Rapport BIPM-08/05

Measurement of the Specific Heat Capacity of Synthetic Sapphire (α-Al_2O_3) from 293 K to 301 K

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ABSTRACT

The specific heat capacity of a sample of synthetic sapphire, α-Al_2O_3, has been measured over the temperature range from 293 K to 301 K. It has a measured value of 768.9 $Jkg^{-1}K^{-1}$ at 295 K with a combined relative standard uncertainty of 9 parts in 10^4, dominated by systematic effects that have been carefully analysed. The experimental temperature-time data were analysed using an empirical physical model designed for this particular application. The new value agrees with the recommended value for the specific heat capacity of sapphire in the range of room temperature. In the context of graphite calorimetry, the measurements confirm that the same apparatus and method can be used to determine the specific heat capacity of graphite to the required accuracy.

1. INTRODUCTION

Within the scope of realizing a primary standard to determine absorbed dose to water using a graphite calorimeter, a series of measurements of the specific heat capacity of graphite has recently been carried out at the BIPM [1-3]. The specific heat capacity of a graphite sample was determined with a combined relative standard uncertainty of 9 parts in 10^4 [2][i]. When studying reported uncertainties of former determinations of specific heat capacity, it is sometimes not possible to distinguish statistical from non-statistical uncertainties and in some cases it is doubtful whether the latter uncertainties have been included [4]. One means of testing the robustness of the present measurement, and assessing its uncertainty in relation to other data, is to apply the adopted experimental methods to a reference material, such as sapphire.

Synthetic sapphire, α-Al_2O_3, is commonly used as reference material for differential scanning calorimeters (DSCs). It has been supported as a standard reference material for specific heat capacity by the National Institute of Standards and Technology (NIST) since the 1970s [5]. Synthetic sapphire can be produced to high purity, is chemically and mechanically stable and provides outstanding electric isolation. Polished, it offers an excellent surface quality. Additionally, its material constants are expected to be highly reproducible.

The thermodynamic properties and former determinations of the heat capacity of sapphire have been reviewed by Archer [6]. This reference constitutes the basis for one of several recommended standard practices for the heat flow calibration of DSCs [7]. These earlier reported measurements were made on samples of various forms. In the present case, a sample of about 30 g was needed to reduce the influence of the heating device and temperature sensors. For this reason, a cylinder of synthetic sapphire was purchased[ii].

This report describes the measurement of the specific heat capacity of α-Al_2O_3 over a 9 K temperature range around ambient temperature. The measurement principle is outlined, followed by a brief description of the major stages of the realization of these measurements. The results are discussed and the experimental uncertainty is examined.

2. EXPERIMENTAL REALIZATION

The measurement technique has many similarities to the method that has been applied by the absorbed-dose calorimetry group at the National Physical Laboratory (UK) to measure the specific heat capacity for graphite samples [8]. It consists of heating a well-known quantity of matter using an accurately determined amount of energy, where the temperature rise can be measured precisely and heat exchanges minimized. The experimental device that was built for this purpose at the BIPM is described in detail in [1].

[i] The uncertainties given in this paper have not been expanded, i.e. the coverage factor $k = 1$.
[ii] Supplied by Roditi International Corporation Ltd, England.

The cylinder of synthetic sapphire acquired for the present experiment has a nominal height of 23 mm that is also its diameter, to minimize the surface-to-volume ratio. Three 0.5 mm diameter holes, 6 mm deep and positioned at the half height of the cylinder, were machined by the manufacturer. A thermistor bead was introduced into each hole: two thermistors act as temperature sensors and the third thermistor is used to heat the sample. A small amount of thermally conducting grease was added to provide thermal contact between the thermistors and the sample. The two sensing thermistors were mounted in opposite arms of a d.c. powered Wheatstone bridge, linked to a calibrated nanovolt-meter, to measure temperature. The total self-heating using a 1.14 V supply is estimated to be less than 60 μK/min. The heating thermistor was connected to a calibrated passive electronic assembly to measure the thermistor power during each measurement cycle via a computer-controlled digital acquisition card. As the thermistor heating is highly localized, the connecting wires were wound around the sapphire sample three times to enable heat re-absorption and hence reduce heat loss by conduction via this path. To assure a good thermal contact between the wires and the sample, cyanoacrylate was used as an adhesive. Previous measurements for a graphite sample indicated that three windings are adequate for this purpose [2].

