GENERALIZATION OF EXPERIMENTAL SPECIFIC HEAT DATA FOR SYNTHETIC CORUNDUM IN THE TEMPERATURE RANGE 80-300°K

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The results of an experimental investigation of the specific heat of corundum on state standard GÉT 70-75 are given. The possibility of generalizing the most accurate data to expanded batches of corundum is discussed.

The reproduction and relaying of the unit of specific heat of solids are effected by means of materials carrying the property. These are special measures contained in state standards, working standards, and standard measures of the second class (see [1], for instance). The property carriers must meet certain requirements to ensure that there is no systematic or random change in the property itself, or in the characteristics of the calorimeter (stability of the property in time, chemical inertness relative to components of measuring devices, etc.). In general, the higher the metrological rank of the carrier material, the more rigorous the demands made on it. In some cases, however, there may be deviations from this rule.

For instance, for a special measure the requirement of homogeneity of the material and the isotropy of its property (specific heat) are not of decisive importance, since the special measure is a weighed portion of material entirely enclosed in the container of the measuring device. In the relaying of the measurement unit to a working standard and then by means of the working standard to standard and precision working means of measurement, however, the question of isotropy of the property may be of fundamental importance if some batch of material (more than the investigated portion) has to be attested as a working standard, or if only part of the investigated portion is to be used in test operations. The answer to this question in both cases necessitates numerous investigations with standard and special standard equipment.

In the Khabarovsk branch of the All-Union Scientific-Research Institute of Physicotechnical and Radiotechnical Measurements (VNIIFTRI) a special standard unit of specific heat of solids in the temperature range 90-273.15°K was produced and in 1975 was ratified by Gosstandart (GÉT 70-75) [2]. The GÉT 70-75 standard consisted of a standard calorimetric apparatus and a special measure composed of synthetic corundum (α-Al_2O_3) of the highest grade (GOST 9618-61) and mass 270 g.

At the time of ratification of the standard three series of measurements of the specific heat of the special measurement were made, involving complete reassembly of the container (Table 1). Subsequently another series of measurements of the specific heat of the special measure was made on the GÉT 70-75 standard (Table 1), and measurements of the specific heat of three new specimens of synthetic corundum were made. Two specimens were taken from the same batch of corundum as the special measure (the whole batch of corundum was obtained from the D. I. Mendeleev Scientific-Research Institute of Metrology), and the third was obtained from a new batch.

It should be noted that as a whole GOST 9618-61 corundum is not homogeneous. The grown "boules" are inhomogeneous in color and have internal stresses, which are removed either by annealing or by splitting the boules into semiboules. The initial material was cut up into granules (cuboidal pieces 2-3 mm long), which were sorted according to their coloration. The special measures was composed of white granules.

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TABLE 1. Experimental Values of Specific Heat of Special Measure

