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**ANALYSIS OF ERRORS IN DETERMINING THE
THERMOELECTRIC PROPERTIES OF MATERIALS BY
THE HARMAN METHOD**

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The results of computer studies of the Harman method accuracy for comprehensive determination of the figure of merit, thermoEMF, electric conductivity and thermal conductivity of thermoelectric materials in the temperature range of 30 – 500 °C were presented. A computer model of the Harman method based on a real physical model was developed. Analysis of possible errors of the method for the case of determining the properties of Bi-Te thermoelectric material was made. The results of calculations of measurement errors due to sample heat exchange with the environment through current conductors and thermocouples, as well as heat exchange by radiation were presented. The possibility of reducing the errors by introducing corrections was considered. Residual values of measurement errors due to inaccuracy in determining these corrections were determined.

Key words: measurements, Harman method, figure of merit, thermoEMF, electric conductivity, thermal conductivity, errors.

Introduction

General characterization of the problem. Progress in thermoelectricity is directly related to increase in the efficiency of thermoelectric power converters which, in turn, is governed by the figure of merit of material of which they are made. For selection of material composition and its optimization for a specific practical task it is necessary to establish clear connection between material properties and its fabrication technique. In so doing, the methods and equipment for measuring material properties will be of vital importance.

Until now in most cases use is made of methods for measuring on different samples the electric conductivity σ , thermoEMF α and thermal conductivity κ [1 – 5] which make it possible to determine by calculation the figure of merit Z of thermoelectric material

$$Z = \frac{\alpha^2 \sigma}{\kappa}. \quad (1)$$

However, finding the figure of merit Z in this way is accompanied by considerable reduction of accuracy as compared to the accuracy of determination of σ , α , κ at least for two reasons.

First, in the calculation of Z by formula (1) in conformity with theory of errors [6] the values of errors are added

$$\delta Z = 2\delta\alpha + \delta\sigma + \delta\kappa,$$

where δZ is the error in determining Z ; $\delta\alpha$, $\delta\sigma$, $\delta\kappa$ the errors in determining σ , α , κ , respectively. As long as these errors are approximately $\delta\alpha = 1 - 2 \%$, $\delta\sigma = 3 - 5 \%$, $\delta\kappa = 5 - 7 \%$, the error in determining Z can reach $\delta Z = 10 - 16 \%$.

Second, measurements of σ , α , κ conducted on various samples that are not identical are the cause for additional errors related to inhomogeneity of the source material of which the samples are made. As a result of inhomogeneity, measurements of σ , α , κ are actually performed on the samples with different thermoelectric properties, through supposed to be identical. In so doing, the greater inhomogeneity of the source material, the larger in proportion is the error in determining Z . Moreover, there will be errors in determining the geometry of the samples and the distances between potential and temperature probes (thermocouples) that will be also different when measuring different samples.

These errors can be considerably reduced when measuring σ , α , κ on the same sample.

Analysis of the literature. As far back as the 50-s of the last century T.C. Harman proposed a method for direct measurement of the figure of merit of thermoelectric materials, subsequently named after him [7, 8]. This method allows measuring directly the figure of merit of material. For this purpose the sample under study is mounted in the thermostat on two conductors (Fig. 1). The electrically and thermally conducting contacts which create homogeneous thermal and electrical fields in the sample are mounted at the sample ends.

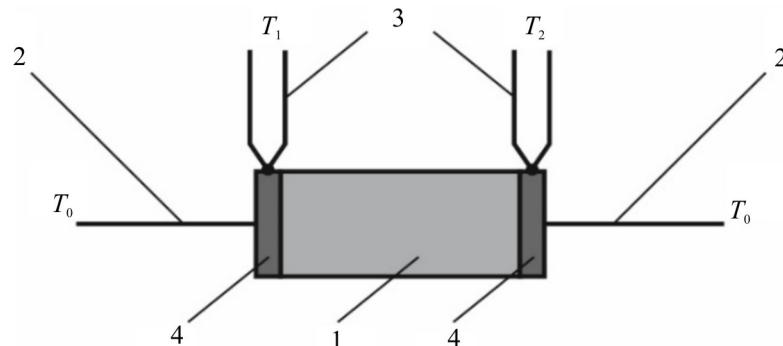


Fig. 1. Schematic of the Harman method
1 – sample; 2 – current conductors; 3 – thermocouples; 4 – contacts.

The measurements reduce to determination of potential difference U_{\approx} on the contacts on the passage of an alternating current through the sample and potential difference $U_=$ on the passage of a direct current. With the identical values of alternating and direct currents I

$$Z = \frac{1}{T} \frac{U_= - U_{\approx}}{U_{\approx}}, \quad (2)$$

where T is average sample temperature.

Moreover, the Harman method allows finding the values of α , σ and κ on this very sample.

The Seebeck coefficient is found from the formula

$$\alpha = \frac{U_= - U_{\approx}}{\Delta T}, \quad (3)$$

where ΔT is temperature difference $T_1 - T_2$ at the sample ends on the passage of a direct current.

The electric conductivity of sample material is determined from expression

$$\sigma = \frac{l_{\approx}}{U_{\approx}} \frac{l}{S}, \quad (4)$$

where I_{\approx} is the value of an alternating current, l is sample length, S is sample cross-section.

