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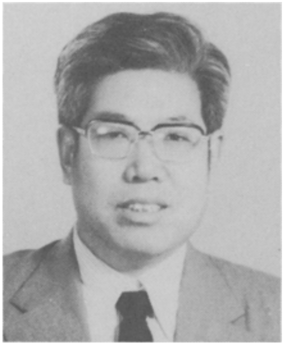

A NEW METHOD OF DETERMINING THE THERMAL CONDUCTIVITIES OF ENERGETIC MATERIALS BY MICROCALORIMETER

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Abstract

A device of measuring the thermal conductivity of pellet of propellants and explosives has been constructed. A method and a calculation formula for determining the thermal conductivity of pellet of propellants and explosives under constant radial heat flow conditions by use of Joule effect is presented. Using this device and a microcalorimeter, type RD496-II, and two standard samples with known thermal conductivity, two instrument constant have been determined and the thermal conductivities of seven materials: plexiglass, teflon, DB propellant DB-2 (nitrocellulose(NC)/nitroglycerine(NG)/dinitrotoluene/dimethyl centralite/vaseline/PbO/$CaCO_3$, 59.6/25/8.8/3/1.2/1.2/1.2), DB propellant SQ(NC/NG/diethyl phthalate(DEP)/binder, 59/29/7/5), DB propellant RHN-149 (NC/NG/triacetin(TA)/binder-I, 52/25/8/15), DB propellant RHN-190 (NC/NG/TA/ binder-II, 52/26/7/15),2,4,6-trinitrotoluene (TNT) at 298 K are measured. The results show that (1) the reproducibility of measurement for the heat (q) retained in investigated system after cutting the Joule current and the amount of heat flux through the wall of the investigated cylinder (Q_s) are less than 0.50% and within 0.10%, respectively; (2) the standard deviation of the thermal conductivity determined by using this method is less than 1.0%; (3) the values of q, Q_s and internal radius of the cylinder are three principal factors affecting the magnitude of the thermal conductivity of these materials.

Keywords: energetic materials, Joule effect, microcalorimetry, thermal conductivity

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Introduction

Thermal conductivity (λ) is an important thermophysical parameter of energetic materials, and its measurement is quite significant for munitions scientific research and production. The basic principle and apparatus for measuring the values of λ of solids with microcalorimetry have been reported [1, 2]. In our previous papers [3, 4], the method and calculation formula of determining the value of λ of solids under constant radial heat flow condition by use of the Peltier and Joule effects were also presented. The aim of this work is to present a new method and a calculation formula for determining the value of λ of energetic materials by using microcalorimetry and to analyse the measuring error of the value of λ using the experimental data of plexiglass, teflon, TNT and DB propellants:DB-2, SQ, RHN-149 and RHN-190.

Derivation of formula of thermal conductivity

If a cylinder shown in Fig. 1 is long enough, the heat conduction in the axial direction may be ignored. In this case, the temperature will only change in the radial direction, and the temperature field will be one-dimensional when the cylinder coordinate is used.

The r_1, r_2, internal and external radii of the cylinder, respectively, m; T_1, T_2, temperature of internal and external walls of the cylinder, respectively, K; r, ar-

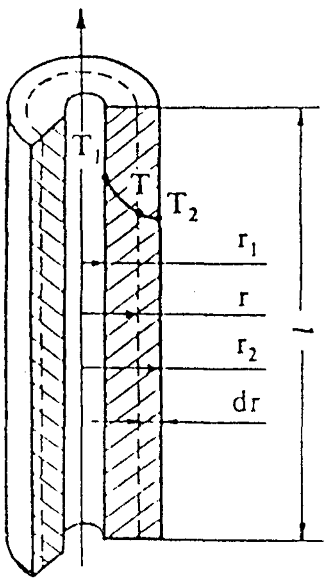

Fig. 1 Single wall cylinder

bitrary radius of the cylinder, *m*; d*r*, thickness of the differential unit cylinder, *m*; *l*, length of the cylinder, *m*.