T, °K	c, J/kg·K	T, °K	c, J/kg·deg K	T, °K	c, J/kg·deg K
First series of measurement					
74,39	54,50	155,38	334,63	237,47	621,98
77,10	60,69	183,08	440,65	239,73	628,51
79,63	66,96	185,54	449,79	242,29	636,06
121,28	201,74	188,22	459,60	244,82	643,26
124,08	212,33	190,86	469,14	273,14	717,98
143,60	288,19	208,84	531,83	275,66	724,16
146,08	298,08	211,27	539,69	278,17	730,06
148,70	308,40	215,12	552,40	303,58	786,80
152,07	321,60	218,86	564,83		
Second series of measurements					
76,90	60,22	162,20	361,47	231,17	603,17
87,13	86,76	173,65	405,51	244,67	642,87
115,10	178,79	187,56	457,10	258,18	679,85
127,62	225,90	200,47	502,98	280,94	736,77
136,52	260,46	213,09	545,90	294,17	766,87
149,26	310,32				
Third series of measurements					
88,28	90,21	147,45	303,31	207,76	527,75
91,35	98,95	150,86	316,68	210,81	537,90
97,02	116,43	153,97	328,84	214,11	548,78
99,71	125,13	156,98	340,78	217,65	560,40
102,29	133,73	159,91	352,20	221,13	571,69
104,88	142,46	163,23	365,17	224,55	582,45
107,63	151,99	166,91	379,35	228,10	593,48
110,45	161,92	170,45	392,98	231,78	604,74
113,40	172,55	173,94	406,24	235,41	615,63
116,47	183,77	177,32	418,91	239,09	626,40
119,69	195,71	180,61	431,20	242,85	637,23
123,05	208,34	183,82	443,04	247,01	649,14
126,26	220,62	186,97	454,73	251,56	661,71
129,34	232,42	190,04	465,88	256,04	673,81
132,42	244,36	193,15	477,07	260,44	685,46
135,51	256,40	196,30	488,32	264,77	696,72
138,49	267,97	199,40	499,12	269,18	707,92
141,41	279,55	202,43	509,62	273,46	718,53
144,41	291,37	204,67	517,20		
Fourth series of meaurements					
90,51	96,49	157,71	343,68	223,91	580,71
92,76	103,22	159,18	349,36	225,70	586,25
94,22	107,66	162,75	363,29	227,54	592,11
97,04	116,51	166,22	376,74	230,16	599,91
99,78	125,39	169,58	389,57	233,94	611,54
105,89	145,96	172,86	402,20	235,37	615,60
108,58	155,32	174,66	409,01	238,24	624,27
111,15	164,46	176,05	414,21	242,18	635,51
113,42	173,36	179,16	425,91	246,21	647,08
115,99	182,03	182,72	439,19	250,18	658,12
118,28	190,47	186,71	453,83	254,06	668,66
120,50	198,73	189,81	465,17	258,04	679,49
123,06	208,40	192,66	475,47	262,39	690,73
125,94	219,42	195,90	486,81	265,23	698,10
128,99	231,15	198,09	494,58	268,76	707,00
132,18	243,47	201,71	507,28	272,13	715,46
135,25	255,43	203,04	511,90	276,17	725,40
138,21	267,00	205,25	519,40	280,47	735,73
141,07	278,23	206,52	523,77	284,70	745,59
144,24	290,68	209,30	533,06	288,86	755,18
147,70	304,33	213,27	546,31	290,49	758,76
151,05	317,55	217,44	559,74	293,48	765,33
154,29	330,30	220,22	568,86	299,24	778,20

The rest of the batch of corundum obtained from the Institute of Metrology was divided into three fractions according to color: white, light grey, and deeply colored. Since there was only 6 g of deeply colored corundum, this specimen was investigated on the standard microcalorimetric apparatus of first class described in [3]. The experimental results revealed a systematic difference between the specific heat of colored corundum and

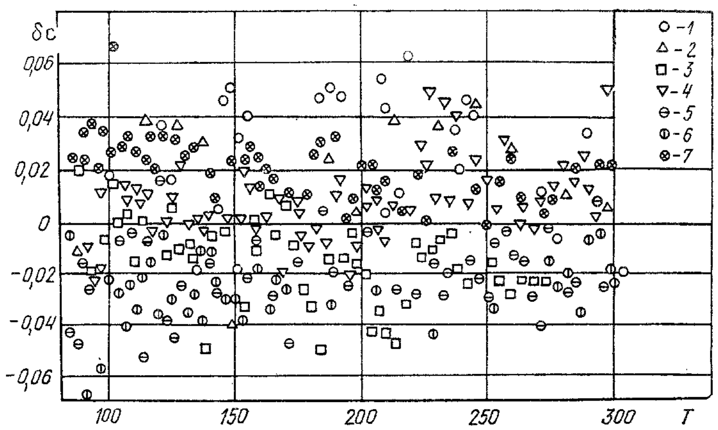

Fig. 1. Deviations of experimental specific heat values for corundum from values calculated from equation $\delta c = [(c_{exp} - c_{calc})/c_{exp}]\cdot 100\%$: 1-4) series of measurements of special measure; 5) working standard VÉT 70-1-78; 6) working standard VÉT 70-2-78; 7) pale pink corundum specimen. T in °K.

the special measure, which at 90°K reached 3% and gradually decreased to 0.6% at 270°K.

