NBS SPECIAL PUBLICATION 260-99

U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

Standard Reference Materials:

Feasibility Study for the Development of Standards Using Differential Scanning Calorimetry

Jane E. Callanan, Sandra A. Sullivan,
and Dominic F. Vecchia

The National Bureau of Standards[1] was established by an act of Congress on March 3, 1901. The Bureau's overall goal is to strengthen and advance the nation's science and technology and facilitate their effective application for public benefit. To this end, the Bureau conducts research and provides: (1) a basis for the nation's physical measurement system, (2) scientific and technological services for industry and government, (3) a technical basis for equity in trade, and (4) technical services to promote public safety. The Bureau's technical work is performed by the National Measurement Laboratory, the National Engineering Laboratory, the Institute for Computer Sciences and Technology, and the Institute for Materials Science and Engineering.

The National Measurement Laboratory

Provides the national system of physical and chemical measurement; coordinates the system with measurement systems of other nations and furnishes essential services leading to accurate and uniform physical and chemical measurement throughout the Nation's scientific community, industry, and commerce; provides advisory and research services to other Government agencies; conducts physical and chemical research; develops, produces, and distributes Standard Reference Materials; and provides calibration services. The Laboratory consists of the following centers:

- Basic Standards[2]
- Radiation Research
- Chemical Physics
- Analytical Chemistry

The National Engineering Laboratory

Provides technology and technical services to the public and private sectors to address national needs and to solve national problems; conducts research in engineering and applied science in support of these efforts; builds and maintains competence in the necessary disciplines required to carry out this research and technical service; develops engineering data and measurement capabilities; provides engineering measurement traceability services; develops test methods and proposes engineering standards and code changes; develops and proposes new engineering practices; and develops and improves mechanisms to transfer results of its research to the ultimate user. The Laboratory consists of the following centers:

- Applied Mathematics
- Electronics and Electrical Engineering[2]
- Manufacturing Engineering
- Building Technology
- Fire Research
- Chemical Engineering[2]

The Institute for Computer Sciences and Technology

Conducts research and provides scientific and technical services to aid Federal agencies in the selection, acquisition, application, and use of computer technology to improve effectiveness and economy in Government operations in accordance with Public Law 89-306 (40 U.S.C. 759), relevant Executive Orders, and other directives; carries out this mission by managing the Federal Information Processing Standards Program, developing Federal ADP standards guidelines, and managing Federal participation in ADP voluntary standardization activities; provides scientific and technological advisory services and assistance to Federal agencies; and provides the technical foundation for computer-related policies of the Federal Government. The Institute consists of the following centers:

- Programming Science and Technology
- Computer Systems Engineering

The Institute for Materials Science and Engineering

Conducts research and provides measurements, data, standards, reference materials, quantitative understanding and other technical information fundamental to the processing, structure, properties and performance of materials; addresses the scientific basis for new advanced materials technologies; plans research around cross-country scientific themes such as nondestructive evaluation and phase diagram development; oversees Bureau-wide technical programs in nuclear reactor radiation research and nondestructive evaluation; and broadly disseminates generic technical information resulting from its programs. The Institute consists of the following Divisions:

- Inorganic Materials
- Fracture and Deformation[3]
- Polymers
- Metallurgy
- Reactor Radiation

---

[1] Headquarters and Laboratories at Gaithersburg, MD, unless otherwise noted; mailing address Gaithersburg, MD 20899.

[2] Some divisions within the center are located at Boulder, CO 80303.

[3] Located at Boulder, CO, with some elements at Gaithersburg, MD.

Standard Reference Materials:

Feasibility Study for the Development of Standards Using Differential Scanning Calorimetry

Jane E. Callanan and Sandra A. Sullivan

Center for Chemical Engineering
National Engineering Laboratory
National Bureau of Standards
Boulder, CO 80303

Dominic F. Vecchia

Center for Applied Mathematics
National Engineering Laboratory
National Bureau of Standards
Boulder, CO 80303

Sponsored by:
Office of Standard Reference Materials
National Measurement Laboratory
National Bureau of Standards
Gaithersburg, MD 20899

U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, Secretary
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Director

Issued August 1985

Library of Congress Catalog Card Number: 85-600567

National Bureau of Standards Special Publication 260-99
Natl. Bur. Stand. (U.S.), Spec. Publ. 260-99, 55 pages (Aug. 1985)
CODEN: XNBSAV