The thermal conductivity of material is found from the Fourier law

$$\kappa = \frac{\alpha I_e T}{\Delta T} \frac{l}{S}. \quad (5)$$

The errors in the Harman method are primarily due to the assumption of an idealized model of sample surfaces adiabaticity which cannot be realized in measurements. The reason for this is the presence of a number of heats which are not taken into account in formula (2). Among them – the Joule heats in the sample, in the contacts and conductors through which electric current is supplied to the sample, thermal fluxes through the conductors from the sample to the thermostat, etc. In order to reduce measurement errors, one must take into account their influence by introducing corrections γ_i into formula (2) for the calculation of the figure of merit, namely

$$Z = \frac{1}{T} \frac{U_e - U_{\approx}}{U_{\approx}} \left(1 + \sum_i \gamma_i \right). \quad (6)$$

Thus, the main complexity of this method is the necessity to determine correction factors, for which purpose one should know a large number of parameters, namely the emissivity factors of the sample, contact plates and conductors, their temperature dependences, precise values of the electric conductivity and thermal conductivity of conductor materials, etc.

Therefore, *the purpose of this paper* is to establish real values of possible errors of the Harman method with regard to corrections for heat exchange between the sample and the thermostat, as well as the influence of errors in the determination of corrections on the residual measurement error.

Physical and computer models of the Harman method

A real physical model of the Harman method is shown in Fig. 2.

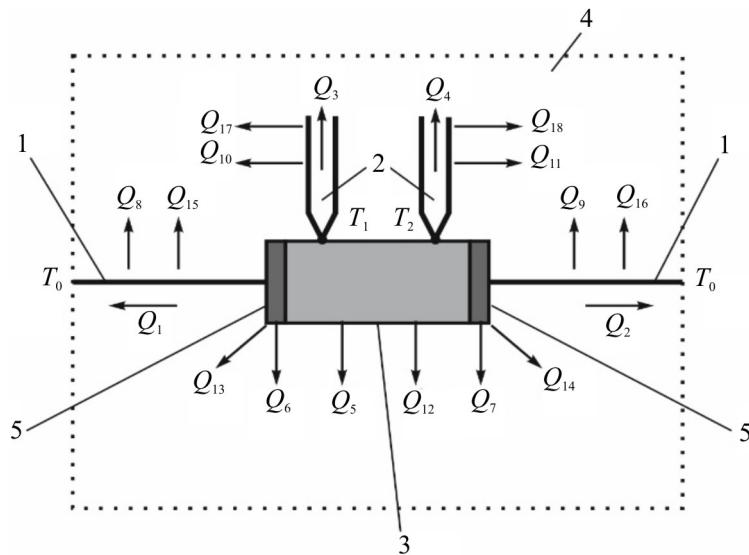


Fig. 2. A real physical model of the Harman method 1 – current conductors, 2 – thermocouples, 3 – sample, 4 – thermostat, 5 – contacts.

The steady-state conditions are created in the sample by virtue of balance of a number of heats, namely the Peltier heat on the contacts, the Joule heat generated in the sample, the contacts and the conductors along which electric current is supplied to the sample, heat flux in the sample and heat fluxes to thermostat with temperature T_0 through current conductors, thermocouple conductors and by heat exchange due to convection and radiation.

Thus, in addition to the Peltier heat one must take into account the Joule heat, the Thomson heat and several more heat fluxes:

- Q_1, Q_2 – heat exchange between the sample and the thermostat through current conductors;
- Q_3, Q_4 – heat exchange between the sample and the thermostat through thermocouple conductors;
- Q_5 – heat exchange by radiation between the sample and the thermostat;
- Q_6, Q_7 – heat exchange by radiation between the contacts and the thermostat;
- Q_8, Q_9 – heat exchange by radiation between current conductors and the thermostat;
- Q_{10}, Q_{11} – heat exchange by radiation between thermocouple conductors and the thermostat;
- Q_{12} – convective heat exchange between the sample and thermostat;
- Q_{13}, Q_{14} – convective heat exchange between the contacts and the thermostat;
- Q_{15}, Q_{16} – convective heat exchange between current conductors and the thermostat;
- Q_{17}, Q_{18} – convective heat exchange between thermocouple conductors and the thermostat.

The possibilities of excluding the above additional kinds of heat are extremely limited. High vacuum created around the sample is the only real condition that can improve this situation. In this case one can assume:

$$Q_{12} = Q_{13} = Q_{14} = Q_{15} = Q_{16} = Q_{17} = Q_{18} = 0. \quad (7)$$

As regards other heats ($Q_1 - Q_{11}$), most of them are practically inevitable, and one must estimate their influence on the measurement results and take into account as a series of corrections.

Calculation of the influence of these thermal fluxes on the error in measuring the figure of merit by the Harman method is a complicated mathematical problem that can be written as system of second-order differential equations in partial derivatives

$$\begin{cases} -\nabla((\kappa_i + \alpha_i^2 \sigma_i T_i) \nabla T_i) - \nabla(\alpha_i \sigma_i T_i \nabla U_i) - \alpha_i ((\nabla U_i)^2 + \alpha_i \nabla T_i \nabla U_i) = 0 \\ \nabla(\sigma_i \nabla U_i) + \nabla(\sigma_i \alpha_i \nabla T_i) = 0, \quad i = 1, 2..5 \end{cases} \quad (8)$$

where σ_i , α_i , κ_i are electric conductivity, thermoEMF and thermal conductivity of physical model elements, U is electrical potential, T is temperature.