The Wheatstone bridge was temperature-calibrated against a platinum resistance thermometer by placing the sapphire sample and thermometer in a temperature-stabilized water tank offering a stability of a few mK. The temperature was varied in 0.5 K intervals over a span from 293 K to 301 K.

The sapphire sample was placed on a three-legged wooden support with minimal contact area, inside a heavy copper housing. The latter not only anchors the system to the surrounding temperature, but also offers reflectivity to reduce heat loss via radiative heat transfer. The copper housing was in turn placed inside, and in good thermal contact with, a vacuum container of stainless steel. This container, and those parts of the electronic equipment that are either physically linked to the sapphire sample or are sensitive to temperature variations, were located in a temperature stabilized insulated cabin.

The measurement routine was computer-controlled. Each heating period was triggered only when specified stability conditions were fulfilled. A series of data was collected from 293 K to 301 K. In figure 1 an example of a recorded temperature-time distribution for sapphire is shown, using a sampling rate of 3.5 Hz. Pre-heating data were first recorded over 60 s. If the pre-heating drift was less than 0.3 μK/s and other conditions required for the temperature stability of the surroundings are met, the heating sequence was triggered and lasted 40 s. After this heating, data were recorded for another 200 s.

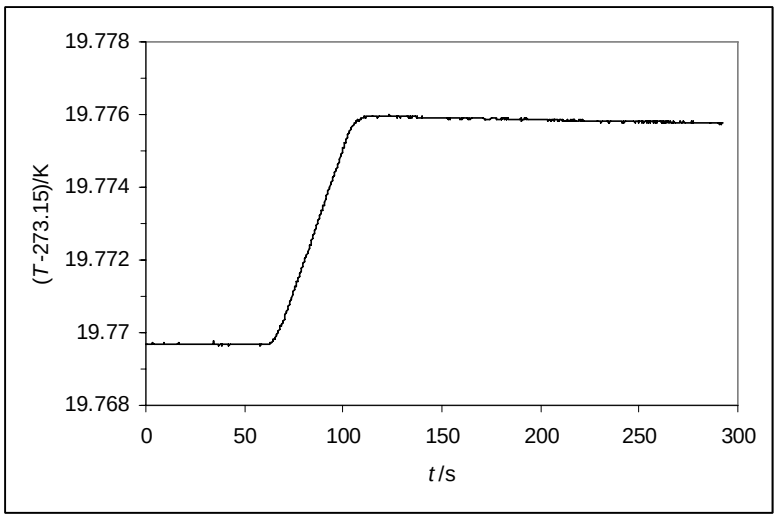

Fig. 1. A typical measured temperature curve for the BIPM sapphire sample.

3. ANALYSIS

The ideal relation between injected energy, E, and the specific heat capacity of sapphire, c_{p}, can be written as

$$E = \Delta T \cdot m_S \cdot c_{\mathrm{p}}\,, \tag{1}$$

where ΔT is the temperature increase and m_{S} represents the mass of the sapphire sample. In practice, any material present that is not sapphire will absorb a part of the injected energy. Heat losses, E_{loss}, may also be present. Hence, the relation can be expressed as

$$E = \Delta T \cdot m_S \cdot \left[c_{\mathrm{p}} + \sum_i \frac{c_i \cdot m_i}{m_S} \right] + E_{loss}\,, \tag{2}$$

where the index i refers to each non-sapphire component present as an added impurity. Experience with graphite samples has shown that heat losses from the heating thermistor wires can be significant, and that care must be taken to ensure good thermal contact between these wires and the sample [2]. The agreement between the two methods used for graphite [2] indicates that heat losses were reduced to a negligible level. This should also be the case for the sapphire sample because of the superior thermal contact that results from the smoother surface of sapphire.

To correct the measured specific heat capacity for added impurities, the mass and physical data for all added impurities must be known, or their relative mass should be sufficiently small that their impact is below the target uncertainty. Therefore, while preparing the sample, the quantity of material added was recorded at each stage. The mass of the sample was determined from the mean value of several determinations. It was corrected for the air buoyancy effect according to [9, 10], where the temperature,

relative humidity and atmospheric pressure were taken into account. The mass m_S of the sapphire sample and its combined standard uncertainty $u_c(m_S)$ were determined as

$$m_S / \text{g} = 38.0595 \qquad u_c(m_S) / \text{g} = 0.0005. \tag{3}$$

The contributions for the added impurities are listed in table 1. The correction factor for c_p is hence estimated to be

$$\left[\sum_i \frac{c_i \cdot m_i}{m}\right] / \{\text{J kg}^{-1}\text{K}^{-1}\} = \frac{3.2 \cdot 10^{-2}}{38.06 \cdot 10^{-3}} = 0.8\,, \tag{4}$$

with a standard uncertainty of

$$\frac{4.0 \cdot 10^{-3}}{38.06 \cdot 10^{-3}}\ \text{J kg}^{-1}\text{K}^{-1} = 0.11\ \text{J kg}^{-1}\text{K}^{-1}. \tag{5}$$

