# Determination of thermal conductivities of solids by microcalorimetry

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## Abstract

A method and a calculation formula for determining the thermal conductivity of solids under constant radial heat flow conditions by use of the Peltier and Joule effects is presented. The instrument constant and coefficient of thermal disequilibrium have been determined using four standard samples with known thermal conductivity: quartz glass, plexiglass, teflon and polyethylene. The reproducibilities of measurements for the heat of thermal disequilibrium in the investigated sample were less than 0.50% and the amount of heat flux through the wall of the investigated cylinder was within 0.07%. The standard deviation, relative error and accuracy of the thermal conductivity determined using this method were 1.8%, 0.22% and 5%, respectively. The thermal conductivities of quartz glass, plexiglass, polyethylene and teflon at 298 K were measured and it was found that the heat of thermal disequilibrium was the principal factor affecting the magnitude of the thermal conductivity of these samples.

# INTRODUCTION

With the development of material engineering, material-heat transfer is of growing interest. As a basic transport property, determination of the thermal conductivity ( $\lambda$ ) of materials becomes important. Many scientists devote their efforts to the measurement of the value of  $\lambda$  of solids. The basic principle and apparatus for measuring the values of  $\lambda$  of solids by microcalorimetry have been reported [1,2]. The aim of this work is to present a method and a calculation formula for determining the value of  $\lambda$ of solids by using microcalorimetry and to analyse the measuring error of the  $\lambda$  value using the experimental data obtained for quartz glass, plexiglass, polyethylene and teflon.

## DERIVATION OF FORMULA OF THERMAL CONDUCTIVITY

If the cylinder shown in Fig. 1 is long enough, the heat conduction in the axial direction may be ignored. In this case, the temperature will change in

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Fig. 1. Single wall cylinder where  $r_1$ ,  $r_2$  are the internal and external radii, respectively, in m;  $T_1$ ,  $T_2$  are the temperatures of the internal and external walls respectively in K; r is the arbitrary radius in m; dr is the thickness of the differential unit cylinder in m and l is the length in m.

the radial direction, and the temperature field will be one-dimensional when the cylinder coordinate is used.

For steady-state conditions the equation which describes onedimensional radial heat conduction in the cylinder coordination is

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}T}{\mathrm{d}r}\right) = 0\tag{1}$$

By integrating eqn. (1) twice, the general solution can be obtained

$$T = c_1 \ln r + c_2 \tag{2}$$

where  $c_1$  and  $c_2$  are the integral constants which are determined by the following boundary conditions

when 
$$r = r_1$$
,  $T = T_1$  (3)

when  $r = r_2$ ,  $T = T_2$  (4)

Substituting eqns. (3) and (4) into eqn. (2), the values of  $c_1$  and  $c_2$  may be obtained. Substituting the values of  $c_1$  and  $c_2$  into eqn. (2), gives the following temperature distribution equation in the cylinder:

$$T = T_1 + \frac{T_2 - T_1}{\ln\left(\frac{r_2}{r_1}\right)} \ln\left(\frac{r}{r_1}\right)$$
(5)

Differentiation of eqn. (5) with respect to r gives

$$\frac{\mathrm{d}T}{\mathrm{d}r} = \frac{1}{r} \frac{T_2 - T_1}{\ln\left(\frac{r_2}{r_1}\right)} \tag{6}$$

For steady-state conditions the amount of heat flux passing through the test sample is a constant, and it can be described by Fourier's law

$$Q_{\rm s} = -\lambda F \frac{\mathrm{d}T}{\mathrm{d}r} = -\lambda 2\pi r l \frac{\mathrm{d}T}{\mathrm{d}r} \tag{7}$$

where  $F(=2\pi rl)$  is the area of the cylinder in m<sup>2</sup> with a radius r,  $Q_s$  is the amount of heat flux passing through the wall of the cylinder in J s<sup>-1</sup>; and  $\lambda$  is the thermal conductivity of the investigated cylindrical sample in W m<sup>-1</sup> K<sup>-1</sup> or J m<sup>-1</sup> s<sup>-1</sup> K<sup>-1</sup>.