Solution of this system of equations with corresponding boundary conditions was obtained by means of computer simulation using Comsol Multiphysics application software package.

Computer simulation results

Determination of the figure of merit

The elaborated computer model was used to obtain the distributions of temperature and electric potential in the sample and the elements of measuring unit intended for determination of thermoelectric properties of material by the Harman method in the temperature range of 30 – 500 °C on the samples of *Bi-Te* based material of diameter 4 mm and length 10 mm. The obtained distributions allowed calculating possible errors in determining the figure of merit by the Harman method without regard to corrections, as well as the values of required corrections and the influence on them of information on the properties and geometry of sample, contacts, current conductors and thermocouples. The results of investigation are given below. If necessary, computer model allows reproducing these results for other materials, temperature ranges and sample dimensions.

Total error in determining the figure of merit Z versus temperature is given in Fig. 3. This dependence was obtained for the case of measurements without regard to correction factors. As is

seen from the plot, the error in determining the figure of merit at room temperature is a little more than 10 % and greatly increases with a rise in temperature. As mentioned above, these errors can be taken into account by introducing into the formula for calculating the figure of merit the correction factors taking into account heat exchange between the sample and the measuring unit elements. However, this requires information on a large number of values characterizing measuring unit, namely precise geometrical dimensions of current conductors, thermocouples and contacts, their thermal conductivity, electric conductivity, thermoEMF, emissivity, thermostat temperature, etc. The errors in determining these values will have a direct influence on the error in determining corrections, hence the figure of merit of the sample. The results of computer simulation of this influence are given below in the form of dependences of errors in determining corrections $\delta\gamma_i$ on the errors in measuring each of the values necessary for their calculation.

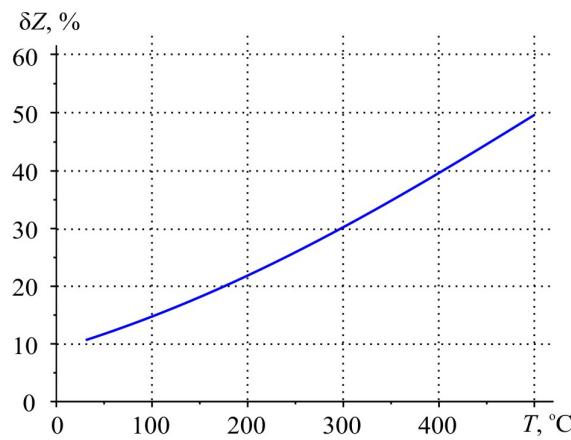


Fig. 3. Total error in determining the figure of merit Z by the Harman method without regard to corrections versus temperature.

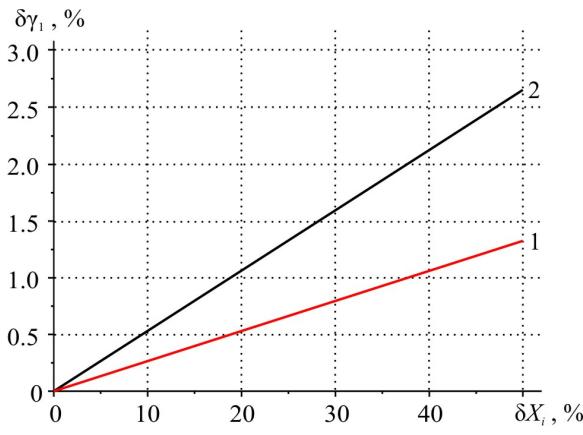


Fig. 4. The error in determining correction γ_1 for heat exchange through current conductors versus the errors in measuring their length L_1 , diameter d_1 , thermal conductivity κ_1 and temperature difference ΔT_1 . δX_i : 1 – δL_1 , $\delta \kappa_1$, $\delta(\Delta T_1)$; 2 – δd_1 .

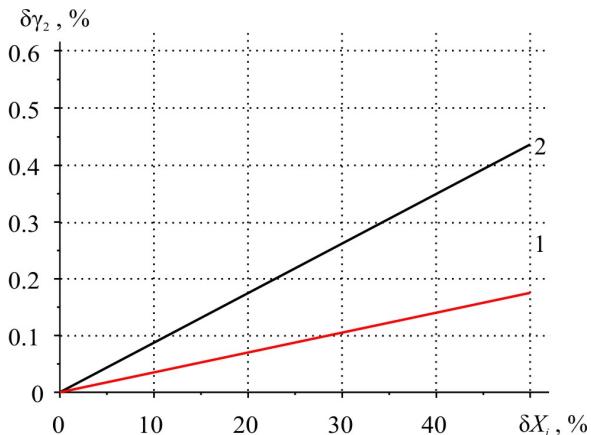


Fig. 5. The error in determining correction γ_2 for heat exchange through thermocouple conductors versus the errors in measuring their lengths L_2 and L_3 , diameters d_2 and d_3 , thermal conductivities κ_2 and κ_3 and temperature differences ΔT_2 and ΔT_3 . δX_i : 1 – δL_2 , δL_3 , $\delta \kappa_2$, $\delta \kappa_3$, $\delta(\Delta T_2)$, $\delta(\Delta T_3)$; 2 – δd_2 , δd_3 .