The uncertainty arising from the impurity correction contributes 1.5 parts in 10^4 to the relative uncertainty.

Table 1. Added impurity contributions for the BIPM sapphire sample, where m_S and m_i are the mass of the sapphire sample and the added impurities, respectively. The specific heat capacities of the added impurities are denoted by the c_i.

		m_S /kg		
α-Al_2O_3		38.0595 (5) $\cdot 10^{-3}$		
Impurity ↓	i	m_i /kg	c_i / J kg^{-1} K^{-1}	($c_i \times m_i$)/ J K^{-1}
3 beads	1	$1.5(1)\cdot10^{-6}$	$6(2)\cdot10^{2}$	$9(3)\cdot10^{-4}$
thermal paste	2	$1.9(2)\cdot10^{-6}$	$9(3)\cdot10^{2}$	$1.7(6)\cdot10^{-3}$
cyano acrylate [2]	3	$7.6(2)\cdot10^{-6}$	$1.42(2)\cdot10^{3}$	$1.08(3)\cdot10^{-2}$
2 turns 80µm	4	$19(1)\cdot10^{-6}$	$9.5(2)\cdot10^{2}$	$1.8(4)\cdot10^{-2}$
$\sum_i$				$3.2(4)\cdot10^{-2}$

Contrary to earlier work in this field, where the temperature rise is usually determined by extrapolations to the mid-time, the data were analysed using an empirical physical model designed for this purpose. Four variable parameters, consisting of the

initial sapphire temperature, the ambient temperature, a heat transfer coefficient and a heat input coefficient, are used to simulate a temperature distribution as a function of time. A fifth parameter is added representing the rate of heat diffusion in the sample, for a specific sample material and geometry. This parameter can be varied, but it is considered as fixed for a given sample. The simulated sample is divided into ten virtual elements, the heat being transported from element to element, representing the temperature along one dimension in the sample from the heating thermistor to the sensing thermistors. The method does not require knowledge of the absolute time when the heat is switched on and off, but only the duration, which is precisely known. The variation of the five parameters continues until a satisfying agreement is achieved between the experimental and simulated distributions. Knowing the final heat input coefficient, the unperturbed temperature rise ΔT can be calculated. The energy input was chosen so that the temperature rise was usually between 8 mK and 20 mK, to maximize the signal-to-noise ratio while avoiding non-linear effects. In figure 2 the difference between the experimental temperature-time distribution of figure 1 and the calculated distribution is shown as a function of time. The standard deviation is 12 µK.

