National Standard and New Reference Material for Specific Heat Capacity Measurements

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Thermal analysis and calorimetry share a close relationship in the field of thermal research. With regards to the specific heat capacity, researchers have been able to realize absolute measurement techniques by utilizing drop, conduction, and adiabatic methods that are used in calorimetry. Furthermore, it is possible to optimize differential scanning calorimetry, which is a comparative measurement technique for the specific heat capacity used in thermal analysis, by improving the absolute measurement techniques. At the National Metrology Institute of Japan (NMIJ), we developed a new certified reference material (CRM) for comparatively measuring the specific heat capacity, the single-crystalline silicon-NMIJ CRM 5806a, using a new type of cryogenic adiabatic calorimeter equipped with a pulse-tube refrigerator working in the temperature range from 50 to 350 K. This CRM was produced in accordance with the quality specifications of NMIJ, and complies with the ISO/IEC 17025, ISO 17034, and ISO GUIDE 35 standards. This paper reports on the procedure for fabricating this CRM and using it to perform specific heat capacity measurements at low temperatures. The specific heat capacity was measured using a differential scanning calorimeter in the temperature range from 280 to 340 K. NMIJ CRM 5806a was used to calibrate the heat flow. It was found that the uncertainty evaluation became easier because one factor of the uncertainty evaluation could be removed using the CRM. We show that the development of the CRM using the adiabatic calorimeter has led to an improvement in the specific heat capacity measurement results obtained by the differential scanning calorimeter.

Keywords Specific heat capacity, reference material, differential scanning calorimeter, adiabatic calorimeter, single-crystalline silicon

(Received September 12, 2020; Accepted November 10, 2020; Advance Publication Released Online by J-STAGE November 20, 2020)

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1 Introduction

Specific heat capacity is one of the main thermophysical properties of materials, as well as an important quantity affecting the realization of energy savings, thermal management, and simulations of the thermal design, among other goals. Materials that require precise and accurate measurements of the specific heat capacity, such as ceramics, acrylic resins, compounds, and porous materials, are diversifying with technological development; consequently, the reliability of specific heat capacity measurements is becoming increasingly important in recent years. The goal of national metrology institutes globally is to promote improvements in documented standards, such as those listed by the international organization for standardization.
Table 1 Documented standards related to specific heat capacity measurements by DSC

| Standard No. | Product No. | Title | Melting temperature | Enthalpy of fusion |
|--------------|-------------|-------|---------------------|-------------------|
| ISO 11357-1  | NIST SRM2232 | Indium | 156.595 ± 0.000341°C | 28.51 ± 0.19 J g⁻¹ |
| ISO 11357-4  | NIST SRM2234 | Gallium | 302.9146 ± 0.0001°C | 80.097 ± 0.032 J g⁻¹ |
| BS EN 1159-3 | NIST SRM2235 | Bismuth | 544.556 ± 0.005°C | 53.146 ± 0.082 J g⁻¹ |
| PTB ZRM31401| LGC2601     | Indium | 156.61 ± 0.02°C | 3.296 ± 0.009 kJ mol⁻¹ |
| PTB ZRM31402| LGC2603     | Naphthalene | 80.25 ± 0.03°C | 18.923 ± 0.083 kJ mol⁻¹ |
| PTB ZRM31403| LGC2605     | Acetanilide | 114.34 ± 0.02°C | 21.793 ± 0.085 kJ mol⁻¹ |
| PTB ZRM31404| LGC2606     | Benzoic acid | 122.35 ± 0.03°C | 17.98 ± 0.04 kJ mol⁻¹ |
| PTB ZRM31405| LGC2607     | Diphenylacetic acid | 147.19 ± 0.03°C | 31.16 ± 0.13 kJ mol⁻¹ |
| PTB ZRM31406| LGC2609     | Tin | 231.92 ± 0.02°C | 7.187 ± 0.011 kJ mol⁻¹ |
| PTB ZRM31407| LGC2610     | Biphenyl | 68.93 ± 0.02°C | 18.60 ± 0.11 kJ mol⁻¹ |
| PTB ZRM31408| LGC2611     | Zinc | 419.53 ± 0.02°C | 7.103 ± 0.012 kJ mol⁻¹ |
| PTB ZRM31409| LGC2612     | Aluminum | 660.33 ± 0.05°C | 10.827 ± 0.042 kJ mol⁻¹ |
| PTB ZRM31410| LGC2613     | Phenyl salicylate | 41.79 ± 0.03°C | 19.18 ± 0.08 kJ mol⁻¹ |
| PTB ZRM31411| PTB ZRM31402| Indium | 429.748 ± 0.004°C | 26.84 ± 0.11 kJ mol⁻¹ |
| PTB ZRM31412| PTB ZRM31403| Tin | 505.078 ± 0.004°C | 60.24 ± 0.27 kJ mol⁻¹ |
| PTB ZRM31413| PTB ZRM31404| Bismuth | 544.550 ± 0.010°C | 53.14 ± 0.22 kJ mol⁻¹ |
| NMIJ CRM 5401-a | NMII CRM 5401-a | Cyclohexane | 279.86 ± 0.035 K | 31.9 ± 0.5 J g⁻¹ |