U.S. GOVERNMENT PRINTING OFFICE
WASHINGTON: 1985

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402

Preface

Standard Reference Materials (SRM's) as defined by the National Bureau of Standards (NBS) are well-characterized materials, produced in quantity and certified for one or more physical or chemical properties. They are used to assure the accuracy and compatibility of measurements throughout the Nation. SRM's are widely used as primary standards in many diverse fields in science, industry, and technology, both within the United States and throughout the world. They are also used extensively in the fields of environmental and clinical analysis. In many applications, traceability of quality control and measurement processes to the national measurement system is carried out through the mechanism and use of SRM's. For many of the Nation's scientists and technologists it is therefore of more than passing interest to know the details of the measurements made at NBS in arriving at the certified values of the SRM's produced. An NBS series of papers, of which this publication is a member, called the NBS Special Publication - 260 Series, is reserved for this purpose.

The 260 Series is dedicated to the dissemination of information on different phases of the preparation, measurement, certification and use of NBS SRM's. In general, much more detail will be found in these papers than is generally allowed, or desirable, in scientific journal articles. This enables the user to assess the validity and accuracy of the measurment processes employed, to judge the statistical analysis, and to learn details of techniques and methods utilized for work entailing the greatest care and accuracy. These papers also should provide sufficient additional information not found on the certificate so that new applications in diverse fields not foreseen at the time the SRM was originally issued will be sought and found.

Inquiries concerning the technical content of this paper should be directed to the author(s). Other questions concered with the availability, delivery, price, and so forth, will receive prompt attention from:

Office of Standard Reference Materials
National Bureau of Standards
Gaithersburg, MD 20899

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

OTHER NBS PUBLICATIONS IN THIS SERIES

Catalog of NBS Standard Reference Materials (1984-85 edition), Catherine H. Hudson, ed., NBS Spec. Publ. 260 (February 1984). $5.50* SN003-003-02558-5.

Michaelis, R. E., and Wyman, L. L. Standard Reference Materials: Preparation of White Cast Iron Spectrochemical Standards. NBS Misc. Publ. 260-1 (June 1964). COM74-11061**

Michaelis, R. E., Wyman, L. L., and Flitsch, R., Standard Reference Materials: Preparation of NBS Copper-Base Spectrochemical Standards. NBS Misc. Publ. 260-2 (October 1964). COM74-11063**

Michaelis, R. E., Yakowitz, H., and Moore, G. A., Standard Reference Materials: Metallographic Characterization of an NBS Spectrometric Low-Alloy Steel Standard. NBS Misc. Publ. 260-3 (October 1964). COM74-11060**

Hague, J. L. Mears, T. W., and Michaelis, R. E., Standard Reference Materials: Sources of Information, NBS Misc. Publ. 260-4 (February 1965). COM74-11059

Alvarez, R., and Flitsch R., Standard Reference Materials: Accuracy of Solution X-Ray Spectrometric Analysis of Copper-Base Alloys. NBS Misc. Publ. 260-5 (March 1965). PB168068**

Shultz, J. I., Standard Reference Materials: Methods for the Chemical Analysis of White Cast Iron Standards, NBS Misc. Publ. 260-6 (July 1965). COM74-11068**

Bell, R. K., Standard Reference Materials: Methods for the Chemical Analysis of NBS Copper-Base Spectrochemical Standards. NBS Misc. Publ. 260-7 (October 1965). COM74-11067**

Richmond, M.S., Standard Reference Materials: Analysis of Uranium Concentrates at the National Bureau of Standards. NBS Misc. Publ. 260-8 (December 1965). COM74-11066**

Anspach, S. C., Cavallo, L. M. Garfinkel, S. B. Hutchinson, J. M. R., and Smith, C. N., Standard Reference Materials: Half Lives of Materials Used in the Preparation of Standard Reference Materials of Nineteen Radioactive Nuclides Issued by the National Bureau of Standards NBS Misc. Publ. 260-9 (November 1965). COM74-11065**

Yakowitz, H., Vieth, D. L., Heinrich, K. F. J., and Michaelis, R. E., Standard Reference Materials: Homogeneity Characterization of NBS Spectrometric Standards II: Cartridge Brass and Low-Alloy Steel, NBS Misc. Publ. 260-10 (December (1965). COM74-11064**