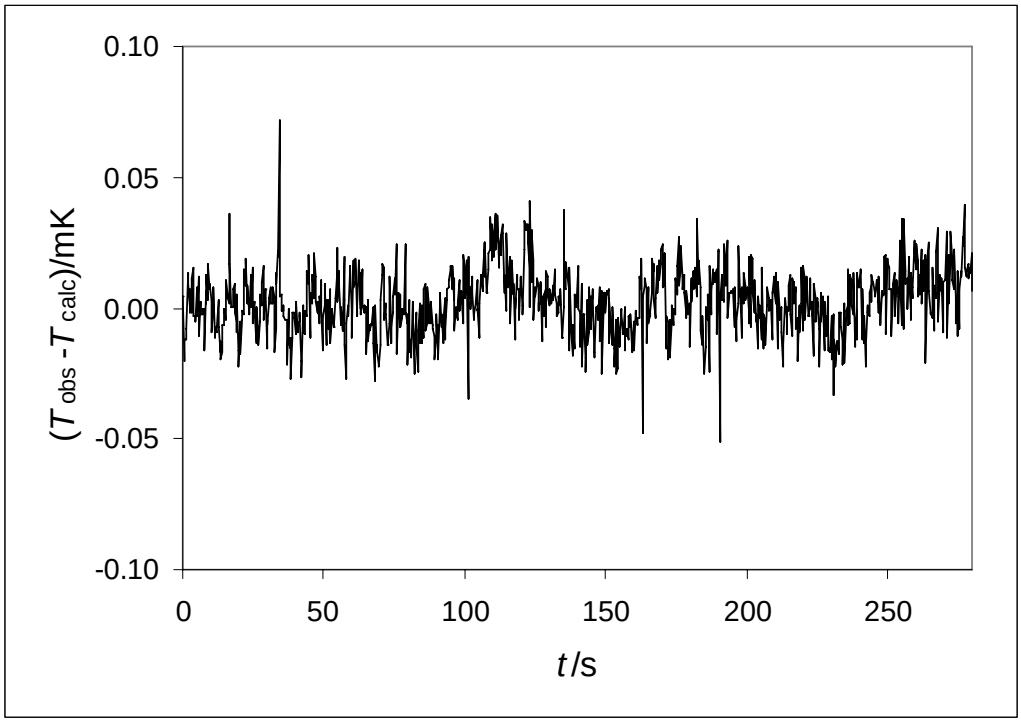

Fig. 2. Temperature difference between observed and calculated temperature curves for a single measurement.

4. RESULTS AND DISCUSSION

The raw data for the specific heat capacity are depicted in figure 3. Each data point was obtained from 15 repeat measurements. The uncertainty bars indicate the statistical standard uncertainty of each mean value.

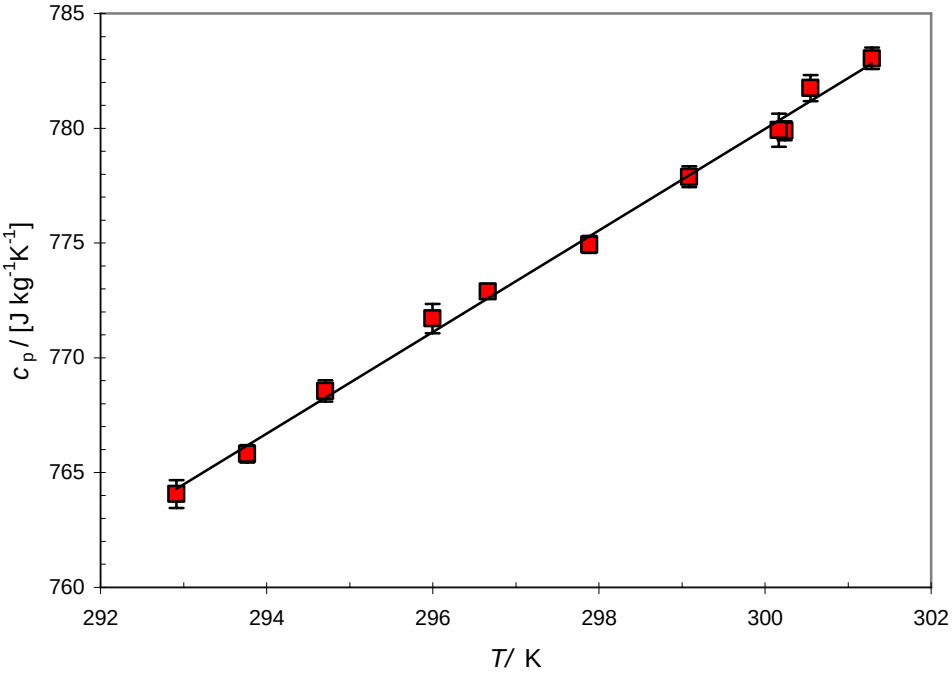

Fig. 3. Measured values for the specific heat capacity, c_p, of synthetic sapphire (α-Al_2O_3) plotted as a function of temperature, T, where no correction for added impurities has been made. The uncertainty bars represent the statistical standard uncertainties.

Fitting a first-order polynomial to these data after correction for added impurities using (4), the relation

$$c_p / \{\mathrm{J\ kg^{-1}K^{-1}}\} = 768.9 + 2.2\cdot(T/\mathrm{K} - 295.0) \qquad (6)$$

is obtained for the temperature region from 293 K to 301 K. The uncertainty budget is given in table 2, where it is evident that the largest contributions are systematic. The combined standard uncertainty is 0.7 J kg^{-1} K^{-1} at 295 K. The uncertainty in the gradient is 0.1 J kg^{-1} K^{-2}.