Fig. 4, 5 show the errors in determining corrections for heat exchange through current conductors, as well as chromel-alumel thermocouple conductors versus the errors in measuring their lengths, diameters and temperature differences.

Further shown are the errors in determining corrections related to radiation from the surface of sample (Fig. 6, 7), contacts (Fig. 8, 9), current conductors and thermocouple conductors (Fig. 10, 11). The figures show the errors in determining corrections versus the errors in measuring the geometry and emissivity of physical model elements for three values of thermostat temperature – 30, 250 and 500 °C.

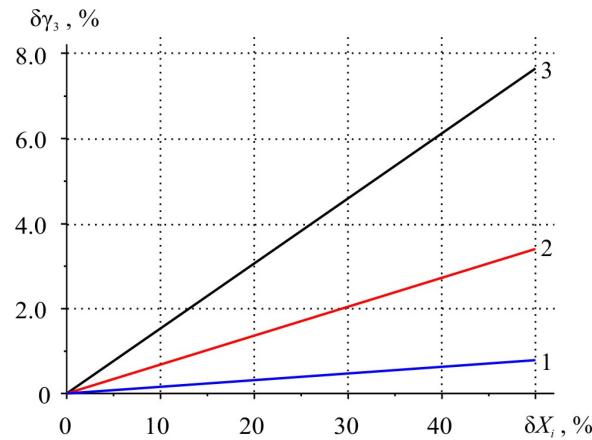


Fig. 6. The error in determining correction γ_3 for heat exchange by radiation between sample and thermostat versus the errors in measuring sample length L_3 and diameter d_3 , sample emissivity ε_3 and thermostat emissivity ε_4 . 1 – 30 °C, 2 – 250 °C, 3 – 500 °C. δX_i : δL_3 , δd_3 , $\delta \varepsilon_3$, $\delta \varepsilon_4$.

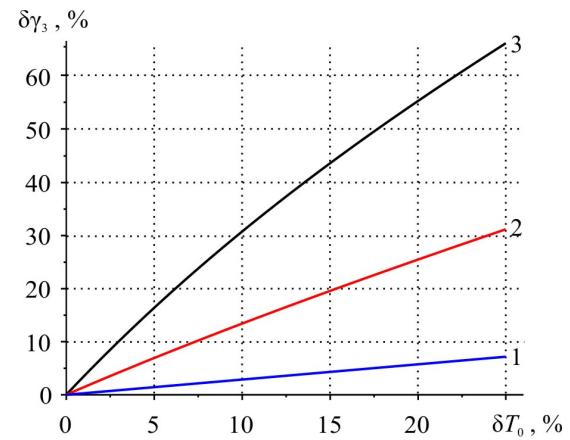


Fig. 7. The error in determining correction γ_3 for heat exchange by radiation between sample and thermostat versus the error in measuring thermostat temperature T_0 . 1 – 30 °C, 2 – 250 °C, 3 – 500 °C.

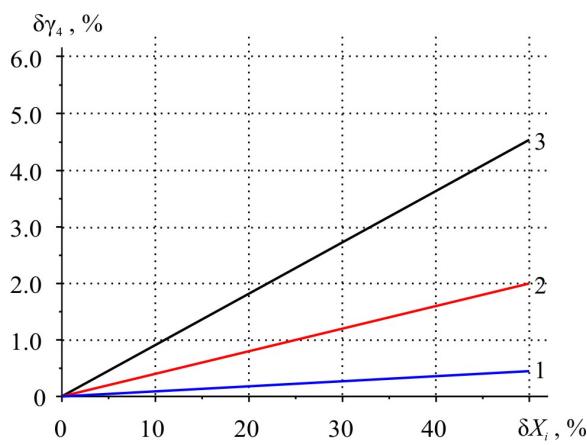


Fig. 8. The error in determining correction γ_4 for heat exchange by radiation between contacts and thermostat versus the errors in measuring thickness L_5 and diameter d_5 of contacts, contact emissivity ε_5 and thermostat emissivity ε_4 . 1 – 30 °C, 2 – 250 °C, 3 – 500 °C. δX_i : δL_5 , δd_5 , $\delta \varepsilon_4$, $\delta \varepsilon_5$.

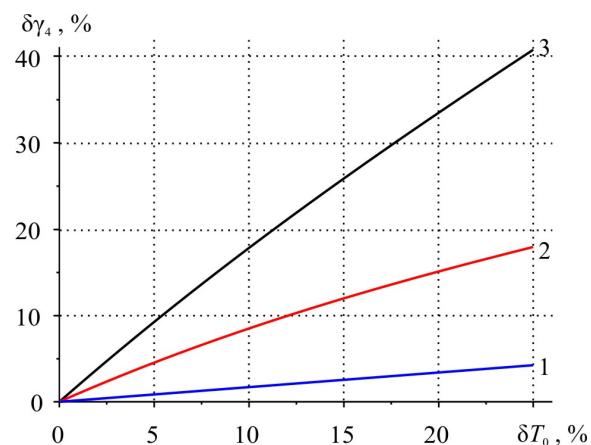


Fig. 9. The error in determining correction γ_4 for heat exchange by radiation between contacts and thermostat versus the error in measuring thermostat temperature T_0 . 1 – 30 °C, 2 – 250 °C, 3 – 500 °C.