Table 2 Temperature and heat flow calibration materials for DSC

| Product No. | Material      | Melting temperature | Enthalpy of fusion |
|-------------|---------------|---------------------|-------------------|
| NIST SRM2232| Indium        | 156.595 ± 0.000341°C | 28.51 ± 0.19 J g⁻¹ |
| NIST SRM2234| Gallium       | 302.9146 ± 0.0001°C | 80.097 ± 0.032 J g⁻¹ |
| NIST SRM2235| Bismuth       | 544.556 ± 0.005°C | 53.146 ± 0.082 J g⁻¹ |
| PTB ZRM31401| Gallium       | 302.930 ± 0.001°C | 80.14 ± 0.32 J mol⁻¹ |
| PTB ZRM31402| Indium        | 429.748 ± 0.004°C | 26.84 ± 0.11 J mol⁻¹ |
| PTB ZRM31403| Tin           | 505.078 ± 0.004°C | 60.24 ± 0.27 J mol⁻¹ |
| PTB ZRM31404| Bismuth       | 544.550 ± 0.010°C | 53.14 ± 0.22 J mol⁻¹ |
| NMIJ CRM 5401-a | Cyclohexane | 279.86 ± 0.035 K | 31.9 ± 0.5 J g⁻¹ |

(ISO), while optimizing various national standards, reference materials (RMs), and certified reference materials (CRMs) for performing specific heat capacity measurements from the view point of industrial and global needs.

The differential scanning calorimeter (DSC) is the most convenient equipment used to measure the specific heat capacity of materials. The documented standards related to specific heat capacity measurements as well as the temperature and heat flow calibration of the DSC are listed in Table 1. There have also been issued by the British Standard European Norm (BS EN), American Society for Testing and Materials (ASTM), and Japanese industrial standards (JIS), in addition to ISO.

Prior to using the DSC, the temperature and heat flow must be calibrated using calibration materials. The DSC calibration materials are listed in Table 2. These materials have primarily been developed by the National Institute of Science and Technology (NIST), United Kingdom Laboratory of the Government Chemist (LCG), Germany Physikalisch-Technische Bundesanstalt (PTB) and National Metrology Institute of Japan (NMIJ). Indium, tin, bismuth, and zinc are predominantly used as components for these materials, and aluminum is useful for the high-temperature calibration; cyclohexane is used for applications requiring low temperature.

The word “Reference Material (RM)” has been used for a long time, but in recent years it has been defined by ISO as follows: “material, sufficiently homogeneous and stable with reference to specified properties, which has been established to be fit for its intended use in measurement or in examination of nominal properties”. RMs of higher quality than those of existing RMs are termed “certified reference materials (CRMs)”, defined as “reference material, accompanied by documentation issued by an authoritative body, and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures”.

