NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
U.S. DEPARTMENT OF COMMERCE

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Reference Material 8103

Adamantane for Subambient DSC Temperature and Enthalpy Calibration

REFERENCE MATERIAL INFORMATION SHEET

Purpose: The non-certified values delivered by this Reference Material (RM) are primarily intended for use in the subambient temperature and enthalpy calibrations of differential scanning calorimeters (DSCs), differential thermal analyzers (DTAs), and similar instruments.

Description: A unit of RM 8103 consists of a single bottle containing approximately 1 g of adamantane.

Non-Certified Values: The non-certified transition temperature and enthalpy of transition values for RM 8103 are provided in Table 1. A NIST non-certified value is suitable for use in method development, method harmonization, and process control but lack either adequate accuracy, sufficient documentation, or traceability to the International System of Units (SI) or other higher order reference system [1]. In this instance, the absence of independent verification currently prevents us from conferring the highest level of confidence in the values' accuracy, which is required for designation as certified values [1]. However, great care has still been taken to account for all known or suspected sources of bias and the resulting estimated expanded uncertainties are included in Table 1. The expanded uncertainty is calculated as $U = ku_c$ where u_c is the combined standard uncertainty and k is the coverage factor corresponding to approximately 95 % confidence [2,3]. For the non-certified values shown in Table 1, k = 1.96 and k = 1.92 for temperature and enthalpy, respectively.

Table 1. Non-Certified Transition Temperature (t_{tran}) and Enthalpy of Transition (ΔH_{tran}) for RM 8103[(a)]

t_{tran}	(–64.58 ± 0.20) °C
ΔH_{tran}	(21.64 ± 0.34) J·g^{-1}

(a) Values are expressed as $x \pm U(x)$, where x is the non-certified value and $U(x)$ is the associated expanded uncertainty. The true value lies within the interval $x \pm U(x)$ with 95 % confidence.

Additional Information: Additional information is provided in Appendix A.

Period of Validity: The non-certified values are valid within the measurement uncertainty specified until **05 August 2034.** The value assignments are nullified if the material is stored or used improperly, damaged, contaminated, or otherwise modified.

Maintenance of Non-Certified Value: NIST will monitor this material to the end of its period of validity. If substantive technical changes occur that affect the non-certified values during this period, NIST will update this Reference Material Information Sheet and notify registered users. RM users can register online from a link available on the NIST SRM website or fill out the user registration form that is supplied with the RM. Registration will facilitate notification. Before making use of any of the values delivered by this material, users should verify they have the most recent version of this documentation, available through the NIST SRM website (https://www.nist.gov/srm).

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Additional Non-Certified Values: The non-certified heating rate dependent temperature of transition and enthalpy of transition values for RM 8103 are provided in Table 2. A NIST non-certified value is defined as being suitable for use in method development, method harmonization, and process control but lacking either adequate accuracy, metrological traceability, or sufficient documentation [1]. As discussed in Appendix A, the heating rate dependent temperature and enthalpy values are considered of limited use for calibration; they are included here simply for reference. Also included in Table 2 are the estimated expanded uncertainties. The expanded uncertainty is calculated as $U = ku_c$, where u_c is the combined standard uncertainty and k is the coverage factor corresponding to approximately 95 % confidence [2,3]. Corresponding k values are shown in Table 2.

Table 2. Non-Certified Heating Rate (β) Dependent Transition Temperature (t_{tran}) and Enthalpy of Transition Values (ΔH_{tran}) for RM 8103

β (a) °C·min^{-1}	t_{tran} (b) °C	k (c)	ΔH_{tran} (b) J·g^{-1}	k (c)
1	–64.55 ± 0.17	1.96	21.70 ± 0.28	1.93
3	–64.49 ± 0.15	1.95	21.82 ± 0.19	1.94
5	–64.44 ± 0.17	1.98	21.93 ± 0.17	1.95
10	–64.30 ± 0.31	1.93	22.23 ± 0.40	1.90

(a) Nominal heating rate.

(b) Values are expressed as $x \pm U(x)$ where x is the non-certified value and $U(x)$ is the associated expanded uncertainty. The true value lies within the interval $x \pm U(x)$ with 95 % confidence.

(c) Coverage factor corresponding to approximately 95 % confidence.

Safety: RM 8103 is intended for research use. Consult the safety data sheet for additional information.

Storage: RM 8103 should be stored in a sealed container at room temperature (20 °C ± 5 °C). An open bottle can be reused until the material reaches its expiration date, provided that the open bottle is resealed and stored at room temperature (20 °C ± 5 °C). Adamantane will absorb atmospheric water. Although no deleterious effects were observed for water concentrations as high as approximately 800 µg g^{-1} during the exploratory testing phase, it is recommended that RM 8103 be stored under dry conditions to ensure optimal performance.

Use: Before use, the contents of the RM 8103 bottle should be thoroughly mixed. A clean spatula or similar instrument can then be used to withdraw the appropriate amount of sample for use in instrument calibration. Every possible effort should be made to avoid contamination during handling procedures.