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

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

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

$$T=c_1\ln r+c_2 \qquad (2)$$

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

$$\text{when } r=r_1,\ T=T_1 \qquad (3)$$

$$\text{when } r=r_2,\ T=T_2 \qquad (4)$$

Substituting the Eqs (3) and (4) into the Eq. (2), the values of c_1 and c_2 can be obtained. Substituting the values of c_1 and c_2 into Eq. (2), the following temperature distribution equation in the cylinder can be obtained

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

Differentiation of Eq. (5) with respect to *r* gives

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

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

$$Q_s=-\lambda F\frac{\mathrm{d}T}{\mathrm{d}r}=-\lambda\cdot 2\pi rl\frac{\mathrm{d}T}{\mathrm{d}r} \qquad (7)$$

where $F=2\pi rl$, is the area of the cylinder with a radius *r*, m^2, Q_s is the amount of heat flux passing through the wall of the cylinder, $J\cdot s^{-1}$; and λ is the thermal conductivity of the investigated cylindrical sample, $W\cdot(m\cdot K)^{-1}$ or $J\cdot(m\cdot s\cdot K)^{-1}$. Substituting the Eq.(6) into Eq.(7) the following equation may be obtained

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

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

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

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

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

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 is arrived at the equilibrium temperature T_e after cutting the power produced in the hole of the cylinder by the Joule effect.

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

$$dq_1 = (dV)\cdot\gamma\cdot(T - T_2) = 2\pi r l dr\cdot\gamma\cdot(T - T_2) \tag{11}$$

where γ is the heat capacity of unit volume of the cylindrical sample, $J\cdot(K\cdot m^3)^{-1}$.

Combining Eqs (10) and (11), we have

$$dq_1 = \frac{\gamma}{\lambda} Q_s r \ln\left(\frac{r_2}{r}\right)\cdot dr = \frac{Q_s}{h} r \ln\left(\frac{r_2}{r}\right)\cdot dr \tag{12}$$

where

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

where h is the coefficient of thermal diffusion of the cylindrical sample, $m^2\cdot s^{-1}$; c is the specific heat of the cylindrical sample, $J(kg\cdot K)^{-1}$; ρ is the density of the cylindrical sample, $kg\cdot m^{-3}$.

Integrating on both sides of the Eq. (12)

$$\int_0^{q_1} dq_1 = \frac{Q_s}{h}\int_{r_1}^{r_2} r\ln\left(\frac{r_2}{r}\right)\cdot dr \tag{14}$$

the calculated formula of the heat accumulated in the whole cylinder (q_1) may be obtained:

$$q_1 = \frac{Q_s}{h}\left[\frac{r_2^2 - r_1^2}{4} - \frac{1}{2}r_1^2\ln\left(\frac{r_2}{r_1}\right)\right] \tag{15}$$

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

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

where T_e is the equilibrium temperature of the cylinder.

Because the value of dq_2 is directly proportional to the amount of the 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, $K/J\cdot s^{-1}$.

Substituting the Eq. (17) into Eq. (16) gives

$$dq_2 = 2\pi r l dr\cdot\gamma\cdot kQ_s \tag{18}$$

Integrating on both sides of the Eq. (18)

$$\int_0^{q_2} dq_2 = 2\pi l\gamma kQ_s\int_{r}^{r_2} r dr \tag{19}$$

the following equation which describes the heat accumulated in the whole cylinder (q_2) can be obtained

$$q_2 = \pi l\gamma kQ_s(r_2^2 - r_1^2) = Vc\rho kQ_s = cmQ_sk \tag{20}$$

where m is mass of the cylindrical sample, kg.

Hence, the equation of heat accumulated in whole cylinder (q_{12}) is as follow

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

When the Joule current is cut, there is the accumulated heat (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, i.e.

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

where D is also a constant of the microcalorimeter.

Thus, the total heat retained in investigated system after cutting the Joule current, q, is to be written as

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

Combining Eqs (13) and (23), we have

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

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

By measuring the values of c, m, Q_s, q, ρ, r_1 and r_2 with two standard cylindrical samples with known thermal conductivity, the values of k and D can be obtained from Eq. (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 ρ obtained with densitometry, and the values of k, D and m into the Eq. (24), the value of λ of the investigated cylindrical sample can be obtained.

Experimental

Sample

The cylindrical samples used to measure the thermal conductivity of plexiglass, teflon, TNT and DB propellants: DB-2, SQ, RHN-149 and RHN-190 have same dimension which is 66.18 mm long with an outer diameter of 14.86 mm and an inner diameter of 2 mm.