To upgrade an RM to a CRM, associated uncertainties and traceabilities of the RM should be clarified. A RM or CRM developed by NIST is called a Standard Reference Material® (SRM) as an exceptional case. The SRMs and CRM for heat capacity are listed in Table 3.

It is only supplied by NIST and NMII. The first SRM is the molybdenum-SRM781D2 developed in 1977, which can be operated at a high temperature range from room temperature to 2800 K. The certified values were decided by operating a
Bunsen ice calorimeter from 273.5 to 1173.15 K, an adiabatic receiving calorimeter from 1170.4 to 2102.4 K, and the high-speed (millisecond) pulse-heating technique from 1500 to 2800 K. The second SRM is the synthetic sapphire-SRM720 developed in 1982, which can be operated at a wide temperature range from 10 to 2250 K. The certified values were decided by operating the adiabatic calorimeter from 10 to 380 K, Bunsen ice calorimeter from 273 to 1173 K, and an adiabatic receiving calorimeter from 1173 to 2250 K. The third SRM is the polystyrene-SRM705a developed in 1990, which can operate at a low temperature range from 10 to 350 K. The certified values were decided using adiabatic calorimetry. These are used for assessing the validity of various calorimeters and for performing specific heat capacity measurements with a differential scanning calorimeter (DSC), which is widely used owing to convenience. However, these SRMs were developed long before and the quality system of CRMs under the present ISO standards has not been established yet. Therefore, it is necessary to develop a new CRM for specific heat capacity measurements. In 2009, the first CRM for performing specific heat capacity measurements, the single-crystalline silicon-NMIJ CRM 5806a, was developed by National Metrology Institute of Japan (NMIJ). To achieve this, we also developed a cryogenic adiabatic calorimeter that operates in the temperature range from 50 to 350 K and evaluated the uncertainty that complies with ISO 17034 and ISO GUIDE 35. Moreover, as an example of the application of CRM 5806a, the specific heat capacity of NIST SRM 781D2-molybdenum was measured using a power-compensated DSC with CRM 5806a or α-alumina that is traceable to NIST SRM 720, as a calibration material. We report the uncertainty evaluated for the DSC measurement and the validity of CRM 5806a.

### Table 3 The SRMs and CRM for heat capacity

| Product No. | Material          | Temperature | Unit of issue | Certified date |
|-------------|-------------------|-------------|---------------|----------------|
| NIST SRM 781D2 | Molybdenum       | 273.15 – 2800 K | 10 cm         | Apr. 1977      |
| NIST SRM720  | Synthetic Sapphire | 10 – 2250 K | 15 g          | Apr. 1982      |
| NIST SRM 705a | Polystyrene      | 10 – 350 K  | 5 g           | Jul. 1990      |
| NMIJ CRM 5806a | Single-crystalline silicon | 50 – 350 K | 50 mg         | Mar. 2009      |

![Fig. 1 Whole view of the adiabatic calorimeter with a pulse-tube refrigerator.](image)

\[ \Delta H = \Delta Q. \]

Therefore,

\[ C_p = \left( \frac{\partial Q}{\partial T} \right)_p. \]

The heat capacity in actual measurements is represented using the amount of heat applied to a sample, \( \Delta Q \), and the temperature increase by heating \( \Delta T \), as follows:

\[ C_p = \left( \frac{\Delta Q}{\Delta T} \right)_p. \]

In other words, the heat capacity at a temperature \( T \) is expressed as

\[ C_p(T) = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}. \]

The specific heat capacity, \( c_p \), is the heat capacity per unit mass. Therefore, for a specimen with mass \( m \), it is

\[ c_p(T) = \left( \frac{C_p(T)}{m} \right). \]

### 3 Cryogenic Adiabatic Calorimeter Developed as the Standard Equipment for Measuring the Specific Heat Capacity

Figure 1 shows the entire setup of the cryogenic adiabatic calorimeter, built using a pulse-tube refrigerator, which was developed as specific heat capacity standard equipment.