The white and light grey fractions were investigated on the state standard and were approved as the working standards VÉT 70-1-78 (of mass 340 g) and VÉT 70-2-78 (of mass 330 g) for the temperature range 90-273.15°K. The results are given in Tables 2 and 3, respectively. A specimen of pale pink corundum (of mass 250 g) was also investigated on the state standard (Table 4). The initial material consisted of semiboules whose internal stresses had been removed mechanically. The experimental data, given in Tables 1-4, were used to obtain an analytical relation for the specific heat of corundum in the range 80-300°K.

The initial relation was approximated by a generalized polynomial by the least-squares method and the system of normal equations was solved by the Jordan—Gauss method. The obtained polynomial of the form

$$c = -61.5774 - 5.29482T + 9.40722\cdot 10^{-2}T^2 - 4.17033\cdot 10^{-4}T^3 + 8.34107\cdot 10^{-7}T^4 - 6.50931\cdot 10^{-10}T^5 + 1.59219\cdot 10^4 T^{-1} - 4.25466\cdot 10^5 T^{-2},\ \text{J/kg}\cdot\text{deg K} \quad (1)$$

TABLE 2. Experimental Values of Specific Heat of Working Standard VÉT 70-1-78

T, °K	c, J/kg • deg K	T, °K	c, J/kg • deg K	T, °K	c, J/kg • deg K
85,21	81,41	143,40	287,31	232,93	608,07
87,99	89,15	152,23	322,08	236,70	619,36
90,59	96,73	155,66	335,55	240,41	630,24
93,06	104,10	158,98	348,58	243,89	640,25
95,40	111,33	162,19	361,12	247,31	649,87
97,87	119,15	165,37	373,33	250,86	659,71
100,43	127,53	168,51	385,47	254,37	669,42
103,83	138,89	171,89	398,29	257,84	678,74
107,40	151,18	175,48	412,02	261,26	687,70
110,15	160,85	178,96	424,84	264,65	696,46
112,77	170,24	185,71	450,20	268,15	705,28
114,55	176,63	189,02	462,19	271,40	713,33
117,43	187,29	192,28	473,94	274,59	721,45
120,19	197,62	195,50	485,38	277,76	729,17
123,09	208,44	198,65	496,51	280,90	736,42
126,12	219,98	202,09	508,54	284,32	744,44
129,04	231,24	214,50	550,17	294,18	766,91
132,01	242,76	218,02	561,61	297,76	774,47
135,00	254,40	221,49	572,84	301,01	781,38
137,89	265,71	225,18	584,41		
140,68	276,66	229,09	596,50		

TABLE 3. Experimental Values of Specific Heat of Working Standard VÉT 70-2-78

T, °K	c, J/kg • deg K	T, °K	c, J/kg • deg K
85,11	81,13	146,76	300,53
88,10	89,54	150,76	316,26
90,90	97,59	154,28	330,07
93,55	105,53	157,67	343,42
96,96	116,22	160,96	356,25
99,31	123,82	164,16	368,61
101,77	131,94	167,26	380,65
104,32	140,53	170,41	392,72
106,77	148,91	188,35	459,67
109,33	157,94	206,50	523,52
112,02	167,50	229,00	596,05
114,66	177,09	252,96	665,41
117,35	187,00	267,29	703,09
120,03	196,92	270,77	711,88
122,61	206,70	274,64	721,47
125,53	217,73	278,89	731,64
128,77	230,18	283,09	741,57
131,87	242,17	287,26	751,10
134,84	253,75	291,33	760,50
137,72	264,99	295,41	769,51
140,49	275,91	299,42	778,06
143,20	286,55	300,13	779,53

represents the initial experimental data with an rmserror of less than 0.03%.