Equipment

Device used for measuring the thermal conductivity of the investigated cylindrical sample is the same as described in Ref. [3]. All measurements are made by using a microcalorimeter, type RD496-II from Southwestern Electronic Engineering Institute, China, which has a sensitivity of 62.66 μV·mW^{-1} and is equipped with two 15 ml vessels. The microcalorimeter is calibrated by the Joule effect before use. The precision of 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 sample are obtained by the testing method presented as a curve in Fig. 2.

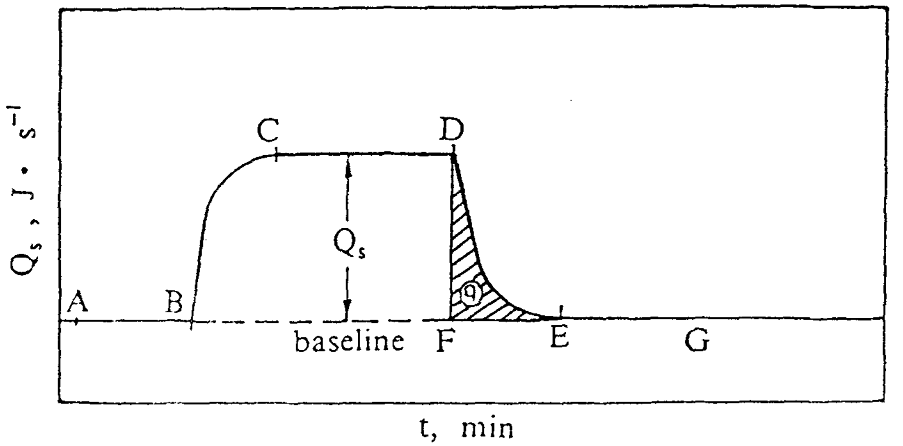

Fig. 2 Schematic thermogram of measuring the thermal conductivity of energetic materials

In Fig. 2, AG is the baseline; at time B, a constant calorific power is generated in the laboratory-cell; at CD, the steady state is established; at the point D, the Joule current is cut; DEF 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 condition; q is the heat retained in the test sample, and all materials in the space around the cylinder after cutting the Joule current.

Determination of the values of c, r_1, r_2 and ρ

The values of c, r_1, r_2 and ρ of the cylindrical sample are obtained as described in Ref. [3].

Results and discussion

The values of Q_s, q, m, c, ρ, r_1, r_2 of plexiglass, teflon, TNT and DB propellants: DB-2, SQ, RHN-149, RHN-190 obtained by using the above-mentioned methods are listed in Table 1. It can be seen in Table 1 that the

Table 1 The original data of standard samples and energetic materials*

Sample	$c \cdot 10^{-3}$	$\rho \cdot 10^{-3}$	$m \cdot 10^{3}$	$r_1 \cdot 10^{3}$	$r_2 \cdot 10^{3}$	q	$\sigma_q \cdot 10^{3}$	$\frac{\sigma_q}{q}$ /%	$Q_s \cdot 10^{3}$	$\sigma_{Q_s} \cdot 10^{6}$	$\frac{\sigma_{Q_s}}{Q_s}$ /%
plexiglass	1.517	1.1900	12.6720	1.25	7.40	3.1281	6.2	0.20	9.075	4.0	0.04
			13.3863	1.00	7.41	3.1633	9.2	0.29	9.088	4.0	0.04
teflon	1.122	2.2124	24.6217	1.06	7.42	3.5909	10.0	0.03	9.055	3.0	0.03
			24.5471	1.07	7.40	3.6073	2.2	0.06	9.083	2.0	0.02
TNT	1.133	1.584	17.5466	1.07	7.45	3.1431	3.2	0.10	9.174	2.0	0.02
DB-2	1.382	1.6150	18.3028	1.00	7.45	3.4690	2.2	0.06	9.062	4.0	0.07
			18.2880	1.00	7.44	3.5044	4.4	0.13	9.074	2.0	0.02
SQ	1.435	1.5840	17.8255	1.00	7.43	3.5833	4.6	0.13	9.089	3.0	0.03
			17.8046	1.00	7.43	3.6082	4.9	0.14	9.173	5.0	0.05
RHN-149	1.523	1.5600	17.6411	1.00	7.45	3.7009	4.3	0.12	9.075	7.0	0.08
			17.6289	1.00	7.43	3.7353	4.7	0.13	9.099	3.0	0.03
RHN-190	1.453	1.555	17.9003	1.00	7.44	3.7028	4.8	0.13	9.073	2.0	0.02
			17.8406	1.00	7.42	3.7252	1.3	0.03	9.173	3.0	0.03