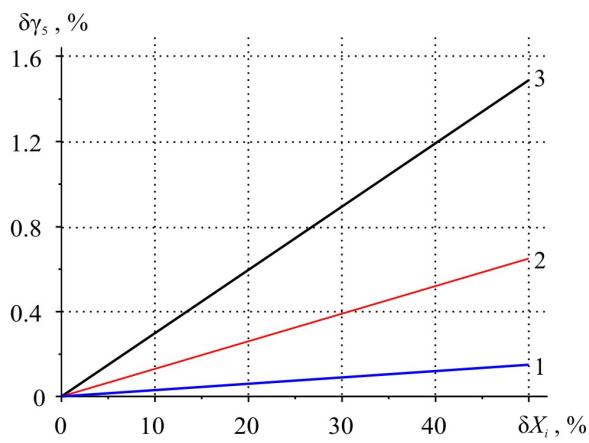


Fig. 10. The error in determining correction γ_5 for heat exchange by radiation between conductors (current and thermocouple) and thermostat versus the errors in measuring length L_6 and diameter d_6 of conductors, conductor emissivity ϵ_6 and thermostat emissivity ϵ_4 . 1 – 30 °C, 2 – 250 °C, 3 – 500 °C.

δX_i : δL_6 , δd_6 , $\delta \epsilon_4$, $\delta \epsilon_6$.

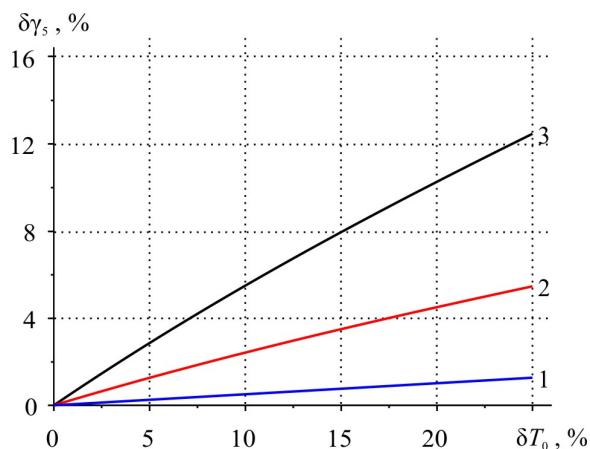


Fig. 11. The error in determining correction γ_5 for heat exchange by radiation between conductors (current and thermocouple) and thermostat versus the error in measuring thermostat temperature T_0 .

1 – 30 °C, 2 – 250 °C, 3 – 500 °C.

From the above dependences one can obtain the expected total error in determining corrections for typical errors in measuring the values necessary for their calculation. The values of errors in determining these corrections are given in Table.

Table

Expected errors in determining corrections for the figure of merit calculation

Nº	Correction	Parameter	Parameter value	Parameter measurement error	Correction determination error
1	2	3	4	5	6
Temperature 30 °C					
1.	γ_1 – account of heat exchange through current conductors	Current conductor length, L_1 , mm	30	3 – 5 %	0.09 – 0.14 %
		Current conductor diameter, d_1 , mm	0.1	5 – 10 %	0.26 – 0.52 %
		Thermal conductivity of conductor material, κ_1 , W/(m*K)	400	5 – 7 %	0.14 – 0.22 %
		Temperature difference on conductor, ΔT_1 , °C	~ 2	~ 5 %	0.14 %
2.	γ_2 – account of heat exchange through thermocouple conductors	Conductor length, L_2 , mm	50 mm	3 – 5 %	< 0.01 %
		Conductor diameter, d_2 , mm	0.1 mm	5 – 10 %	0.02 – 0.08 %
		Thermal conductivity of conductor material, κ_2 , W/(m*K) – chromel – alumel	18 27	5 – 7 % 5 – 7 %	0.01 – 0.02 % 0.01 – 0.02 %
		Temperature difference on conductor, ΔT_2 , °C	~ 2	~ 5 %	< 0.01 %

Table (continued)