Napolitano, A., and Hawkins, E. G., Standard Reference Materials: Viscosity of Standard Lead-Silica Glass, NBS Misc. Publ. 260-11 (November 1966). NBS Misc. Publ. 260-11**

Yakowitz, H., Vieth, D. L., and Michaelis, R. E., Standard Reference Materials: Homogeneity Characterization of NBS Spectrometric Standards III: White Cast Iron and Stainless Steel Powder Compact, NBS Misc. Publ. 260-12 (September 1966). NBS Misc. Publ. 260-12**

Spijkerman, J. L., Snediker, D. K., Ruegg, F. C., and DeVoe, J. R., Standard Reference Materials: Mossbauer Spectroscopy Standard for the Chemical Shift of Iron Compounds, NBS Misc. Publ. 260-13 (July 1967). NBS Misc. Publ. 260-13**

Menis, O., and Sterling, J. T., Standard Reference Materials: Determination of Oxygen in Ferrous Materials - SRM 1090, 1091, and 1092, NBS Misc. Publ. 260-14 (September 1966). NBS Misc. Publ. 260-14**

Passaglia, E., and Shouse, P. J., Standard Reference Materials: Recommended Method of Use of Standard Light-Sensitive Paper for Calibrating Carbon Arcs Used in Testing Textiles for Colorfastness to Light, NBS Misc.. Publ. 260-15 (June 1967). (Replaced by NBS Spec. Publ. 260-41.)

Yakowitz, H., Michaelis, R. E., and Vieth, D. L., Standard Reference Materials: Homogeneity Characterization of NBS Spectrometric Standards IV: Preparation and Microprobe Characterization of W-20% MO Alloy Fabricated by Powder Metallurgical Methods, NBS Spec. Publ. 260-16 (January 1969). COM74-11062**

Catanzaro, E. J., Champion, C. E., Garner, E. L., Marinenko, G., Sappenfield, K. M., and Shields, W. R., Standard Reference Materials: Boric Acid; Isotopic and Assay Standard Reference Materials, NBS Spec. Publ. 260-17 (February 1970). Out of Print.

Geller, S. B., Mantek, P.A., and Cleveland, N. G., Standard Reference Materials: Calibration of NBS Secondary Standard Magnetic Tape (Computer Amplitude Reference) Using the Reference Tape Amplitude Measurement "Process A," NBS Spec. Publ. 260-18 (November 1969). (See NBS Spec. Publ. 260-29.)

Paule, R. C., and Mandel, J., Standard Reference Materials: Analysis of Interlaboratory Measurements on the Vapor Pressure of Gold (Certification of Standard Reference Material 745). NBS Spec. Publ. 260-19 (January 1970). PB190071**

Paule, R. C., and Mandel, J., Standard Reference Materials: Analysis of Interlaboratory Measurements on the Vapor Pressures of Cadmium and Silver, NBS Spec. Publ. 260-21 (January 1971). COM74-11359**

Yakowitz, H., Fiori, C. E., and Michaelis, R. E., Standard Reference Materials: Homogeneity Characterization of Fe-3 Si Alloy, NBS Spec. Publ. 260-22 (February 1971). COM74-11357**

Napolitano, A., and Hawkins, E. G., Standard Reference Materials: Viscosity of a Standard Borosilicate Glass, NBS Spec. Publ. 260-23 (December 1970). COM71-00157**

Sappenfield, K. M., Marineko, G., and Hague, J. L., Standard Reference Materials: Comparison of Redox Standards, NBS Spec. Publ. 260-24 (January 1972). COM72-50058**

Hicho, G. E., Yakowitz, H., Rasberry, S. D., and Michaelis, R. E., Standard Reference Materials: A Standard Reference Material Containing Nominally Four Percent Austenite, NBS Spec. Publ. 260-25 (February 1971). COM74-11356**

Martin, J. F., Standard Reference Materials: National Bureau of Standards-US Steel Corporation Joint Program for Determining Oxygen and Nitrogen in Steel, NBS Spec. Publ. 260-26 (February 1971). 85 cents* PB 81176620

Garner, E. L., Machlan, L. A., and Shields, W. R., Standard Reference Materials: Uranium Isotopic Standard Reference Materials, NBS Spec. Publ. 260-27 (April 1971). COM74-11358**

Heinrich, K. F. J., Myklebust, R. L., Rasberry, S. D., and Michaelis, R. E., Standard Reference Materials: Preparation and Evaluation of SRM's 481 and 482 Gold-Silver and Gold-Copper Alloys for Microanalysis, NBS Spec. Publ. 260-28 (August 1971). COM71-50365**