\[ \Delta H = \Delta Q. \]

Therefore,

\[ C_p = \left( \frac{\partial Q}{\partial T} \right)_p. \]

- In other words, the heat capacity at a temperature \( T \) is expressed as
  \[ C_p(T) = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}. \]
  The specific heat capacity, \( c_p \), is the heat capacity per unit mass. Therefore, for a specimen with mass \( m \), it is
  \[ c_p(T) = \left( \frac{C_p(T)}{m} \right). \]

### 2 Definition of Specific Heat Capacity

The heat capacity, \( C_p \), for solid materials is defined as

\[ C_p = \left( \frac{\partial H}{\partial T} \right)_p, \]

where the enthalpy, \( H \), is given by

\[ H = Q + pV. \]

Here, \( Q \) is the internal energy, \( p \) is the pressure, and \( V \) is the volume. Generally, the specific heat capacity of solid materials is considered as the constant pressure specific heat capacity according to the following expression:

\[ \Delta H = \Delta Q + p \Delta V \]

\( \Delta H \) can be negligible in the case of solid materials because the thermal expansion hardly changes.
The pulse-tube refrigerator, SRP-052A-W71C, was manufactured by Sumitomo Heavy Industries, Ltd., with a cooling capacity of 0.5 W at 4.2 K. The adiabatic calorimeter could be cooled without helium cryogens by this pulse-tube refrigerator; thus, cost reduction and simplification of the arrangement for the measurements and a long stable endurance run became possible. Figure 2 shows the internal structure of the adiabatic calorimeter. This equipment was able to mitigate the influence of vibration caused by operation of the refrigerator by separating the rotary valve unit from the cold head. The body of the calorimeter, located in the lower part of the refrigerator, consisted of a vacuum chamber, radiation shield, high-vacuum chamber, an outer shield, inner shields in two parts (side and bottom), and a sample cell. To suppress heat exchange between the outside and inside of the calorimeter, the sample cell and inner and outer shields were hung by nylon thread. The cell is shown in Fig. 3. It mainly comprises oxygen-free copper, and the surface of the cell is plated with gold. The mass of the cell was 18.8 g and, the volume was 4.16 cm³. A platinum resistance thermometer and a main heater were embedded in the center of the cell by means of a low-melting-point solder. The thermometer was a capsule-type S1059 made by MINCO Products, Inc., with a diameter of 3.2 mm and length of 9.7 mm. The thermometer resistance was measured at fixed temperature points, defined by ITS-90 or by comparison with a calibrated platinum resistance thermometer traceable to NIST. The minimum temperature at which a measurement was possible was 13.8033 K, but the actual measurement was carried out from approximately 30 K due to various factors such as self-heating of the system. A strain gauge with a small film shape was used as the main heater. A specimen was set by an indium seal in a sample cell filled with helium gas. The ideal specimen dimensions for which measurement was possible were an outer diameter of 17 mm, an inner diameter of 5 mm, and a height of 15 mm.

The adiabatic control system around the cell is shown in Fig. 4. The temperature difference between the sample cell and inner shield (side) was detected by a differential thermocouple (TC1), and a shield heater (H1) was controlled by a software proportional-integral-differential (PID) controller system to offset the temperature difference. The temperature differences between the two-part inner shield (side and bottom), and between the inner shield (side) and the outer shield, were also controlled using two differential thermocouples (TC2 and TC3) and two shield heaters (H2 and H3). Thus, temperature control around the cell could be performed efficiently by these three pairs of systems.