Substituting eqn. (6) into eqn. (7) the following equation may be obtained:

$$Q_{\rm s} = \frac{2\pi\lambda l(T_1 - T_2)}{\ln\left(\frac{r_2}{r_1}\right)} \tag{8}$$

Similarly, the following equation which describes the amount of heat flux passing through the test sample from r to  $r_2$  can be obtained

$$Q = \frac{2\pi\lambda l(T - T_2)}{\ln\left(\frac{r_2}{r}\right)}$$
(9)

For steady-state conditions,  $Q = Q_s$ , that is

$$Q_{\rm s} = \frac{2\pi\lambda l(T-T_2)}{\ln\left(\frac{r_2}{r}\right)} \tag{10}$$

The accumulated heat in the differential unit cylinder shown in Fig. 1 is composed of  $dq_1$  and  $dq_2$  if the following experimental conditions are satisfied: (a) the length of the cylinder is much greater than its diameter, i.e.  $l \gg 2r_2$  and its top and bottom are covered by thermal insulation; (b) the temperature of the test cylinder arrives at the equilibrium temperature  $T_e$ after simultaneously cutting the power produced in the hole of the cylinder by the Joule effect and the compensated power produced in the thermoelectric pile by the Peltier effect.

The value of  $dq_1$  caused by  $T > T_2$  is given by

$$dq_1 = (dV) \gamma (T - T_2) = 2\pi r l \, dr \, \gamma (T - T_2)$$
(11)

where  $\gamma$  is the heat capacity of unit volume of the cylindrical sample in J K<sup>-1</sup> m<sup>-3</sup>.

Combining eqns. (10) and (11), we have

$$dq_{1} = \frac{\gamma}{\lambda} Q_{s} r \ln\left(\frac{r_{2}}{r}\right) dr = \frac{Q_{s}}{h} r \ln\left(\frac{r_{2}}{r}\right) dr$$
(12)

where

$$h = \frac{\lambda}{\gamma} = \frac{\lambda}{c\rho} \tag{13}$$

where *h* is the coefficient of thermal diffusion of the cylindrical sample in  $m^2 s^{-1}$ ; *c* is the specific heat of the cylindrical sample in  $J kg^{-1} K^{-1}$  and  $\rho$  is the density of the cylindrical sample in kg m<sup>-3</sup>.

Integrating on both sides of eqn. (12)

$$\int_{0}^{q_{1}} dq_{1} = \frac{Q_{s}}{h} \int_{r_{1}}^{r_{2}} r \ln\left(\frac{r_{2}}{r}\right) dr$$
(14)

the calculated formula of the heat of thermal disequilibrium  $(q_1)$  accumulated in the whole cylinder may be obtained as

$$q_{1} = \frac{Q_{s}}{h} \left[ \frac{r_{2}^{2} - r_{1}^{2}}{4} - \frac{1}{2}r_{1}^{2}\ln\left(\frac{r_{2}}{r_{1}}\right) \right]$$
(15)

The value of  $dq_2$  caused by  $T_2 > T_e$  is given by

$$dq_2 = 2\pi r l \, dr \, \gamma (T_2 - T_e) \tag{16}$$

where  $T_{\rm e}$  is the equilibrium temperature of the cylinder.

Because the value of  $dq_2$  is directly proportional to the amount of heat flux passing through the wall of the cylinder  $(Q_s)$  the temperature difference  $(T_2 - T_e)$  is also directly proportional to the value of  $Q_s$ , i.e.

$$T_2 - T_e = kQ_s \tag{17}$$

where k is a constant of the microcalorimeter in  $K J^{-1} s$ .

Substituting eqn. (17) into eqn. (16) gives

$$dq_2 = 2\pi r l \, dr \gamma k Q_s \tag{18}$$

Integrating on both sides of eqn. (18) gives

$$\int_{0}^{q_{2}} \mathrm{d}q_{2} = 2\pi l \gamma k Q_{\rm s} \int_{r_{1}}^{r_{2}} r \,\mathrm{d}r \tag{19}$$

and the following equation which describes heat of thermal disequilibrium

 $q_2$  accumulated in the whole cylinder can be obtained

$$q_2 = \pi l \gamma k Q_{\rm s} (r_2^2 - r_1^2) = V c \rho k Q_{\rm s} = {\rm cm} Q_{\rm s} k \tag{20}$$

where m is mass of the cylindric sample in kg.

Hence, the heat of thermal disequilibrium  $q_{12}$  accumulated in the whole cylinder is

$$q_{12} = q_1 + q_2 = \frac{Q_s}{h} \left[ \frac{r_2^2 - r_1^2}{4} - \frac{1}{2} r_1^2 \ln\left(\frac{r_2}{r_1}\right) \right] + cm Q_s k$$
(21)

When the Joule current and the Peltier current are cut simultaneously, there is the heat of thermal disequilibrium  $q_3$  within the all materials in the space around the cylinder. The value of  $q_3$  is also directly proportional to the value of  $Q_{s_1}$  i.e.

$$q_3 = DQ_s \tag{22}$$

Where D is the coefficient of thermal disequilibrium.

