, excellent agreement with pulse diffusivity-derived conductivity is also obtained. Using the modified Pyrex conductivity and the least-squares data reduction method, the maximum fractional difference between any of our derived conductivity relations for either material is found to be less than 5%. We conclude either that the Pyrex conductivity function needs to be modified as we have suggested or that we still do not completely understand the operation of the thermal comparative system.

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