4 Verification of the Reliability of the Measurement by the Cryogenic Adiabatic Calorimeter

First, the heat capacity of the empty sample cell was measured in the temperature range from 50 to 350 K. A basic measurement program that repeats the isothermal condition and the temperature rise by heating the cell is shown in Fig. 5. The specific heat capacity can be obtained as follows:

\[
c(T_m) = \frac{c(T_m)}{m} = \frac{\Delta Q}{m(T_f - T_i)} = \frac{\Delta Q}{m\Delta T},
\]

\[
T_m = \frac{T_i + T_f}{2},
\]

where, \(T_m\) measurement temperature; \(\Delta Q\) Joule heating from the cell heater; \(T_i\) initial temperature at which heating begins; \(T_f\) final temperature at which heating ends; \(m\) mass of a specimen. The temperature interval, \(\Delta T\), was set to 1 K for temperatures
below 90, and 2 K for temperatures above 90 K. The time interval from \( t_1 \) to \( t_2 \) (and from \( t_3 \) to \( t_4 \)) was 20 min and that from \( t_2 \) to \( t_3 \) was set to 40 min as shown in Fig. 5. The results of the three temperature-dependent measurements are shown in Fig. 6(a). A comparison of the deviation between the reproducibility, obtained by resetting the cell after every measurement, and the repeatability, obtained by repeating the measurement while keeping the cell set, is shown in Fig. 6(b). The deviation of the two results was found to be within 1%.

Next, the specific heat capacity measurement of NIST SRM 720 was performed to verify the reliability of measurement.\(^{26–28}\) The measurement specifications are the same as those for the empty cell. The heat capacity of the synthetic sapphire was obtained by subtracting from that of the empty sample cell. The deviation between the measurement result and the certified value was within 1%. The preliminary measurement results are in good agreement with the certified values.

5 Estimation of Single-crystalline Silicon as a Certified Reference Material

The candidate material for the CRM is single-crystalline silicon, which is well known to be homogeneous and stable. Test specimens for measurement by the adiabatic calorimeter were cut from the midsections and three edges of an ingot, as shown in Fig. 7 (No. 1 (upper part), No. 2 (center), No. 3 (lower part), and No. 4 (side piece)). Each test specimen had an outer diameter of 17 mm, an inner diameter of 5 mm, a height of 15 mm, and a mass of approximately 7 g. Specimens for the DSC were also cut to a diameter of 5 mm and a thickness of 1 mm from the underside where No. 1 – No. 4 were cut. This shape was suitable for measurement with the DSC. Figure 8 shows the measurement results for the four specimens, obtained using the adiabatic calorimeter in the temperature range from 50 to 350 K. The characteristic value was fitted using a regression curve for the temperature function using the least-squares method. The temperature range beyond 50 K was divisible into three areas as a function of temperature, and the characteristic values are as follows:

\[
\begin{align*}
50 \text{ K} & \leq T < 100 \text{ K} \\
C_p,_{\text{CRM}} & = 4.0206 \times 10^{-2} - 5.8826 \times 10^{-5} T + 2.4772 \times 10^{-7} T^2 \\
& - 3.1655 \times 10^{-8} T^3 + 2.4772 \times 10^{-10} T^4 \\
& - 4.9465 \times 10^{-11} T^5, \\
100 \text{ K} & \leq T < 200 \text{ K} \\
C_p,_{\text{CRM}} & = -4.0837 \times 10^{-2} + 1.7123 \times 10^{-3} T - 2.0234 \times 10^{-5} T^2 \\
& - 7.1941 \times 10^{-7} T^3 - 6.3602 \times 10^{-10} T^4 \\
& + 3.8280 \times 10^{-11} T^5, \\
200 \text{ K} & \leq T < 350 \text{ K} \\
C_p,_{\text{CRM}} & = -0.81477 + 1.6542 \times 10^{-4} T - 3.8727 \times 10^{-6} T^2 \\
& + 2.6977 \times 10^{-7} T^3 - 4.5515 \times 10^{-10} T^4 \\
& + 3.1789 \times 10^{-13} T^5.
\end{align*}
\]