REFERENCES

[1] Beauchamp, C.R.; Camara, J.E.; Carney, J.; Choquette, S.J.; Cole, K.D.; DeRose, P.C.; Duewer, D.L.; Epstein, M.S.; Kline, M.C.; Lippa, K.A.; Lucon, E.; Molloy, J.; Nelson, M.A.; Phinney, K.W.; Polakoski, M.; Possolo, A.; Sander, L.C.; Schiel, J.E.; Sharpless, K.E.; Toman, B.; Winchester, M.R.; Windover, D.; *Metrological Tools for the Reference Materials and Reference Instruments of the NIST Material Measurement Laboratory*; NIST Special Publication (NIST SP) 260-136, 2021 edition; National Institute of Standards and Technology, Gaithersburg, MD (2021); available at https://nvlpubs.nist.gov/nistpubs/SpecialPublications/NIST.SP.260-136-2021.pdf (accessed Nov 2024).

[2] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (2008); available at https://www.bipm.org/en/committees/jc/jcgm/publications (accessed Nov 2024).

[3] Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at https://www.nist.gov/pml/nist-technical-note-1297 (accessed Nov 2024).

[4] Chang, S.-S.; Westrum, E.F.; *Heat Capacities and Thermodynamic Properties of Globular Molecules. I. Adamantane and Hexamethylenetetramine*; J. Phys. Chem., Vol. 64, pp. 1547–1551 (1960).

[5] Westrum, E.F.; *The Thermophysical Properties of Three Globular Molecules*; J. Phys. Chem. Solids, Vol. 18, pp. 83–85 (1961).

[6] Fortin, T.J.; Koepke, A.A.; Splett, J.D.; *Development of Reference Material 8103: Adamantane for Subambient DSC Temperature and Enthalpy Calibration*; NIST SP 260-241; National Institute of Standards and Technology: Gaithersburg, MD (2024); available at https://nvlpubs.nist.gov/nistpubs/SpecialPublications/NIST.SP.260-241.pdf (accessed Nov 2024).

[7] Boerio-Goates, J.; Callanan, J.E.; Differential Thermal Methods; In *Physical Methods of Chemistry, Volume VI: Determination of Thermodynamic Properties*; Rossiter, B.W.; Baetzold, R.C.; Eds.; John Wiley & Sons: New York, NY, pp. 621–717 (1992).
[8] Gmelin, E.; Sarge, S.M.; *Calibration of Differential Scanning Calorimeters*; Pure Appl. Chem., Vol. 67, pp. 1789 –1800, (1995).
[9] Höhne, G.W.H.; Hemminger, W.; Flammersheim, H.J.; *Differential Scanning Calorimetry: An Introduction for Practitioners*; Springer-Verlag: Berlin, Germany (1996).

If you use this RM in published work, please reference:

Fortin TJ, Koepke AA, Splett JD (2024) Development of Reference Material 8103: Adamantane for Subambient DSC Temperature and Enthalpy Calibration. (National Institute of Standards and Technology, Gaithersburg, MD), NIST Special Publication (SP) 260-241. https://doi.org/10.6028/NIST.SP.260-241

Certain commercial equipment, instruments, or materials may be identified in this Reference Material Information Sheet to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Users of this RM should ensure that the Reference Material Information Sheet in their possession is current. This can be accomplished by contacting the Office of Reference Materials 100 Bureau Drive, Stop 2300, Gaithersburg, Maryland 20899-2300; telephone (301) 975-2200; e-mail srminfo@nist.gov; or the Internet at https://www.nist.gov/srm.

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Appendix A

Source and Preparation: The material for RM 8103 was sourced from a single lot (lot # MKCL1826) of high-purity (≥99 %) adamantane purchased from Sigma-Aldrich Inc., St. Louis, MO. As purchased, the material was packaged in sealed plastic bottles, each containing 100 g. A purity of ≥99.9 % was independently confirmed via gas chromatography-mass spectrometry analysis conducted by NIST. Additionally, Karl Fischer (KF) titration was performed by NIST to determine sample water content. A total of six randomly selected samples were tested. Within estimated combined expanded uncertainties, water content was consistent across all six samples with an average value of (416.6 ± 39.1) $\mu g \cdot g^{-1}$. NIST's Office of Reference Material packaged the source material as approximately 1 g aliquots sealed in 10 mL amber glass bottles for distribution as RM 8103. The contents of the supplier's source bottles were combined prior to repackaging to ensure homogeneity.

Temperature and Enthalpy Analysis: Adamantane undergoes a crystalline rearrangement, from a face-centered cubic to a body-centered tetragonal lattice, at approximately –64 °C [4,5]. Value assignments for both the temperature and enthalpy of this transition for RM 8103 were based on DSC measurements, with all analyses performed at NIST [6]. Measurements were made on 15 samples randomly selected from RM 8103 material. The DSC used for these measurements was calibrated for both temperature and enthalpy using certified reference materials from two different national metrology institutes: NIST and Physikalish-Technische Bundesanstalt (PTB). Because DSC measurements are highly sensitive to experimental parameters such as heating rate (β) [7–9], measurements on the 15 RM 8103 samples were made at four different heating rates (1 °C min^{-1}, 3 °C min^{-1}, 5 °C min^{-1}, and 10 °C min^{-1}), and a β-dependent transition temperature and enthalpy of transition value determined for each (see Table 2). However, since individual instruments will presumably exhibit their own particular dependency, β-dependent information is only of limited use; for a reference material the temperature and enthalpy at thermal equilibrium are the values of interest. Therefore, the β-dependent values were extrapolated to determine the temperature of transition and the enthalpy of transition at β = 0 °C min^{-1}. These values are reported as t_{tran} and ΔH_{tran} in Table 1. Additional details can be found in reference 6.

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