* c, the specific heat of the cylindrical sample, J·$(kg \cdot K)^{-1}$; ρ, the density of the cylindrical sample $kg \cdot m^{-3}$; m, the mass of the cylindrical sample, kg; r_1, the internal radius of the cylindrical sample, m; r_2, the external radius of the cylindrical sample, m; q, the heat of thermal disequilibrium, J; σ_q, the standard deviation of the heat of thermal disequilibrium J; Q_s the amount of the heat flux under the steady state, $J \cdot s^{-1}$; σ_{Q_s}, the standard deviation of the amount of the heat flux, $J \cdot s^{-1}$; q and Q_s are the average values of nine measurements, respectively; the values of σ_q and σ_{Q_s} are obtained with

$$\sigma = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}, \; x = q, \; Q_s, \; n = 9.$$

reproducibilities of the values of Q_s and q are within 0.10% and less than 0.5%, respectively.

By substituting the values of Q_s, q, c, m, ρ, r_1 r_2 listed in Table 1 and the reported values of λ of 0.192 $W\cdot m^{-1}\cdot K^{-1}$ for plexiglass and of 0.251 $W\cdot m^{-1}\cdot K^{-1}$ for teflon listed in Table 2, into Eq. (24), the corresponding values of k of 5.4343 $K/J\cdot s^{-1}$ and of D of 124.61 s, and of the correlation coefficient of 0.9911 may be obtained. By substituting the values of Q_s, q, m, c, ρ, r_1, r_2 listed in Table 1 and the values of k and D into Eq. (24), the corresponding values of λ of seven materials can be obtained (data seen Table 2).

Table 2 Comparison of the experimental values λ with literature ones λ_l of thermal conductivity of standard samples and energetic materials at 298 K

Sample	λ_l / $W\cdot m^{-1}\cdot K^{-1}$		λ / $W\cdot m^{-1}\cdot K^{-1}$	$\frac{\lvert\lambda-\lambda_l\rvert}{\lambda_l}$ / %
plexiglass	0.192 [3]		0.186	
			0.199	
		ave	0.192	0
teflon	0.251 [3]		0.252	
			0.248	
		ave	0.250	0.40
TNT	0.203 [4]		0.204	0.49
DB-2	0.230 [4]		0.233	
			0.226	
		ave	0.230	0
SQ	0.220 [4]		0.218	
			0.220	
		ave	0.219	0.45
RHN-149	0.214 [4]		0.219	
			0.213	
		ave	0.216	0.93
RHN-190	0.205 [4]		0.200	
			0.201	
		ave	0.201	1.9

To check the accuracy, the thermal conductivities of seven materials are compared with the reported values [3, 4]. The comparison is shown in Table 2. The result for seven materials accord excellently with that reported. Because the reported methods have a relative error of 1.5% in measuring solids, it is reasonable to believe that the relative error of the microcalorimetry is less than 2.0%.

Table 3 The values of the standard deviation, error propagation coefficient used for calculating the values of σ_λ, and the overall standard deviation σ_λ