Thus, the total heat of thermal disequilibrium q is written as

$$q = q_{12} + q_3 = \frac{Q_s}{h} \left[ \frac{r_2^2 - r_1^2}{4} - \frac{1}{2} r_1^2 \ln\left(\frac{r_2}{r_1}\right) \right] + cm Q_s k + DQ_s$$
(23)

Combining eqns. (13) and (23), we have

$$\lambda = \frac{c\rho}{\frac{q}{Q_{\rm s}} - (cmk + D)} \left[ \frac{r_2^2 - r_1^2}{4} + \frac{r_1^2}{2} \ln\left(\frac{r_1}{r_2}\right) \right]$$
(24)

Equation (24) is known as the calculated formula of thermal conductivity of the cylindric sample.

By measuring the values of c, m,  $Q_s$ , q,  $\rho$ ,  $r_1$  and  $r_2$  with four standard cylindrical samples of known thermal conductivity, the values of k and D can be obtained from eqn. (24).

By substituting the values of  $Q_s$ , q and c obtained by using microcalorimetry, the values of  $r_1$  and  $r_2$  obtained with a vernier callipers, the value of  $\rho$  obtained with densitometry, and the values of k, D and m into eqn. (24), the value of  $\lambda$  of the investigated cylindrical sample can be obtained.

To gain the value of specific heat of the sample in eqn. (24), the empty cell (system I), the cell containing sample with unknown specific heat c (system II), the cell containing first standard substance with known specific heat  $c_1$  (system III), and the cell containing the second standard substance with known specific heat  $c_2$  (system IV) are uniformly heated by the Peltier current of  $10\sqrt{10}$  mA for 1 h. When thermal equilibrium of systems I–IV is established, it can be shown that, (a) the temperature is uniform within the cell, and (b) the equilibrium temperature  $\theta$  is the same for a given Peltier

current, whatever the cell contents. When the Peltier current is cut off, the quantities of heat,  $Q_1$ ,  $Q_2$ ,  $Q_3$  and  $Q_4$  retained by the systems I–IV are given by the following equations.

For system I	$Q_1 = KS_0 = a\theta$	(25)
For system II	$Q_2 = KS = (a + mc)\theta$	(26)
For system III	$Q_3 = KS_1 = (a + m_1c_1)\theta$	(27)
For system IV	$Q_4 = KS_2 = (a + m_2c_2)\theta$	(28)
where K is a ca experimental tem capacity of the e	loric constant of the microcalorimeter perature in J (integral number) <sup>-1</sup> ; <i>a</i> is empty cell in J K <sup>-1</sup> ; <i>m</i> , $m_1$ and $m_2$ and the first standard substance and the	er used under the the apparent heat are masses of the

investigated sample, the first standard substance and the second standard substance, respectively, in kg; S is the area under the curve on its return to the experimental zero after cutting off the Peltier current, (integral number); and subscripts 0, 1 and 2 express the systems I, III and IV, respectively.

From eqns. (25) and (26), we have

$$mc\theta = K(S - S_0) \tag{29}$$

From eqns. (25) and (27), we have

$$m_1 c_1 \theta = K(S_1 - S_0) \tag{30}$$

From eqns. (29) and (30), we have

$$c = \frac{(S - S_0)m_1c_1}{(S_1 - S_0)m}$$
(31)

Similarly, we have

$$c = \frac{(S - S_0)m_2c_2}{(S_2 - S_0)m}$$
(32)

From eqns. (31) and (32), we can obtain

$$c = \frac{S - S_0}{2m} \left( \frac{m_1 c_1}{S_1 - S_0} + \frac{m_2 c_2}{S_2 - S_0} \right)$$
(33)

The value of c of the investigated sample can be obtained from eqn. (33) if the values of  $c_1$  and  $c_2$  of two standard substances are known.

## EXPERIMENTAL

#### Sample

The cylindrical samples used to measure the thermal conductivity of quartz glass, plexiglass, polyethylene and teflon have same dimensions: 66.18 mm long with a outer diameter of 14.86 mm and an inner diameter of 2 mm (see Fig. 2).



Fig. 2. Device used for measuring the thermal conductivity of the investigated cylindrical samples. 1, Teflon cover; 2, wooden rod; 3, enamel-insulated manganin wire; 4, calorimetric cell; 5, investigated cylindrical sample; 6, thermal insulation.

# Electric heater

The electric heater is placed in the hole of the cylinder (inner diameter 2 mm) and is composed of a wooden rod of length 66.18 mm and diameter 1.40 mm and an enamel-insulated manganin wire  $(85.4 \Omega m^{-1})$  of 0.08 mm diameter which has a very low resistance-temperature coefficient. The wire is compactly wrapped in the wooden rod in the form of two layers. The leads of the heater are fixed onto the teflon cover. The two electric heaters used in the measurements have same resistance.