1	2	3	4	5	6
3.	γ_3 – account of heat exchange by radiation between sample and thermostat	Sample length, L_3 , mm	10	0.5 %	< 0.01 %
		Sample diameter, d_3 , mm	4	0.25 %	< 0.01 %
		Sample emissivity, ϵ_3	0.7	20 – 30 %	0.28 – 0.42 %
		Thermostat emissivity, ϵ_3	0.7	20 – 30 %	0.28 – 0.42 %
		Thermostat temperature, T_0 , °C	30	1 – 2 %	0.34 – 0.68 %
4.	γ_4 – account of heat exchange by radiation between contacts and thermostat	Contact thickness, L_4 , mm	2	0.5 %	< 0.01 %
		Contact diameter, d_4 , mm	4	0.25 %	< 0.01 %
		Contact emissivity, ϵ_4	0.7	20 – 30 %	0.16 – 0.24 %
		Thermostat emissivity, ϵ_4	0.7	20 – 30 %	0.16 – 0.24 %
		Thermostat temperature, T_0 , °C	30	1 – 2 %	0.2 – 0.4 %
5.	γ_5 – account of heat exchange by radiation between conductors and thermostat	Length – current conductors, L_1 , mm – thermocouple conductors, L_2 , mm	30 50	3 – 5 % 3 – 5 %	< 0.01 % < 0.01 %
		Diameter – current conductors, d_1 , mm – thermocouple conductors, d_2 , mm	0.1 0.1	5 – 10 % 5 – 10 %	0.01 – 0.03 % 0.01 – 0.03 %
		Emissivity – current conductors, ϵ_1 – thermocouple conductors, ϵ_2	0.7 0.7	20 – 30 % 20 – 30 %	0.06 – 0.09 % 0.06 – 0.09 %
		Thermostat emissivity, ϵ_4	0.7	20 – 30 %	0.06 – 0.09 %
		Thermostat temperature, T_0 , °C	30	1 – 2 %	0.06 – 0.11 %
		Sum $\gamma_1 - \gamma_5$, %			2.3 – 4.0 %
		Temperature 250 °C			
		Current conductor length, L_1 , mm	30	3 – 5 %	0.08 – 0.12 %
		Current conductor diameter d_1 , mm	0.1	5 – 10 %	0.21 – 0.42 %
		Thermal conductivity of conductor material, κ_1 , W/(m*K)	385	5 – 7 %	0.09 – 0.19 %
1.	γ_1 – account of heat exchange through current conductors	Temperature difference on conductor, ΔT_1 , °C	~ 2	~ 5 %	0.12 %
		Conductor length, L_2 , mm	50 mm	3 – 5 %	< 0.01 %
		Conductor diameter, d_2 , mm	0.1 mm	5 – 10 %	0.02 – 0.06 %
		Thermal conductivity of conductor material, κ_2 , W/(m*K) – chromel – alumel	22.7 32	5 – 7 % 5 – 7 %	< 0.01 % < 0.01 %
		Temperature difference on conductor, ΔT_2 , °C	~ 2	~ 5 %	< 0.01 %
2.	γ_2 – account of heat exchange through thermocouple conductors	Sample length, L_3 , mm	10	0.5 %	0.03 %
		Sample diameter, d_3 , mm	4	0.25 %	0.01 %
		Sample emissivity, ϵ_3	0.7	20 – 30 %	1.19 – 1.78 %
		Thermostat emissivity, ϵ_3	0.7	20 – 30 %	1.19 – 1.78 %
		Thermostat temperature, T_0 , °C	250	1 – 2 %	1.45 – 2.9 %
3.	γ_3 – account of heat exchange by radiation between sample and thermostat	Sample length, L_3 , mm	10	0.5 %	0.03 %
		Sample diameter, d_3 , mm	4	0.25 %	0.01 %
		Sample emissivity, ϵ_3	0.7	20 – 30 %	1.19 – 1.78 %
		Thermostat emissivity, ϵ_3	0.7	20 – 30 %	1.19 – 1.78 %
		Thermostat temperature, T_0 , °C	250	1 – 2 %	1.45 – 2.9 %

Table (continued)

1	2	3	4	5	6
4.	γ_4 – account of heat exchange by radiation between contacts and thermostat	Contact thickness, L_4 , mm	2	0.5 %	0.02 %
		Contact diameter, d_4 , mm	4	0.25 %	0.01 %
		Contact emissivity, ϵ_4	0.7	20 – 30 %	0.68 – 1.02 %
		Thermostat emissivity, ϵ_4	0.7	20 – 30 %	0.68 – 1.02 %
		Thermostat temperature, T_0 , °C	250	1 – 2 %	0.85 – 1.7 %
5.	γ_5 – account of heat exchange by radiation between conductors and thermostat	Length – current conductors, L_1 , mm – thermocouple conductors, L_2 , mm	30 50	3 – 5 % 3 – 5 %	< 0.01 % < 0.01 %
		Diameter – current conductors, d_1 , mm – thermocouple, d_2 , mm	0.1 0.1	5 – 10 % 5 – 10 %	0.04 – 0.12 % 0.04 – 0.12 %
		Emissivity – current conductors, ϵ_1 – thermocouple conductors, ϵ_2	0.7 0.7	20 – 30 % 20 – 30 %	0.25 – 0.38 % 0.25 – 0.38 %
		Thermostat emissivity, ϵ_4	0.7	20 – 30 %	0.25 – 0.38 %
		Thermostat temperature, T_0 , °C	250	1 – 2 %	0.25 – 0.46 %
		Sum $\gamma_1 - \gamma_5$, %			7.7 – 13.1 %
		Temperature 500 °C			
1.	γ_1 – account of heat exchange through current conductors	Current conductor length, L_1 , mm	30	3 – 5 %	0.06 – 0.09 %
		Current conductor diameter, d_1 , mm	0.1	5 – 10 %	0.17 – 0.34 %
		Thermal conductivity of conductor material, κ_1 , W/(m*K)	366	5 – 7 %	0.07 – 0.15 %
		Temperature difference on conductor, ΔT_1 , °C	~ 2	~ 5 %	0.17 %
2.	γ_2 – account of heat exchange through thermocouple conductors	Conductor length, L_2 , mm	50 mm	3 – 5 %	< 0.01 %
		Conductor diameter, d_2 , mm	0.1 mm	5 – 10 %	0.01 – 0.03 %
		Thermal conductivity of conductor material, κ_2 , W/(m*K) – chromel – alumel	27.8 37.5	5 – 7 % 5 – 7 %	< 0.01 % < 0.01 %
		Temperature difference on conductor, ΔT_2 , °C	~ 2	~ 5 %	< 0.01 %
3.	γ_3 – account of heat exchange by radiation between sample and thermostat	Sample length, L_3 , mm	10	0.5 %	0.07 %
		Sample diameter, d_3 , mm	4	0.25 %	0.04 %
		Sample emissivity, ϵ_3	0.7	20 – 30 %	2.72 – 4.07 %
		Thermostat emissivity, ϵ_3	0.7	20 – 30 %	2.72 – 4.07 %
		Thermostat temperature, T_0 , °C	500	1 – 2 %	3.29 – 6.59 %
4.	γ_4 – account of heat exchange by radiation between contacts and thermostat	Contact thickness, L_4 , mm	2	0.5 %	0.04 %
		Contact diameter, d_4 , mm	4	0.25 %	0.02 %
		Contact emissivity, ϵ_4	0.7	20 – 30 %	1.55 – 2.33 %
		Thermostat emissivity, ϵ_4	0.7	20 – 30 %	1.55 – 2.33 %
		Thermostat temperature, T_0 , °C	500	1 – 2 %	1.94 – 3.88 %