To develop a CRM, it is necessary to estimate the uncertainty in the measurement, \( u_{\text{meas}} \), the uncertainty in the homogeneity of the master material, \( u_{\text{homo}} \), the stability of the characteristic value, \( u_{\text{stab}} \), and the regression curve of the temperature dependence of the specific heat capacity, \( u_{\exp} \). The all-inclusive uncertainty present in the CRM, \( u_{\text{CRM}} \), is determined as
An uncertainty evaluation method for specific heat capacity measurement using the adiabatic calorimeter, $u_{\text{meas}}$, has not been realized thus far; therefore, a formula for the uncertainty calculation model is proposed as follows:

$$
C = \frac{\Delta Q_{\text{Joule}} + \Delta Q_{\text{loss}}}{\Delta T} = \frac{I_m V_m \Delta_T + \delta Q_{\text{loss}}}{\Delta R} \frac{dR}{dT} + \delta Q_{\text{loss}}
$$

where, $C$, heat capacity; $\Delta Q_{\text{Joule}}$, Joule heating; $\delta Q_{\text{loss}}$, heat loss; $\Delta T$, temperature increase; $\Delta R$, resistance change; $R_m$, resistance before heating; $R_f$, resistance after heating; $dR/dT$, temperature coefficient of resistance thermometer; $I_m$, current of Joule heating; $V_m$, voltage of Joule heating; $\Delta_T$, time of Joule heating; $R_m$, standard resistance for monitor current; $V_m$, voltage for monitor resistance; $\delta Q_{\text{loss}}$, heat loss during adiabatic control; $\delta Q_{\text{loss}1}$, heat loss due to temperature drift.

To estimate the uncertainty in the homogeneity, $u_{\text{homo}}$, the measurements using the four specimens were repeated three times. Variance analysis was performed using these results, and it was found that the four specimens were sufficiently uniform statistically. For the stability, a characteristic value change due to long-term storage and multiple temperature fluctuations was confirmed. The uncertainty in the stability, $u_{\text{stab}}$, was sufficiently smaller than the uncertainty in the measurement. The uncertainty in the regression curve, $u_{\text{exp}}$, was estimated using the deviation between the regression curve and the characteristic value at the measurement temperature. In the results, $u_{\text{homo}}$, $u_{\text{stab}}$, and $u_{\text{exp}}$ were much smaller than $u_{\text{meas}}$; hence, it was determined that $u_{\text{CRM}}$ was mainly dependent on $u_{\text{meas}}$. The typical characteristic values and expanded uncertainties are shown in Table 2. The relative expanded uncertainty is 1% at 350 K and 4% at 50 K.

The temperature dependence of the expanded uncertainty, $U_{\text{CRM}}$, with the coverage factor $k = 2$, is expressed using a

![Fig. 6](image1.png)  (a) Heat capacity of the empty cell (three blank measurements), (b) deviation in case of three reset and repetition measurements of the empty cell.

![Fig. 7](image2.png)  Sampling for specimens of the CRM.

![Fig. 8](image3.png)  Temperature dependence of NMIJ CRM 5806a.
fourth-order polynomial fitting:

\[ U_{CRM} = 0.0017509 + 2.1144 \times 10^{-5}T + 1.9668 \times 10^{-7}T^2 - 1.0623 \times 10^{-9}T^3 + 1.3595 \times 10^{-12}T^4. \]

A comparison with seven reference data sources (29–35) for the specific heat capacity of silicon is shown in Fig. 9. The Committee on Data for Science and Technology (CODATA) and the National Institute of Standard and Technology, Joint Army-Navy-Air Force (NIST-JANAF) data (30) are well known and reliable. The reference data and the certified values agreed within the expanded uncertainty \( k = 2 \).

Long-term stability monitoring of the characteristic value was continued periodically based on ISO 17034 (23). It was found that the stability of the CRM was high if the difference between the measurement value when monitoring, \( c_p,\text{meas} \), and the certified value, \( c_p,\text{CRM} \), was within the expanded uncertainty \( U_{CRM} \):

\[ |c_p,\text{meas} - c_p,\text{CRM}| \leq U_{CRM}. \]

The monitoring results of specimen No. 2 from 2008 to 2019 are shown in Fig. 10. Each monitoring result is plotted as a deviation from the characteristic value, and the symmetric dotted lines show the upper and lower limits of the expanded uncertainty \( k = 2 \) of the characteristic value at each temperature. It was confirmed that the change in the significant characteristic value in the past for eleven years was not more than this result.