## Experimental equipment

All measurements were made using a microcalorimeter, type RD496-II from Southwestern Electronic Engineering Institute, China, which has a sensitivity of 46.49  $\mu$  V mW<sup>-1</sup> and is equipped with two 15 ml vessels. The microcalorimeter was calibrated by the Joule effect before use. The variation in enthalpy measurement is less than 1%.

# Determination of the values of $Q_s$ and q

The values of  $Q_s$  and q used to calculate the thermal conductivity of the sample are obtained by the testing method presented as a thermogram in Fig. 3. In Fig. 3, AH is the baseline; at time B, a constant calorific power is generated in the laboratory cell; at CD, the steady state is established; at point D, the Peltier effect begins; at EF, the calorific power produced by the Joule effect is totally compensated by the Peltier effect; at point F, the Joule and Peltier effects are simultaneously cut; FGH is the resulting curve, corresponding to a heat evolution;  $Q_s$  is the amount of heat flux passing through the wall of the test sample under the steady-state conditions; q is the heat of thermal disequilibrium accumulated in the test sample, and all materials in the space around the cylinder.

Determination of the values of c,  $r_1$ ,  $r_2$  and  $\rho$ 

The value c of the cylindrical sample was obtained using a microcalorimeter. The values of  $r_1$  and  $r_2$  were obtained with vernier callipers and  $\rho$  was obtained by densitometry.



Fig. 3. Schematic thermogram of measurement of the thermal conductivity of solids.

## EXPERIMENTAL RESULTS AND DISCUSSION

The values of  $Q_s$ , q, m, c,  $\rho$ ,  $r_1$ ,  $r_2$ ,  $S_0$ , S,  $S_1$ ,  $S_2$ ,  $m_1$ ,  $m_2$ ,  $c_1$  and  $c_2$  of quartz glass, plexiglass, teflon and polyethylene obtained using the abovementioned methods are listed in Tables 1 and 2. It can be seen in Table 1 that the reproducibilities of the values of  $Q_s$  and q are within 0.07% and within less than 0.5% respectively.

By substituting the values of  $Q_s$ , q, c, m,  $\rho$ ,  $r_1$ ,  $r_2$  listed in Table 1 and the reported values of  $\lambda$  of 1.37 W m<sup>-1</sup> K<sup>-1</sup> for quartz glass, of 0.192 W m<sup>-1</sup> K<sup>-1</sup> for plexiglass, of 0.251 W m<sup>-1</sup> K<sup>-1</sup> for teflon, and of 0.460 W m<sup>-1</sup> K<sup>-1</sup> for polyethylene listed in Table 3 into eqn. (24), the corresponding values of k

The original da	ita of four star	idard samples							
Sample	$c^{ m a}  imes 10^{-3}$	$ ho^{b}  imes 10^{-3}$	$m^{\rm c}  imes 10^3$	$r_1^{\rm d}  imes 10^3$	$r_2^{e}  imes 10^3$	q <sup>tj</sup>	$\frac{\sigma_{q}^{g,k}}{q}$ in %	$Q_{\rm s}^{\rm h,j}  imes 10^3$	$rac{\sigma_{Q_s}}{Q_s}$ in %
Quartz glass	0.8409	2.2027	24.5948 24.8210	1.01	7.42 7.43	0.6094 0.6143	0.46 0.49	9.237 9.236	0.05
Plexiglass	1.517	1.1900	12.6720	1.25	7.40	1.4498	0.27 0.23	9.200 9.192	0.05 <sup>1</sup> 0.04
Teflon	1.122	2.2124	24.6217	1.06	7.42	1.7251	0.17	9.177 9.101	0.02
Polyethylene	1.834	0.9707	10.7744 10.7762	1.07 1.07	0 <del>4</del> .7 1.40	0.8677	0.25 0.26	9.199	0.03
<sup>a</sup> c, Specific heat cylindrical sample disequilibrium in values of nine me	of cylindrical sat $r_2$ , Exte J. <sup>h</sup> $Q_s$ , Amount sasurements. <sup>k</sup> V	nple in J kg <sup>-1</sup> K <sup>-1</sup> rnal radius of the of heat flux under $a_q$ and $a_q$ and $a_q$	$\frac{1}{r}$ , <sup>b</sup> $\rho$ , Density cylindrical sam r the steady sta $\sigma_{Q_s}$ arc obtaino	of cylindrical i pple in m. $f_q$ , 1 te in J s <sup>-1</sup> , $\sigma_q$	sample in kg 1 Heat of therm $Q_{0,}$ , Standard d $\Sigma(x_i - x)^2/(n$	$m^{-3}$ . $^{c}m$ , Ma al disequilib eviation of tl $-1)]^{1/2}$ , $x =$	iss of cylindrical rium in J. <sup>8</sup> $\sigma_q$ , S he amount of he: $q$ , $Q_s$ , $n = 9$ ; <sup>1</sup> D	sample in kg. <sup>d</sup> $r_1$ , tandard deviation at flux in $\int s^{-1} \int q dt$	Internal radius of the of the heat of the heat of thermal and $Q_s$ are the average - analysis.