Table (continued)

1	2	3	4	5	6	
5.	γ_5 – account of heat exchange by radiation between conductors and thermostat	Length – current conductors, L_1 , mm	30 50	3 – 5 % 3 – 5 %	< 0.01 % < 0.01 %	
		Diameter – current conductors, d_1 , mm	0.1 0.1	5 – 10 % 5 – 10 %	0.09 – 0.26 % 0.09 – 0.26 %	
		Emissivity – current conductors, ε_1 – thermocouple conductors, ε_2				
			0.7 0.7	20 – 30 % 20 – 30 %	0.58 – 0.87 % 0.58 – 0.87 %	
		Thermostat emissivity, ε_4	0.7	20 – 30 %	0.58 – 0.87 %	
Thermostat temperature, T_0 , °C				500	1 – 2 %	
Sum $\gamma_1 - \gamma_5$, %					16.9 – 28.6 %	

From Table it follows that the expected total error in determining corrections for typical errors in measuring the values necessary for their calculation will increase with a rise in temperature from $\sim 2.3 – 4.0\%$ at room temperature to $\sim 16.9 – 28.6\%$ at 500°C (for the above indicated geometrical dimensions of sample and measuring unit elements).

The error in measuring figure of merit by the Harman method, apart from the errors in determining corrections for heat exchange with the environment, will also include other errors, namely the errors in measuring voltages U_{\approx} ($\sim 1.5\%$), $U_{=}$ ($\sim 0.1\%$) and average temperature of sample ($\sim 0.5\%$). Therefore, total error in measuring figure of merit by the Harman method will make from $\sim 4.4 – 6.1\%$ at room temperature to $\sim 19 – 30.7\%$ at 500°C .

Determination of thermoEMF, electric conductivity and thermal conductivity

There were also calculated possible errors in determining by the Harman method of other thermoelectric parameters of material, namely thermoEMF, electric conductivity and thermal conductivity.

The errors in measuring thermoEMF and electric conductivity are mainly governed by instrumental errors in measuring the values which enter into formulae (3) and (4) – the errors in measuring voltage U_{\approx} on the passage of an alternating current through the sample ($\sim 1.5\%$), voltage $U_{=}$ on the passage of a direct current through the sample ($\sim 0.15\%$), sample length ($\sim 0.25\%$), sample cross-sectional area ($\sim 0.5\%$), temperature difference on the sample ($\sim 3\%$), the Seebeck coefficient of chromel ($\sim 2\%$), the value of an alternating current I_{\approx} ($\sim 0.5\%$).

Additional error in measuring electric conductivity is also introduced by current density inhomogeneity in the sample ($\sim 1\%$). As regards the influence of thermoEMF on electric conductivity measurement, the use of an alternating current due to thermal inertia at not very low frequencies eliminates the influence of the Peltier effect on temperature distribution in the sample and, accordingly, the influence of thermoEMF on the measurements.

Thus, total error in measuring the Seebeck coefficient will make $\sim 6.7\%$, electric conductivity $\sim 3.8\%$.

The situation with thermal conductivity measurement is more difficult. As in the case of the

figure of merit, the errors in determining thermal conductivity will depend on the accuracy of finding corrections for heat exchange between the sample and the environment. The resulting distributions of temperature and electric potential in the sample and measurement unit elements allowed calculating possible errors in measuring thermal conductivity by the Harman method without regard to corrections, the values of the necessary corrections and the influence on them of precise information on the properties and geometry of sample, contacts, current conductors and thermocouples. The error in measuring thermal conductivity related to thermal losses versus temperature is shown in Fig. 12.