	Plexiglass		Teflon		TNT
	No. 1	No. 2	No. 1	No. 2	
σ_{r_1}	5.77×10^{-6}	5.77×10^{-6}	5.77×10^{-6}	5.77×10^{-6}	5.77×10^{-6}
σ_{r_2}	5.77×10^{-6}	5.77×10^{-6}	5.77×10^{-6}	5.77×10^{-6}	5.77×10^{-6}
σ_q	6.2×10^{-3}	9.2×10^{-3}	10×10^{-3}	2.2×10^{-3}	3.2×10^{-3}
σ_{Q_s}	4.0×10^{-6}	4.0×10^{-6}	3.0×10^{-6}	2.0×10^{-6}	2.0×10^{-6}
σ_c	1.42×10^{-2}	1.42×10^{-2}	1.42×10^{-2}	1.42×10^{-2}	1.42×10^{-2}
σ_m	5.77×10^{-8}	5.77×10^{-8}	5.77×10^{-8}	5.77×10^{-8}	5.77×10^{-8}
σ_ρ	5.77×10^{-8}	5.77×10^{-8}	5.77×10^{-8}	5.77×10^{-8}	5.77×10^{-8}
$\frac{\partial\lambda}{\partial r_1}$	-3.47×10	-3.20×10	-4.20×10	-4.18×10	-3.39×10
$\frac{\partial\lambda}{\partial r_2}$	5.61×10	5.81×10	7.41×10	7.32×10	5.95×10
$\frac{\partial\lambda}{\partial q}$	-1.77×10^{-1}	-1.94×10^{-1}	-2.29×10^{-1}	-2.23×10^{-1}	-2.02×10^{-1}
$\frac{\partial\lambda}{\partial Q_s}$	6.11×10	6.74×10	9.07×10	8.84×10	6.92×10
$\frac{\partial\lambda}{\partial c}$	2.33×10^{-4}	2.48×10^{-4}	5.02×10^{-4}	4.91×10^{-4}	3.56×10^{-4}
$\frac{\partial\lambda}{\partial m}$	1.33×10	1.39×10	1.26×10	1.23×10	1.14×10
$\frac{\partial\lambda}{\partial\rho}$	1.56×10^{-4}	1.60×10^{-4}	1.14×10^{-4}	1.12×10^{-4}	1.27×10^{-4}
σ_λ	1.2×10^{-3}	1.8×10^{-3}	2.4×10^{-3}	7.1×10^{-4}	7.7×10^{-4}
λ	0.186	0.199	0.252	0.248	0.204
$\frac{\sigma_\lambda}{\lambda}$, %	0.65	0.90	0.95	0.29	0.38

Table 3 (continued)

	DB-2		SQ	
	No. 1	No. 2	No. 1	No. 2
σ_{r_1}	5.77×10^{-6}	5.77×10^{-6}	5.77×10^{-6}	5.77×10^{-6}
σ_{r_2}	5.77×10^{-6}	5.77×10^{-6}	5.77×10^{-6}	5.77×10^{-6}
σ_q	2.2×10^{-3}	4.4×10^{-3}	4.6×10^{-3}	4.9×10^{-3}
σ_{Q_s}	6.0×10^{-6}	2.0×10^{-6}	3.0×10^{-6}	5.0×10^{-6}
σ_c	1.42×10^{-2}	1.42×10^{-2}	1.42×10^{-2}	1.42×10^{-2}
σ_m	5.77×10^{-8}	5.77×10^{-8}	5.77×10^{-8}	5.77×10^{-8}
σ_ρ	5.77×10^{-8}	5.77×10^{-8}	5.77×10^{-8}	5.77×10^{-8}
$\frac{\partial\lambda}{\partial r_1}$	-3.71×10	-3.61×10	-3.49×10	-3.51×10
$\frac{\partial\lambda}{\partial r_2}$	6.76×10	6.56×10	6.35×10	6.38×10
$\frac{\partial\lambda}{\partial q}$	-2.13×10^{-1}	-2.01×10^{-1}	-1.84×10^{-1}	-1.84×10^{-1}
$\frac{\partial\lambda}{\partial Q_s}$	8.16×10	7.74×10	7.25×10	7.25×10
$\frac{\partial\lambda}{\partial c}$	3.61×10^{-4}	3.44×10^{-4}	3.14×10^{-4}	3.17×10^{-4}
$\frac{\partial\lambda}{\partial m}$	1.45×10	1.45×10	1.30×10	1.32×10
$\frac{\partial\lambda}{\partial\rho}$	1.45×10^{-4}	1.44×10^{-4}	1.38×10^{-4}	1.39×10^{-4}
σ_λ	8.1×10^{-4}	10×10^{-4}	9.7×10^{-4}	11×10^{-4}
λ	0.233	0.226	0.218	0.220
$\frac{\sigma_\lambda}{\lambda}$, %	0.35	0.44	0.44	0.50

Table 3 (continued)