TABLE 1

	Empty cell	Benzoic acid	Distilled water	Quartz glass	Plexiglass	Teflon	Polyethylene
So <sup>a,d</sup>	2994						
S <sub>1</sub> <sup>a,d</sup>		3246	5116				
$S_2$ S <sup>a,d</sup>			5110	4064	3644	3977	3662
$m_1 \times 10^{3 \text{ b}}$		3.0284		1001	5044	5711	5002
$m_2 \times 10^{3}$ b			7.3857				
m <sup>b</sup>				19.1310	6.4395	12.9555	5.4793
$c_1 \times 10^{-3}$		1.253 [3]					
$c_2 \times 10^{-3}$ $c \times 10^{-3}$			4.180 [4]	0.8409	1.5173	1.1220	1.8337

Original data used for calculating the values of c

<sup>a</sup>  $S_0$ ,  $S_1$ ,  $S_2$  and S, are the areas under the curve on its return to the experimental zero after cutting off the Peltier current for the empty cell, the cell containing first standard sample (benzoic acid), the cell containing second standard sample (distilled water), and the cell containing investigated sample, respectively, (integral number). <sup>b</sup>  $m_1$ ,  $m_2$  and m are the masses of benzoic acid, distilled water, and the investigated sample, respectively in kg. <sup>c</sup>  $c_1$ ,  $c_2$  and c are the specific heats of benzoic acid, distilled water, and the investigated sample, respectively in J kg<sup>-1</sup> K<sup>-1</sup>. <sup>d</sup>  $S_0$ ,  $S_1$ ,  $S_2$  and S, Average value of six measurements.

of 2.3265 K J<sup>-1</sup> s<sup>-1</sup> and of *D* of 0.9668 s, and of the correlation coefficient of 0.9998 may be obtained. By substituting the values of  $Q_s$ , q, m, c,  $\rho$ ,  $r_1$ ,  $r_2$  listed in Table 1 and the values of k and D into eqn. (24), the corresponding value of  $\lambda$  can be obtained (data shown in Table 3).

To check the accuracy of measurements, the thermal conductivities of quartz glass, teflon, plexiglass and polyethylene were measured and compared with the reported values [5–8]. The comparison is shown in

TABLE 3

Sample	$\lambda_1/W m^{-1} K^{-1}$		$\lambda/W m^{-1} K^{-1}$	$\frac{ \lambda-\lambda_1 }{\lambda_1} \text{ in } \%$
Quartz glass	1.37 [5]		1.37	
-			1.37	
		Av.	1.37	0
Plexiglass	0.192 [6]		0.192	
-			0.192	
		Av.	0.192	0
Teflon	0.251 [7]		0.251	
			0.251	
		Av.	0.251	0
Polyethylene	0.460 [8]		0.462	
•••			0.459	
		Av.	0.461	0.22

Comparison of the experimental values of  $\lambda$  with literature ones  $\lambda_1$  of thermal conductivity of four standard solids at 298 K

TABLE 2

Table 3. The results for quartz glass, plexiglass, teflon and polyethylene are in excellent accord with those reported in the literature. Because the reported methods have a relative error of 1% in measuring solids, it is reasonable to believe that the relative error of the microcalorimetry is less than 1.5%.

In order to gain the overall standard deviation of results obtained by microcalorimeter, we made the data treatment of indirect measuring quantities by using the functional eqns. (34) and (35), the overall standard deviation formulae (36) and (37), the propagation coefficient eqns. (38)–(53), the calculated formula,  $\sigma = \Delta d/\sqrt{3}$  where  $\Delta d$  is the value of the minimal scale division of the measuring equipment), for the single measurement quantities,  $r_1, r_2, m, m_1, m_2$  and  $\rho$ , and the standard deviation equation  $\sigma = \sqrt{\{\sum[(x_i - x)^2]/(n-1)\}}, x = q, Q_s, S_0, S_1$  and  $S_2$ , for the repeatable measurement quantities,  $q, S_s, S_0, S_1$  and  $S_2$  and the results are shown in Table 4.