Previous measurements for sapphire by other groups were made on specific Calorimetry Conference Samples (1948)[iii] or SRM 720 samples, all distributed by the NIST. The purity of such samples was examined at that time, the impurities approximated to 2 parts in 10^4 and estimated to contribute less than 0.02 % to the relative uncertainty of the specific heat capacity [11]. The sample used in the present work originated from a different source. Unfortunately, the manufacturer of the sample was not disclosed by the supplier. However, information on representative impurity contents was available, obtained from measurements using glow discharge mass spectroscopy. These indicate in total 20 ppm, i.e. 2 parts in 10^5, excluding Al and O impurities.

The reference data on specific heat capacity for synthetic sapphire listed by the NIST [5] was revised by Archer in 1993 [6]. Enthalpy measurements made by Archer and Rudtsch ten years later agree within 5 parts in 10^4 with those of the revision [12]. This revision includes eight sources of data, spanning over more than thirty years and covering a total temperature region from 10 K to 2250 K. The revised data are given in steps of 10 K. The data obtained in the present work span only 9 K. Therefore, to compare these data, a second order polynomial was fitted to the data of Archer using nine data points centred on the temperature of the present measurement series, i.e. from 250 K to 330 K. The relation

$$c_p / \{\mathrm{J\,kg^{-1}K^{-1}}\} = 768.5 + 2.2\cdot(T/\mathrm{K} - 295.0) - 0.6\cdot10^{-2}\cdot(T/\mathrm{K} - 295.0)^2 \qquad (7)$$

is obtained. The present value at 295 K is 5 parts in 10^4 higher than that derived in this way from Archer [6]. The measured temperature dependence of the BIPM sapphire in (6) is in agreement with (7).

A new series of measurements on the specific heat capacity of synthetic sapphire was later published by Stølen et *al*. [13], reporting data for temperatures above 307 K. Fitting a second order polynomial to their listed data from 307 K to 340 K the relation

$$c_p / \{\mathrm{J\,kg^{-1}K^{-1}}\} = 769.2 + 2.2\cdot(T/\mathrm{K} - 295.0) - 0.6\cdot10^{-2}\cdot(T/\mathrm{K} - 295.0)^2 \qquad (8)$$

is obtained, where c_p at 295 K is obtained by extrapolation as 769.2 $\mathrm{J\cdot kg^{-1}\cdot K^{-1}}$. The present value is 4 parts in 10^4 lower than this extrapolated value of Stølen et *al*. The value for the specific heat capacity at 295 K measured in the present work and those obtained from Archer [6] and Stølen et *al*. [13] are shown in figure 4. The uncertainty estimation, using a coverage factor $k = 1$, for the value obtained by Stølen et *al*. is dominated by the extrapolation that was made for the present comparison.

[iii] Produced by Linde Air Products Company, later Union Carbide and Carbon Co.

Table 2. Uncertainty budget for the measurement of the specific heat capacity c_S of a synthetic sapphire sample over the temperature range from 292 K to 301 K, where u represents the relative standard uncertainty and u_c the combined relative standard uncertainty at T = 295 K.

	u
statistical uncertainties	2×10^{-4}
energy determination (including calibration of heating circuit resistance, integration method, influence of instrument resolution and sample speed)	2×10^{-4}
mass	1×10^{-4}
added impurity correction	2×10^{-4}
absolute temperature calibration	1×10^{-4}
calibration of temperature difference	5×10^{-4}
simulation of temperature curve	4×10^{-4}
long term stability of power supply	1×10^{-4}
voltmeter calibration, time stability	1×10^{-4}
residual losses from heat source	5×10^{-4}
$\boldsymbol{u_c}$	$\mathbf{9 \times 10^{-4}}$

The overlap between these data for sapphire demonstrates the agreement of the present result with former measurements. This enhances confidence in the validity of the uncertainty budget listed in table 2, in particular the estimation of systematic effects; the three values presented in figure 4 have been obtained by different methods and on different samples, hence systematic effects are unlikely to be of the same origin.