6 Application of CRM5806a to the Calibration Material of DSC

The DSC is known to be a useful thermal-analytical system that can measure the melting temperature, enthalpy of fusion, and specific heat capacity of various materials, among other features. The specific heat capacity measurement by the DSC involves three runs, namely the blank run, calibration run, and specimen run for the same temperature change program (36–38). A typical DSC in the furnace consists of a twin-type holder, with two holders called “sample” and “reference.” If the furnace is heating at a rate \( \beta \), we have the following equation relating the heat flow, \( \phi \), and \( \rho \), and the heat capacities, \( C_1 \) and \( C_2 \), in the “sample” and “reference” holders, respectively:

\[ \phi - \rho = \beta(C_1 - C_2). \]

In the three runs, while the “reference” holder remains a blank crucible for each run, the “sample” holder changes from being a blank crucible to having a calibration material in the crucible, and finally having a specimen. The equations for these three runs can be written as follows:

\[ \phi_{s,b} - \phi_{r,b} = \beta(C_{s,b} - C_{r,b}), \]
\[ \phi_{s,c} - \phi_{r,b} = \beta(C_{s,c} - C_{r,b}), \]
\[ \phi_{s,s} - \phi_{r,b} = \beta(C_{s,s} - C_{r,b}). \]

where, \( \phi_{s,b} \), heat flow rate for the blank in the reference holder; \( \phi_{s,c} \), heat flow rate for the calibration material in the sample holder; \( \phi_{s,s} \), heat flow rate for the specimen in the sample holder; \( C_{r,b} \), heat capacity of the blank in the reference holder; \( C_{s,b} \), heat capacity of the blank in the sample holder; \( C_{s,c} \), heat capacity of the calibration material in the sample holder; \( C_{s,s} \), heat capacity of the specimen in the sample holder.

From the above three formulas, we obtain

\[ \frac{\phi_{s,s} - \phi_{s,b}}{\phi_{s,c} - \phi_{s,b}} = \frac{C_{s,s} - C_{s,b}}{C_{s,c} - C_{s,b}}. \]

Here,

\[ C_{s,s} - C_{s,b} = m_1 c_s, \]
\[ C_{s,s} - C_{s,b} = m_2 c_s, \]

where, \( c_s \), specific heat capacity of the specimen; \( c_c \), specific heat capacity of the calibration material; \( m_1 \), mass of the specimen; \( m_2 \), mass of the calibration material.

Therefore, we obtain the following formula:

\[ c_s = m_1 c_c \times \frac{\phi_{s,s} - \phi_{s,b}}{\phi_{s,c} - \phi_{s,b}}. \]

Figure 11 shows an example of the DSC curves for runs of a blank, calibration material, and specimen. Thus, the specific
The accuracy of measurement using DSC and analyzed the present data. The measurement must be corrected by an analytical software with the DSC. Each isothermal baseline does not always match, and therefore, the DSC curves in the present data. In the actual measurement, 20 K/min using the stepwise-scan mode in the temperature range from 280 to 340 K. Figure 12 shows an example of the DSC curves. The apparatus was a power-compensated DSC (Diamond DSC, PerkinElmer Co.). The measurement was programmed for an isothermal time of 10 min and the heating rate was set to 20 K/min using the stepwise-scan mode in the temperature range from 280 to 340 K. Figure 12 shows an example of the DSC curves in the present data. In the actual measurement, each isothermal baseline does not always match, and therefore, must be corrected by an analytical software with the DSC system like in Fig. 11. At NMIJ, we developed an original analytical program for the specific heat capacity measurement by the DSC and analyzed the present data. The measurement results of the temperature dependence and the deviation from the certified values of NIST SRM 781D2 are shown in Fig. 13(a) and (b), respectively. The accuracy of measurement using α-alumina was within ±0.5% and that using CRM 5806a was within ±0.2%.