## TABLE 4

Values of the standard deviation, error propagation coefficient used for calculating the values of  $\sigma_{\lambda}$ , and the overall standard deviation  $\sigma_{\lambda}$ 

	Quartz glass	Plexiglass	Teflon	Polyethylene
$\sigma_{r_1}$	$5.77 \times 10^{-6}$ $5.77 \times 10^{-6}$	$5.77 \times 10^{-6}$ $5.77 \times 10^{-6}$	$5.77 \times 10^{-6}$ $5.77 \times 10^{-6}$	$5.77 \times 10^{-6}$ $5.77 \times 10^{-6}$
$\sigma_q$	$2.76 \times 10^{-3}$	$3.50 \times 10^{-3}$	$2.90 \times 10^{-3}$	$2.20 \times 10^{-3}$
$\sigma_{\mathcal{Q}_s}$	$5.00 \times 10^{-6}$ 1 42 × 10 <sup>-2</sup>	$4.00 \times 10^{-6}$ 1 42 × 10^{-2}	$2.00 \times 10^{-6}$ 1 42 × 10 <sup>-2</sup>	$4.00 \times 10^{-5}$ 1 42 × 10^{-2}
$\sigma_m$	$5.77 \times 10^{-8}$	$5.77 \times 10^{-8}$	$5.77 \times 10^{-8}$	$5.77 \times 10^{-8}$
$\sigma_{ ho}$	$5.77 \times 10^{-8}$	$5.77 \times 10^{-8}$	5.77 × 10 *	$5.77 \times 10^{-8}$
$\frac{\partial \lambda}{\partial r_1}$	$-2.21 \times 10^{2}$	$-3.59 \times 10$	$-4.17 \times 10$	$-7.78 \times 10$
$\frac{\partial \lambda}{\partial r_2}$	$3.99 \times 10^{2}$	5.80 × 10	$7.35 \times 10$	$1.36 \times 10^{2}$
$\frac{\partial \lambda}{\partial q}$	-8.78	$-1.87 \times 10^{-1}$	$-2.22 \times 10^{-1}$	-1.06
$rac{\partial \lambda}{\partial Q_{\mathrm{s}}}$	$5.79 \times 10^2$	2.94 × 10	$4.18 \times 10$	$1.00 \times 10^{2}$
$\frac{\partial \lambda}{\partial c}$	$6.36 \times 10^{-3}$	$1.78 \times 10^{-4}$	$3.42 \times 10^{-4}$	$5.02 \times 10^{-4}$
$\frac{\partial \lambda}{\partial m}$	$1.59 \times 10^{2}$	6.06	5.33	4.17 × 10
$rac{\partial \lambda}{\partial  ho}$	$6.22 \times 10^{-4}$	$1.61 \times 10^{-4}$	$1.13 \times 10^{-4}$	$4.76 \times 10^{-4}$
$\sigma_{\star}$	$2.5 \times 10^{-2}$	$7.7 \times 10^{-4}$	$8.1 \times 10^{-4}$	$2.5 \times 10^{-3}$

$$\lambda = f(r_1, r_2, q, Q_s, c, m, \rho, k, D)$$
(34)

$$c = f(S, m, S_0, m_1, c_1, S_1, m_2, c_2, S_2)$$
(35)

$$\sigma_{\lambda} = \left[ \left( \frac{\partial \lambda}{\partial r_{1}} \right)^{2} \sigma_{r_{1}}^{2} + \left( \frac{\partial \lambda}{\partial r_{2}} \right)^{2} \sigma_{r_{2}}^{2} + \left( \frac{\partial \lambda}{\partial q} \right)^{2} \sigma_{q}^{2} + \left( \frac{\partial \lambda}{\partial Q_{s}} \right)^{2} \sigma_{Q_{s}}^{2} + \left( \frac{\partial \lambda}{\partial c} \right)^{2} \sigma_{c}^{2} + \left( \frac{\partial \lambda}{\partial m} \right)^{2} \sigma_{m}^{2} + \left( \frac{\partial \lambda}{\partial \rho} \right)^{2} \sigma_{\rho}^{2} + \left( \frac{\partial \lambda}{\partial k} \right)^{2} \sigma_{k}^{2} + \left( \frac{\partial \lambda}{\partial D} \right)^{2} \sigma_{D}^{2} \right]^{1/2}$$
(36)

$$\sigma_{c} = \left[ \left( \frac{\partial c}{\partial S} \right)^{2} \sigma_{S}^{2} + \left( \frac{\partial c}{\partial m} \right)^{2} \sigma_{m}^{2} + \left( \frac{\partial c}{\partial S_{0}} \right)^{2} \sigma_{S_{0}}^{2} + \left( \frac{\partial c}{\partial m_{1}} \right)^{2} \sigma_{m_{1}}^{2} + \left( \frac{\partial c}{\partial c_{1}} \right)^{2} \sigma_{c_{1}}^{2} + \left( \frac{\partial c}{\partial m_{2}} \right)^{2} \sigma_{m_{2}}^{2} + \left( \frac{\partial c}{\partial c_{2}} \right)^{2} \sigma_{c_{2}}^{2} + \left( \frac{\partial c}{\partial S_{2}} \right)^{2} \sigma_{s_{2}}^{2} \right]^{1/2}$$
(37)