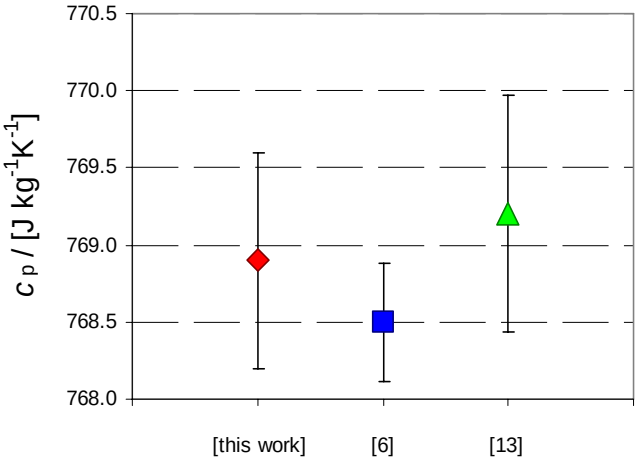

Fig. 4. Values for the specific heat capacity of synthetic sapphire at 295.0 K obtained from this work, interpolated from Archer [6] and extrapolated from Stølen et *al.* [13]. The standard uncertainties are depicted.

In the present measurement, the thermal conductivity of sapphire, λ_S, was not explicitly measured. However, when applying the empirical model, the simulation of temperature-time distributions for a given sample requires a choice to be made for the parameter representing heat transport in the material. A comparison of the heat transport in sapphire and graphite samples, derived from the empirical model, results in a ratio of the thermal heat conductivities of 5:13. The manufacturer of the graphite sample specifies its thermal heat conductivity as λ_g = 75 $Wm^{-1}K^{-1}$ [iv]. This implies a thermal heat conductivity for sapphire of 29 $Wm^{-1}K^{-1}$. Data tables on the thermal heat conductivity of sapphire at room temperature indicate a value between 25 $Wm^{-1}K^{-1}$ and 35 $Wm^{-1}K^{-1}$. This agreement between these estimates gives increased confidence in the empirical model.

5. CONCLUSION

An experimental method designed to measure the specific heat capacity of macroscopic solid samples has been applied to sapphire. An analysis of the uncertainties demonstrates that the absolute value can be determined with a relative combined standard uncertainty of 9 parts in 10^4. The stated purity of the sample allows comparison of the present data with previous measurements made by other groups on samples from a reference batch. The measured value for the specific heat capacity of sapphire of 768.9 $Jkg^{-1}K^{-1}$ at 295 K, as well as the measured temperature dependence, agrees with former results within the stated standard uncertainty. The present result was

[iv] Carbone Lorraine, UHP 5.

obtained using an experimental method and analysis that differ from those used by former groups. In addition, when applied to graphite samples, the present method agrees well with a second, differential method also developed recently at the BIPM [2]. The results of these two experiments give added confidence in the ability of the BIPM to determine specific heat capacity at the stated uncertainty, not only concerning the experimental method itself, but also the empirical analysis technique that is applied to measured temperature-time data.

REFERENCES

[1] Picard S., Burns D.T., Roger P., Measurement of the specific heat capacity of graphite, ***Rapport BIPM-2006/01***, 31 pp

[2] Picard S., Burns D.T., Roger P., Determination of the Specific Heat Capacity of a Graphite Sample Using Absolute and Differential Methods, ***Metrologia* 44 (2007) 294-302.**

[3] Picard S., Burns D.T., Roger P., Measurement of the Specific Heat Capacity of an Ensemble of Graphite Samples, *to be published*.

[4] Gmelin E., Sarge St.M., *Pure & Appl. Chem*. **67** (1995) 1789-1800.

[5] National Bureau of Standards certificate, standard reference material 720 synthetic sapphire (α-Al_2O_3) http://nist.gov

[6] Archer D.G., *J. Phys. Chem*. Ref. Data **22** (1993) 1441-1453.

[7] Standard practice for heat flow calibration of differential scanning calorimeters E968-02 (2002, West Conshohocken: ASTM International)

[8] Williams A.J., Burns D.T., McEwen M., Measurement of the specific heat capacity of the electron-beam graphite calorimeter *NPL Report RSA(EXT) 40* (1993, Teddington: National Physical Laboratory)

[9] Giacomo P., *Metrologia* **18** (1982) 33-40.

[10] Davis R.S., *Metrologia* **29** (1992) 67-70.

[11] Ditmars D.A., Douglas T.B., *J. Res. Nat. Bur. Stand*. **75A** (1971) 401-420, and references therein.

[12] Archer D.G., Rudtsch S., *J. Chem. Eng.* Data **48** (2003) 1157-1163.

[13] Stølen S., Glöckner R., Grønvold F., *J. Chem. Thermodynamics* **28** (1993) 1263-1281.