	RHN-149		RHN-190	
	No. 1	No. 2	No. 1	No. 2
σ_{r_1}	5.77×10^{-6}	5.77×10^{-6}	5.77×10^{-6}	5.77×10^{-6}
σ_{r_2}	5.77×10^{-6}	5.77×10^{-6}	5.77×10^{-6}	5.77×10^{-6}
σ_q	4.3×10^{-3}	4.7×10^{-3}	4.8×10^{-3}	1.3×10^{-3}
σ_{Q_s}	7.0×10^{-6}	3.0×10^{-6}	2.0×10^{-6}	3.0×10^{-6}
σ_c	1.42×10^{-2}	1.42×10^{-2}	1.42×10^{-2}	1.42×10^{-2}
σ_m	5.77×10^{-8}	5.77×10^{-8}	5.77×10^{-8}	5.77×10^{-8}
σ_ρ	5.77×10^{-8}	5.77×10^{-8}	5.77×10^{-8}	5.77×10^{-8}
$\frac{\partial\lambda}{\partial r_1}$	-3.48×10	-3.40×10	-3.19×10	-3.22×10
$\frac{\partial\lambda}{\partial r_2}$	6.33×10	6.19×10	5.81×10	5.83×10
$\frac{\partial\lambda}{\partial q}$	-1.76×10^{-1}	-1.67×10^{-1}	-1.55×10^{-1}	-1.56×10^{-1}
$\frac{\partial\lambda}{\partial Q_s}$	7.16×10	6.86×10	6.33×10	6.33×10
$\frac{\partial\lambda}{\partial c}$	2.96×10^{-4}	2.86×10^{-4}	2.75×10^{-4}	2.77×10^{-4}
$\frac{\partial\lambda}{\partial m}$	1.32×10	1.26×10	1.11×10	1.13×10
$\frac{\partial\lambda}{\partial\rho}$	1.40×10^{-4}	1.37×10^{-4}	1.29×10^{-4}	1.29×10^{-4}
σ_λ	10×10^{-4}	9.1×10^{-4}	8.5×10^{-4}	4.7×10^{-4}
λ	0.219	0.213	0.200	0.201
$\frac{\sigma_\lambda}{\lambda}$, %	0.46	0.43	0.43	0.23

Table 4 Percentage that the percentage error of seven direct measurement quantities accounts for the overall error

%	Plexiglass		Teflon		TNT
	No. 1	No. 2	No. 1	No. 2	
$\left(\frac{\partial\lambda\,\sigma_{r_1}}{\partial r_1\,\sigma_\lambda}\right)^2$	2.78	1.05	1.02	11.5	6.45
$\left(\frac{\partial\lambda\,\sigma_{r_2}}{\partial r_2\,\sigma_\lambda}\right)^2$	7.27	3.47	3.17	35.4	19.9
$\left(\frac{\partial\lambda\,\sigma_q}{\partial q\,\sigma_\lambda}\right)^2$	83.63	98.32	91.04	47.75	70.5
$\left(\frac{\partial\lambda\,\sigma_{Q_s}}{\partial Q_s\,\sigma_\lambda}\right)^2$	4.15	2.24	1.29	6.20	3.23
$\left(\frac{\partial\lambda\,\sigma_c}{\partial c\,\sigma_\lambda}\right)^2$	7.60×10^{-4}	3.83×10^{-4}	8.82×10^{-4}	9.64×10^{-3}	4.31×10^{-3}
$\left(\frac{\partial\lambda\,\sigma_m}{\partial m\,\sigma_\lambda}\right)^2$	4.09×10^{-5}	1.99×10^{-5}	9.18×10^{-6}	9.99×10^{-5}	7.30×10^{-5}
$\left(\frac{\partial\lambda\,\sigma_\rho}{\partial \rho\,\sigma_\lambda}\right)^2$	5.63×10^{-15}	2.63×10^{-15}	7.51×10^{-16}	8.28×10^{-14}	9.06×10^{-15}

Table 4 (continued)

%	DB-2		SQ	
	No. 1	No. 2	No. 1	No. 2
$\left(\frac{\partial\lambda\,\sigma_{r_1}}{\partial r_1\,\sigma_\lambda}\right)^2$	6.97	4.34	4.31	3.39
$\left(\frac{\partial\lambda\,\sigma_{r_2}}{\partial r_2\,\sigma_\lambda}\right)^2$	23.2	14.3	14.3	11.2
$\left(\frac{\partial\lambda\,\sigma_q}{\partial q\,\sigma_\lambda}\right)^2$	33.47	78.22	76.14	67.18
$\left(\frac{\partial\lambda\,\sigma_{Q_s}}{\partial Q_s\,\sigma_\lambda}\right)^2$	36.54	2.40	5.03	10.86
$\left(\frac{\partial\lambda\,\sigma_c}{\partial c\,\sigma_\lambda}\right)^2$	4.01×10^{-3}	2.39×10^{-3}	1.08×10^{-3}	1.67×10^{-3}
$\left(\frac{\partial\lambda\,\sigma_m}{\partial m\,\sigma_\lambda}\right)^2$	1.07×10^{-4}	7.00×10^{-5}	5.98×10^{-5}	4.79×10^{-5}
$\left(\frac{\partial\lambda\,\sigma_\rho}{\partial \rho\,\sigma_\lambda}\right)^2$	1.07×10^{-14}	6.90×10^{-15}	6.74×10^{-15}	5.32×10^{-15}