$$\frac{\partial c}{\partial S} = \frac{1}{2m} \left( \frac{m_1 c_1}{S_1 - S_0} + \frac{m_2 c_2}{S_2 - S_0} \right) \tag{38}$$

$$\frac{\partial c}{\partial m} = -\frac{S - S_0}{2m^2} \left( \frac{m_1 c_1}{S_1 - S_0} + \frac{m_2 c_2}{S_2 - S_0} \right)$$
(39)

$$\frac{\partial c}{\partial S_0} = \frac{1}{2m} \left[ \frac{m_1 c_1 (S - S_1)}{(S_1 - S_0)^2} + \frac{m_2 c_2 (S - S_2)}{(S_2 - S_0)^2} \right]$$
(40)

$$\frac{\partial c}{\partial m_1} = \frac{c_1(S - S_0)}{2m(S_1 - S_0)} \tag{41}$$

$$\frac{\partial c}{\partial c_1} = \frac{m_1(S - S_0)}{2m(S_1 - S_0)} \tag{42}$$

$$\frac{\partial c}{\partial S_1} = -\frac{m_1 c_1 (S - S_0)}{2m(S_1 - S_0)^2}$$
(43)

$$\frac{\partial c}{\partial m_2} = \frac{c_2(S - S_0)}{2m(S_2 - S_0)} \tag{44}$$

$$\frac{\partial c}{\partial c_2} = \frac{m_2(S - S_0)}{2m(S_2 - S_0)} \tag{45}$$

$$\frac{\partial c}{\partial S_2} = -\frac{m_2 c_2 (S - S_0)}{2m(S_2 - S_0)^2}$$
(46)

$$\frac{\partial \lambda}{\partial r_1} = \frac{\rho c}{\frac{q}{Q_s} - cmk - D} r_1 \ln\left(\frac{r_1}{r_2}\right)$$
(47)

$$\frac{\partial \lambda}{\partial r_2} = \frac{\rho c}{\frac{q}{Q_s} - cmk - D} \frac{r_2^2 - r_1^2}{2r_2}$$
(48)

$$\frac{\partial \lambda}{\partial q} = -\frac{\rho c}{\left(\frac{q}{Q_{\rm s}} - cmk - D\right)^2 Q_{\rm s}} \left[\frac{r_2^2 - r_1^2}{4} + \frac{r_1^2}{2}\ln\left(\frac{r_1}{r_2}\right)\right] \tag{49}$$

$$\frac{\partial \lambda}{\partial Q_{s}} = \frac{\rho cq}{\left(\frac{q}{Q_{s}} - cmk - D\right)^{2} Q_{s}^{2}} \left[\frac{r_{2}^{2} - r_{1}^{2}}{4} + \frac{r_{1}^{2}}{2} \ln\left(\frac{r_{1}}{r_{2}}\right)\right]$$
(50)

$$\frac{\partial \lambda}{\partial c} = \frac{\rho q}{\left(\frac{q}{Q_{\rm s}} - cmk - D\right)^2 Q_{\rm s}} \left[\frac{r_2^2 - r_1^2}{4} + \frac{r_1^2}{2}\ln\left(\frac{r_1}{r_2}\right)\right]$$
(51)

$$\frac{\partial \lambda}{\partial m} = \frac{\rho c^2 k}{\left(\frac{q}{Q_s} - cmk - D\right)^2} \left[\frac{r_2^2 - r_1^2}{4} + \frac{r_1^2}{2} \ln\left(\frac{r_1}{r_2}\right)\right]$$
(52)

$$\frac{\partial \lambda}{\partial \rho} = \frac{c}{\left(\frac{q}{Q_{\rm s}} - cmk - D\right)} \left[\frac{r_2^2 - r_1^2}{4} + \frac{r_1^2}{2}\ln\left(\frac{r_1}{r_2}\right)\right]$$
(53)

Because k and D are two constants,  $\partial \lambda / \partial k = 0$  and  $\partial \lambda / \partial D = 0$ .

The percentages that the percentage error of eight direct measurement quantities accounts for of the overall error for quartz glass, plexiglass, teflon and polyethylene are shown in Table 5. It can be seen from Table 5 that the value of q in eight direct measurement quantities is the principal factor affecting the  $\lambda$  value of solids.