Figure 1 shows the relative deviations δc of the experimental values of the specific heat of the special measure (all four series), the working standards VÉT 70-1-78 and VÉT 70-2-78, and the pale pink corundum specimen of the new batch from the values calculated from Eq. (1). Figure 1 shows that when the above-indicated requirements regarding selection of the granules are met the reproducibility of the data is very high. Within the limits of measurement error the investigated specimens were practically indistinguishable as regards specific heat. This indicates that there is no point in continuing individual attestation of specific heat working standards composed of GOST 9618-61 uncolored and slightly colored corundum.

The working standards VÉT 70-1-78 and VÉT 70-2-78 are now used, in accordance with [1], for the ratification and testing of standard means of the first class and precision working means of measurement with containers up to 150 cm^3. The testing of means of measurement with containers of more than 150 cm^3 necessitates the investigation and attestation of a batch of corundum of at least 1 kg as a working standard. Such a set of working standards is quite sufficient for all practical cases where testing of corundum is required.

TABLE 4. Experimental Values of Specific Heat of Pale Pink Corundum Specimen

T, °K	c, J/kg • deg K	T, °K	c, J/kg • deg K	T, °K	c, J/kg • deg K
83,13	75,85	140,80	277,21	206,76	524,62
86,03	83,71	142,88	285,36	209,99	535,51
88,75	91,39	144,92	293,35	213,42	546,82
91,31	98,91	148,87	308,99	216,79	557,80
93,74	106,25	152,78	324,37	220,10	568,42
96,06	113,46	154,85	332,52	223,36	578,92
98,45	121,11	156,89	340,52	226,34	588,11
100,64	128,29	158,89	348,33	236,47	618,99
102,94	135,92	160,85	355,94	245,42	644,79
105,56	144,84	163,34	365,65	250,59	659,15
108,33	154,50	166,34	377,25	255,68	673,12
110,99	163,90	172,13	399,43	259,88	684,33
113,55	173,11	175,38	411,75	264,02	695,02
116,24	182,98	179,01	425,42	272,13	715,46
119,06	193,41	182,14	437,13	276,11	725,21
121,77	203,60	184,75	446,81	280,52	735,80
126,91	223,16	187,72	457,67	285,36	747,16
129,39	232,70	191,05	469,77	290,13	758,12
131,80	242,02	194,32	481,30	294,84	768,48
134,10	250,99	197,52	492,66	299,48	778,51

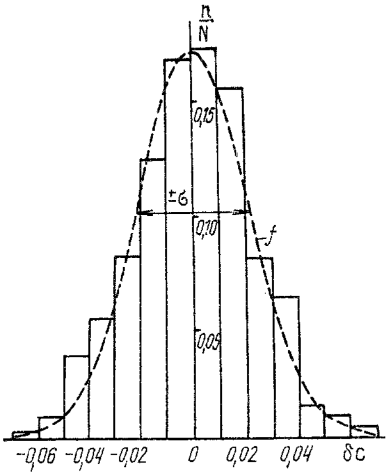

Fig. 2. Histogram showing distribution of relative errors relative to the mean of all the experimental points.

From the results of the comparison we can also draw the following conclusions regarding the metrological characteristics of the standard GÉT 70-75. The distribution of random errors in the investigated temperature range indicates that the specific heat measurements are equally accurate as regards relative error.

The histogram (Fig. 2) representing the distribution of relative errors relative to the mean of all the experimental points* confirms that the distribution is normal and allows determination of the variance and standard deviation. The relative standard deviation is less than 0.03%, which is much smaller than the value given in the specifications of GÉT 70-75 (0.05%). The obtained results indicate that the investigated specimens, including the working standards VÉT 70-1-78 and VÉT 70-2-78, can be combined into one working standard, consisting of the combined batch of material. The subsequent investigation of new batches of corundum will settle the question of whether the confidence interval of the specific heat data recommended as a whole for GOST 9618-61 synthetic corundum [4] can be significantly reduced.