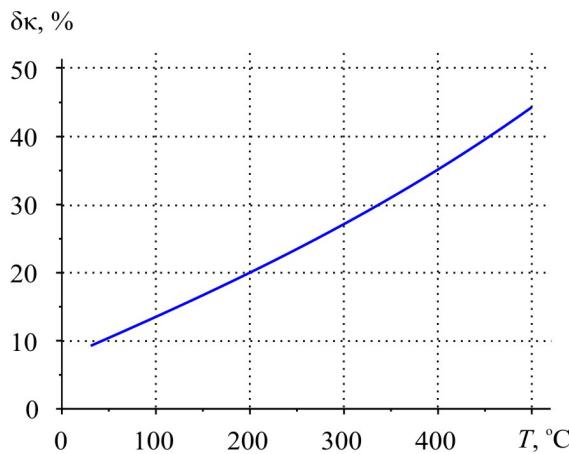


Fig. 12. Total error in determining thermal conductivity by the Harman method versus temperature (without regard to corrections).

The error in determining thermal conductivity at room temperature is of the order of 9.5 % and, similar to the error in measuring figure of merit, increases with a rise in temperature to ~ 45 % at 500 °C. These errors can be reduced by introducing corrections. Dependences of the accuracy in determining these corrections on the accuracy in measuring the values necessary for their calculation were obtained. It was established that total error in determining corrections for thermal conductivity calculation by the Harman method increases from ~ 2.2 – 3.7 % at room temperature to ~ 15.3 – 26 % at 500 °C. The error in measuring thermal conductivity, apart from the errors in determining corrections for heat exchange with the environment, will also include the errors in measuring sample length (~ 0.25 %), cross-sectional area (~ 0.5 %), voltages U_z (~ 1.5 %) and U_- (~ 0.1 %), current I_- (~ 0.1 %), sample average temperature (~ 0.5 %) and temperature difference on sample (~ 3 %). Total error in measuring thermal conductivity by the Harman method will make from ~ 8.2 – 9.7 % at room temperature to ~ 21.3 – 32 % at 500 °C.

Thus, the possibility of using the Harman method for a comprehensive determination of thermoelectric properties of material is essentially restricted by the necessity to know additional accurate information on many values, as well as by a narrow range of temperatures with acceptable values of measurement errors.

Conclusions

1. By computer simulation of a real physical model of the Harman method it was established that the error in determining the figure of merit of thermoelectric materials based on *Bi-Te* by this method at room temperature is ~ 10 % and drastically increases with a rise in temperature to ~ 50 % at 500 °C.

2. The influence of the accuracy of information on the geometry and physical properties of the sample and measuring unit elements on the accuracy of determining corrections for the figure of merit calculation was determined. It was established that total error in determining corrections for the case of measuring the figure of merit of thermoelectric materials based on *Bi-Te* and typical errors in measuring the values necessary for calculation of these errors increases from ~ 2.3 – 4.0 % at room temperature to ~ 16.9 – 28.6 % at 500 °C. Total error in measuring the figure of merit with regard to instrumental errors of measured values is from ~ 4.4 – 6.1 % at room temperature to ~ 19 – 30.7 % at 500 °C.
3. Possible errors in measuring other thermoelectric properties by the Harman method were evaluated. It was established that total error in measuring the Seebeck coefficient is ~ 6.7 %, electric conductivity ~ 3.8 %, thermal conductivity – from ~ 8.2 – 9.7 % at room temperature to ~ 21.3 – 32 % at 500 °C.

References

1. L.I.Anatychuk, *Thermoelements and Thermoelectric Devices* (Kyiv: Naukova Dumka, 1979), 768 p.
2. H. Czichos, T. Saito, and L. Smith, *Springer Handbook of Metrology and Testing* (Springer, 2011), 1500 p.
3. T.Tritt, Electrical and Thermal Transport Measurement Techniques for Evaluation of the Figure-of-Merit of Bulk Thermoelectric Materials, in: *Thermoelectric Handbook: Macro to Nano*, ed. by D.M. Rowe (CRC Press, 2006).
4. L.I.Anatychuk, S.V.Pervozvansky, and V.V.Razinkov, Precise Measurement of Cooling Thermoelectric Material Parameters: Methods, Arrangements and Procedures, *Proc. of the 12th Intern. Conf. Thermoelectrics (Japan, 1993)*, pp. 553 – 564.
5. A.S.Okhotin, A.S.Pushkarsky, R.P.Borovikova, and V.A.Simonov, *Methods for Measuring Characteristics of Thermoelectric Materials and Converters* (Moscow: Nauka, 1974).
6. E.S.Polischuk, M.M.Dorozhovets, V.O.Yatsuk et al., *Metrology and Measuring Equipment*, Ed. by prof. E.S.Polischuk (Lviv: Beskyd Bit Publ., 2004), 544p.
7. T.C. Harman, J.H. Cahn, and M.J. Logan, Measurement of Thermal Conductivity by Utilization of the Peltier Effect, *J. Applied Physics* **30**(9), 1351 – 1359 (1959).
8. US 2994818, T.C.Harman, Method and Apparatus for Measuring Thermoelectric Properties, 1959.

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