Table 4 (continued)

	RHN-149		RHN-190	
%	No. 1	No. 2	No. 1	No. 2
$\left(\frac{\partial\lambda\,\sigma_{r_1}}{\partial r_1\,\sigma_\lambda}\right)^2$	4.03	4.67	4.73	15.36
$\left(\frac{\partial\lambda\,\sigma_{r_2}}{\partial r_2\,\sigma_\lambda}\right)^2$	13.34	15.40	15.70	50.37
$\left(\frac{\partial\lambda\,\sigma_q}{\partial q\,\sigma_\lambda}\right)^2$	57.27	74.40	77.34	18.31
$\left(\frac{\partial\lambda\,\sigma_{Q_s}}{\partial Q_s\,\sigma_\lambda}\right)^2$	25.12	5.11	14.89	16.32
$\left(\frac{\partial\lambda\,\sigma_c}{\partial c\,\sigma_\lambda}\right)^2$	1.77×10^{-3}	1.99×10^{-3}	2.11×10^{-3}	7.00×10^{-3}
$\left(\frac{\partial\lambda\,\sigma_m}{\partial m\,\sigma_\lambda}\right)^2$	5.80×10^{-5}	6.38×10^{-5}	5.68×10^{-5}	1.92×10^{-4}
$\left(\frac{\partial\lambda\,\sigma_\rho}{\partial \rho\,\sigma_\lambda}\right)^2$	6.53×10^{-15}	7.55×10^{-15}	7.67×10^{-15}	2.51×10^{-14}

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 Eq. (25), the overall standard deviation formula (26), the propagation coefficient Eqs (27)~(33), the calculated formula, $\sigma = \Delta d/\sqrt{3}$ (Δd, the value of the minimal scale division of measuring equipment), for the single measurement quantities, r_1, r_2, m, m_1, m_2 and ρ, and the standard deviation equation,

$$\sigma = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n-1}},$$

$x = q$, and Q_s, for the repeatable measurement quantities, q, and Q_s. The results are shown in Table 3. The percentages that the percentage error of seven direct measurement quantities accouts for of the overall error for plexiglass and teflon, TNT and four kinds of double propellants are shown in Table 4.

$$\lambda = f(r_1, r_2, q, Q_s, c, m, \rho, k, D) \tag{25}$$

$$\sigma_\lambda = \left[\left(\frac{\partial\lambda}{\partial r_1}\right)^2 \sigma_{r_1}^2 + \left(\frac{\partial\lambda}{\partial r_2}\right)^2 \sigma_{r_2}^2 + \left(\frac{\partial\lambda}{\partial q}\right)^2 \sigma_q^2 + \left(\frac{\partial\lambda}{\partial Q_s}\right)^2 \sigma_{Q_s}^2 + \right.$$

$$\left. \left(\frac{\partial\lambda}{\partial c}\right)^2 \sigma_c^2 + \left(\frac{\partial\lambda}{\partial m}\right)^2 \sigma_m^2 + \left(\frac{\partial\lambda}{\partial \rho}\right)^2 \sigma_\rho^2 + \left(\frac{\partial\lambda}{\partial k}\right)^2 \sigma_k^2 + \left(\frac{\partial\lambda}{\partial D}\right)^2 \sigma_D^2 \right]^{1/2} \tag{26}$$

$$\frac{\partial\lambda}{\partial r_1} = \frac{\rho c}{\frac{q}{Q_s} - cmk - D} r_1 \ln\left(\frac{r_1}{r_2}\right) \tag{27}$$

$$\frac{\partial\lambda}{\partial r_2} = \frac{\rho c}{\frac{q}{Q_s} - cmk - D} \cdot \frac{r_2^2 - r_1^2}{2r_2} \tag{28}$$

$$\frac{\partial\lambda}{\partial q} = -\frac{\rho c}{\left(\frac{q}{Q_s} - cmk - D\right)^2 \cdot Q_s} \left[\frac{r_2^2 - r_1^2}{4} + \frac{r_1^2}{2} \ln\left(\frac{r_1}{r_2}\right)\right] \tag{29}$$