To check the effects of dimension of the cylinder and concentricity of the hole of the cylinder on the value of  $\lambda$ , we measured the values of the thermal conductivities of plexiglass with different dimensions and concentricity. It can be seen from Table 6 that the relative error and reproducibilities of the thermal conductivities of plexiglass determined by using this method are within than 1.1% and within 0.60% when the internal radius is changed from 1.00 mm to 1.25 mm, the external radius from 7.40 mm to 7.46 mm, and the concentricity from 0.02 mm to 0.12 mm.

	Quartz glass	Plexiglass	Teflon	Polyethylene
$\overline{\left(\frac{\partial \lambda}{\partial r_1}\frac{\sigma_{r_1}}{\sigma_{\lambda}}\right)^2}$	0.26	7.19	8.79	3.15
$\left(\frac{\partial \lambda}{\partial r_2}\frac{\sigma_{r_2}}{\sigma_{\lambda}}\right)^2$	0.88	18.77	27.32	9.60
$\left(\frac{\partial\lambda}{\partial q}\frac{\sigma_q}{\sigma_\lambda}\right)^2$	97.50	71.74	62.83	84.75
$\left(\frac{\partial \lambda}{\partial Q_{\rm s}}\frac{\sigma_{Q_{\rm s}}}{\sigma_{\lambda}}\right)^2$	1.38	2.30	1.06	2.50
$\left(\frac{\partial \lambda}{\partial c}\frac{\boldsymbol{\sigma}_c}{\boldsymbol{\sigma}_{\boldsymbol{\lambda}}}\right)^2$	$1.34 \times 10^{-3}$	$1.07 \times 10^{-3}$	$3.58 \times 10^{-3}$	$7.91 \times 10^{-4}$
$\left(\frac{\partial \lambda}{\partial m}\frac{\sigma_m}{\sigma_\lambda}\right)^2$	$1.40 \times 10^{-5}$	$2.04 \times 10^{-4}$	$1.44 \times 10^{-5}$	$9.02 \times 10^{-5}$
$\left(\frac{\partial \lambda}{\partial \rho}\frac{\sigma_{\rho}}{\sigma_{\lambda}}\right)^2$	$2.14 \times 10^{-16}$	$1.45 \times 10^{-14}$	$6.45 \times 10^{-15}$	$1.17 \times 10^{-14}$

# TABLE 5

Percentage that the percentage error of eight direct measurement quantities accounts for of the overall error

## TABLE 6

The effects of dimension of the cylinder and concentricity of the hole of the cylinder on the  $\lambda$  values of plexiglass <sup>a</sup>

	$N_1$	$N_2$	$N_3$	$N_4$	$N_5$	$N_6$	
r <sub>1</sub> /mm	1.25	1.00	1.25	1.02	1.1	1.25	
$r_2/mm$	7.40	7.41	7.44	7.45	7.45	7.44	
$\overline{Ct}/mm$ $\lambda/W m^{-1} K^{-1}$	0.12 0.192	0.02 0.192	0.04 0.191	0.12 0.190	0.05 0.190	0.04 0.192	

<sup>a</sup>  $N_{1-6}$  are experimental values and Ct is the concentricity of the hole of the cylinder.

## CONCLUSIONS

The method of determining the thermal conductivity of solids under constant radial heat flux conditions by use of the Peltier and Joule effects is very satisfactory in accuracy, relative error and reproducibility. The results for quartz glass, plexiglass, teflon and polyethylene determined using this method agree with data available in the literature. The heat of thermal disequilibrium is the principal factor affecting the magnitude of the thermal conductivity of solids.

## REFERENCES

- 1 E. Calvet and H. Prat, Recent Progress in Microcalorimetry, Pergamon Press, Oxford, 1963, p. 67.
- 2 E. Calvet, J.P. Bros and H. Pinelli, C. R. Acad. Sci., 260(4) (1965) 1164-1167.
- 3 Chilton, Chemical Engineer's Handbook, 55th edn., McGraw Hill, New York, 1973, pp. 3-131.
- 4 Robert C. Weast, CRC Handbook of Chemistry and Physics, 55th edn., CRC Press, Boca Raton, FL, 1974, p. D-137.
- 5 Y.S. Touloukian, R.W. Powell, C. Y. Ho and P.G. Klemens, Thermophysical Properties of Matter, Vol. 2, IFI/Plenum, New York–Washington, 1970, p. 190.
- 6 Y.S. Touloukian, R.W. Powell, C.Y. Ho and P.G. Klemens, Thermophysical Properties of Matter, Vol. 2, IFI/Plenum, New York-Washington, 1970, p. 962.
- 7 J.A. Deam, Lange's Handbook of Chemistry, McGraw Hill, New York, 1979, p. 7-453.
- 8 Bacon Ke, Thermal Analysis of High Polymers, Interscience, Inc., New York, 1964, p. 160.