In conclusion we note that the results of our generalization were compared with the results of measurements of the specific heat of the working standard VÉT 70-1-78 at VNIIFTRI [5]. The two groups of data agreed sufficiently well. At temperatures above 140°K, however, there was a systematic deviation of the data of [5] of 0.08% on the average, which can be accounted for by the less favorable ratio of specific heats of the empty and full container than in the state standard. Thus, the estimates of the errors given in [5] are slightly underestimated.

NOTATION

c, specific heat; T, absolute temperature; c_{calc}, calculated values of specific heat; c_{exp}, experimental values; $\delta c = [(c_{exp} - c_{calc})/c_{exp}]\cdot 100\%$, relative deviations of experimental values of specific heat; f, theoretical normal curve of relative errors.

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*Some of the experimental points (142) are omitted from Tables 1-4, since they were obtained at temperatures very close to those indicated in the tables. The purpose of obtaining these data was to investigate the reproducibility and spread of the measurement results.

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THERMAL EXPANSIVITY OF TEFLON UNDER HIGH PRESSURE

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Results of $(\partial T/\partial P)_S$ measurements are presented involving Teflon. The dependence of its thermal expansivity α on the pressure has been determined within the stability range for various modifications of this material ($P \leq 13$ kbar, $0 \leq T \leq 50°C$).

Polymer materials are nowadays widely used. In high-pressure technology, e.g., Teflon (polytetrafluoroethylene, fluoroplastic-4) has been widely accepted as a structural material. Naturally, it seems worthwhile to more thoroughly study the behavior of this material under extreme pressures and temperatures.

Several studies have dealt with the properties of Teflon under high pressure: its phase diagram was determined [1], its equations of state were derived [2-4], and the pressure dependence of its thermal conductivity as well as of its specific heat was determined [5, 6]. The trend of the V(T) relation, determined at various pressures, suggests that the thermal expansivity of the initial low-temperature Teflon modification (II) under pressure is negative [2]. In a later study [4] this apparent negative value of α has been explained by a slow II → III transition. The high-temperature modification (III) is characterized by a high density, the transition causing the volume of a specimen to decrease with rising temperature, which could indeed lead to incorrect readings. Estimates of α on the basis of the equation of state [3] have yielded positive values for all three modifications, but the change of α during the transition cannot be easily determined from the results of that study. The thermal expansivity of Teflon under pressure at room temperature was also measured directly [6]. It was found to be positive over the entire range of measurements ($P \leq 40$ kbar), but the poor accuracy (∿10%) of these measurements made a determination of its change during the transition impossible.

In this study was measured the pressure dependence of the derivative $(\partial T/\partial P)_S$. With this derivative known, and also the specific heat $C_P(P)$ [or $K_S(P)$] known, it is possible to determine α (or γ) from the relation

$$(\partial T/\partial P)_S = \frac{TV}{C_P}\alpha = \frac{T}{K_S}\gamma,$$

where K_S is the adiabatic modulus of isotropic compression and γ is the Grüneisen parameter.

The method of measurements was based on recording the temperature jump in a specimen due to a sharp change of pressure in the chamber [7]. The measurements were made in a high-pressure apparatus of the cylinder-piston type, under hydrostatic conditions. The pressure jump (≈100 bars) was measured with a Manganin probe and the corresponding temperature change was measured with a Chromel—Alumel thermocouple. The accuracy of a $\Delta T/\Delta P$ determination was of the order of 2%. The specimen of Teflon had been prepared in the form of a cylinder ≈10 mm high and ≈8 mm in diameter.

The graph in Fig. 1 depicts experimental values of the derivative $(\partial T/\partial P)_S$ for Teflon under pressures up to 13 kbar at three different temperatures (curves 1-3), based on measurements during forward and reverse cycles. This range covers the stability ranges for all

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