$$\frac{\partial\lambda}{\partial Q_s} = \frac{\rho c q}{\left(\frac{q}{Q_s} - cmk - D\right)^2 \cdot Q_s^2} \left[\frac{r_2^2 - r_1^2}{4} + \frac{r_1^2}{2} \ln\left(\frac{r_1}{r_2}\right)\right] \tag{30}$$

$$\frac{\partial\lambda}{\partial c} = \frac{\rho\left(\frac{q}{Q_s} - D\right)}{\left(\frac{q}{Q_s} - cmk - D\right)^2} \left[\frac{r_2^2 - r_1^2}{4} + \frac{r_1^2}{2} \ln\left(\frac{r_1}{r_2}\right)\right] \tag{31}$$

$$\frac{\partial\lambda}{\partial m} = \frac{\rho c^2 k}{\left(\frac{q}{Q_s} - cmk - D\right)^2} \left[\frac{r_2^2 - r_1^2}{4} + \frac{r_1^2}{2} \ln\left(\frac{r_1}{r_2}\right)\right] \tag{32}$$

$$\frac{\partial\lambda}{\partial \rho} = \frac{c}{\left(\frac{q}{Q_s} - cmk - D\right)} \left[\frac{r_2^2 - r_1^2}{4} + \frac{r_1^2}{2} \ln\left(\frac{r_1}{r_2}\right)\right] \tag{33}$$

Because both k and D are constants, $\frac{\partial\lambda}{\partial k} = 0$, $\frac{\partial\lambda}{\partial D} = 0$.

It can be seen from Tables 3 and 4 that the standard deviation of the thermal conductivity determined by using this method is less than 1.0%, and that the values of q, Q_s and r_2 in seven direct measurement quantities is three principal factors affecting the value of λ of energetic materials.

Conclusion

The method of determining the thermal conductivity of energetic materials under constant radical heat flux conditions by use of the Joule effect is very satisfactory in accuracy, relative error and reproducibility. The result of plexiglass, teflon, TNT and four kinds of double propellants determined by using this method agree with data available in the literature.

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Zusammenfassung — Es wurde ein Gerät zur Messung der thermischen Leitfähigkeit von Granulat aus Treibstoffen und Explosivstoffen konstruiert. Es wird eine Methode und eine Berechnungsformel zur Bestimmung der thermischen Leitfähigkeit von Granulat aus Treibstoffen und Explosivstoffen unter den Bedingungen eines konstanten radialem Wärmeflusses unter Anwendung des Joule'schen Effektes vorgestellt. Unter Verwendung dieser Apparatur und eines Mikrokalorimeters vom Typ RD496-II sowie von zwei Standardproben mit bekannter thermische Leitfähigkeit wurden zwei Gerätekonstanten bestimmt und bei 298 K die thermische Leitfähigkeit von sieben Substanzen: Plexiglas, Teflon, DB-Treibstoff DB2 (Nitrozellulose(NC)/Nitroglycerin(NG)/Dinitrotoluol/Dimethylzentralit/Vaseline/PbO/$CaCO_3$, 59.6/25/8.8/3/1.2/1.2/1.22), DB-Treibstoff SQ(NC/NG/Diethylphthalat(DEP)/Bindemittel, 59/29/7/5), DB-Treibstoff RHN-149 (NC/NG /Triacetin(TA)/Bindemittel-I, 52/25/8/15), DB-Treibstoff RHN-190 (NC/NG/TA / Bindemittel-II, 52/26/7/15), 2,4,6-Trinitrotoluol (TNT) gemessen. Die Ergebnisse zeigen, daß (1) die Reproduzierbarkeit der Messung für die nach Abtrennen des Joule'schen Stromes im untersuchten System verbleibende Wärme (q) und die Größe des Wärmeflusses durch die Wand des untersuchten Zylinders (Q_3) geringer als 0,50% und innerhalb von 0.10% liegen; (2) die Standarddeviation der nach dieser Methode bestimmten thermischen Leitfähigkeit ist geringer als 1.0%; (3) die Werte für q, Q_3 und der innere Radius des Zylinders sind drei grundlegende Faktoren, welche die Größe der thermischen Leitfähigkeit dieser Substanzen beeinflussen.