The uncertainty evaluation of the specific heat capacity measurement by the DSC, $u_{\text{meas}}$, was first proposed by Rudtsch. 39

\[
\varphi_s = \frac{m_s c_s}{m} \times \left( \varphi_b + \Delta \varphi_s \right) - \left( \varphi_b + \Delta \varphi_s \right) + \left( \frac{\partial \varphi_c}{\partial T} \right) \Delta T, 
\]

where \( \varphi_{s,b} \), value after baseline correction of \( \varphi_b \); \( \varphi_{s,c} \), value after baseline correction of \( \varphi_c \); \( \varphi_{s,s} \), value after baseline correction of \( \varphi_s \); \( \Delta \varphi_s \), correction of \( \varphi_s \); \( \Delta \varphi_c \), correction of \( \varphi_c \); \( \Delta \varphi_b \), correction of \( \varphi_b \); \( c_s \), specific heat capacity of the calibration material; \( c_r \), specific heat capacity of the reference material; \( \delta \), correction in temperature.

The propagation rule of the uncertainty was calculated for individual factors using the formula for the uncertainty calculation model and makes an uncertainty budget possible. Table 5 shows an example of the uncertainty budgets using the CRM 5806a as the calibration material in the specific heat capacity measurement of Molybdenum-NIST SRM 781D2 with the DSC at 340 K. The relative expanded uncertainty \( (k = 2) \) of the specific heat capacity measurement is estimated to be.

| Temperature \( T/\text{K} \) | Certified value \( c_p/\text{CRM/J K}^{-1} \text{g}^{-1} \) | Expanded uncertainty \( U_{\text{CRM}}/\text{J K}^{-1} \text{g}^{-1} \) |
|-----------------|-----------------|-----------------|
| 50              | 0.0786          | 0.0032          |
| 100             | 0.2583          | 0.0049          |
| 150             | 0.4253          | 0.0065          |
| 200             | 0.5562          | 0.0075          |
| 250             | 0.6480          | 0.0080          |
| 273.15          | 0.6805          | 0.0081          |
| 293.15          | 0.7045          | 0.0081          |
| 300             | 0.7119          | 0.0081          |
| 350             | 0.7568          | 0.0081          |
| 350             | 0.7568          | 0.0081          |

Fig. 12 Example of experimental DSC curves.
approximately 1.6% in the CRM 5806a. On the other hand, in measurements using the α-alumina as the calibration material, the relative expanded uncertainty \((k = 2)\) is estimated to be approximately 1.9%, including an uncertainty in \(\delta c_c\). The addition of one factor slightly increases the overall relative expanded uncertainty \((k = 2)\).

### 7 Conclusions

This paper is a review concerning specific heat capacity measurements from the viewpoints of the national standard and reference material. A new type of cryogenic adiabatic calorimeter using a pulse-tube cryocooler was developed for the national standard of specific heat capacity measurements in the temperature range from 50 to 350 K in order to develop the single-crystalline silicon-NMIJ CRM5806a, which is often used for comparative measurements of DSCs. It was also developed as a CRM by absolute measurements of the specific heat capacity using an adiabatic calorimeter in the temperature range from 50 to 350 K. This CRM was available in the form shown in Fig. 14. To confirm the validity of CRM 5806a, the specific heat capacity of NIST SRM 781D2 was measured using CRM 5806a or α-alumina as a calibration material in the temperature range from 280 to 340 K. The measurement results agreed with the certified value of NIST SRM 781D2 within \(\pm 0.2\%\) in the case of CRM 5806a and within \(\pm 0.5\%\) in the case of α-alumina. It is also clear that the relative expanded uncertainty was reduced and simplified by using CRM 5806a as a calibration material because one factor of the uncertainty could be removed. The specific heat capacity measurement by the DSC can be more precise using the CRM with the uncertainty.

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