Geller, S. B., Standard Reference Materials: Calibration of NBS Secondary Standard Magnetic Tape (Computer Amplitude Reference) Using the Reference Tape Amplitude Measurement "Process A-Model 2," NBS Spec. Publ. 260-29 (June 1971). COM71-50282

Gorozhanina, R. S., Freedman, A. Y., and Shaievitch, A. B. (translated by M. C. Selby), Standard Reference Materials: Standard Samples Issued in the USSR (A Translation from the Russian). NBS Spec. Publ. 260-30 (June 1971). COM71-50283**

Hust, J. G., and Sparks, L. L., Standard Reference Materials: Thermal Conductivity of Electrolytic Iron SRM 734 from 4 to 300 K, NBS Spec. Publ. 260-31 (November 1971). COM71-50563**

Mavrodineanu, R., and Lazar, J. W., Standard Reference Materials: Standard Quartz Cuvettes, for High Accuracy Spectrophotometry, NBS Spec. Publ. 260-32 (December 1973). 55 cents* SN003-003-01213-1

Wagner, H. L., Standard Reference Materials: Comparison of Original and Supplemental SRM 705, Narrow Molecular Weight Distribution Polystyrene, NBS Spec. Publ. 260-33 (May 1972). COM72-50526**

Sparks, L. L., and Hust, J. G., Standard Reference Materials: Thermoelectric Voltage, NBS Spec. Publ. 260-34, (April 1972). COM72-50371**

Sparks, L. L., and Hust, J. G., Standard Reference Materials: Thermal Conductivity of Austenitic Stainless Steel, SRM 735 from 5 to 280 K, NBS Spec. Publ. 260-35 (April 1972.) 35 cents* COM72-50368**

Cali, J. P., Mandel, J., Moore, L. J., and Young, D. S., Standard Reference Materials: A Referee Method for the Determination of Calcium in Serum, NBS SRM 915, NBS Spec. Publ. 260-36 (May 1972). COM72-50527**

Shultz, J. I. Bell., R. K. Rains, T. C., and Menis, O., Standard Reference Materials: Methods of Analysis of NBS Clay Standards, NBS Spec. Publ. 260-37 (June 1972). COM72-50692**

Richmond, J. C., and Hsia, J. J., Standard Reference Materials: Preparation and Calibration of Standards of Spectral Specular Reflectance, NBS Spec. Publ. 260-38 (May 1972). COM72-50528**

Clark, A. F., Denson, V.A., Hust, J. G., and Powell, R. L., Standard Reference Materials: The Eddy Current Decay Method for Resistivity Characterization of High-Purity Metals, NBS Spec. Publ. 260-39 (May 1972). COM72-50529**

McAdie, H. G., Garn, P.D., and Menis, O., Standard Reference Materials: Selection of Thermal Analysis Temperature Standards Through a Cooperative Study (SRM 758, 759, 760), NBS Spec. Publ. 260-40 (August 1972.) COM72-50776**

Wood, L. A., and Shouse, P. J., Standard Reference Materials: Use of Standard Light-Sensitive Paper for Calibrating Carbon Arcs Used in Testing Textiles for Colorfastness to Light, NBS Spec. Publ. 260-41 (August 1972) COM72-50775**

Wagner, H. L. and Verdier, P. H., eds., Standard Reference Materials: The Characterization of Linear Polyethylene, SRM 1475, NBS Spec. Publ. 260-42 (September 1972). COM72-50944**

Yakowitz, H., Ruff, A. W., and Michaelis, R. E., Standard Reference Materials: Preparation and Homogeneity Characterization of an Austenitic Iron-Chromium-Nickel Alloy, NBS Spec. Publ. 260-43 (November 1972). COM73-50760**

Schooley, J. F., Soulen, R. J., Jr., and Evans, G. A., Jr., Standard Reference Materials: Preparation and Use of Superconductive Fixed Point Devices, SRM 767, NBS Spec. Publ. 260-44 (December 1972). COM73-50037**

Greifer, B., Maienthal, E. J., Rains, T. C., and Rasberry, S. D., Standard Reference Materials: Powdered Lead-Based Paint, SRM 1579, NBS Spec. Publ. 260-45 (March 1973). COM73-50226**

Hust, J. G., and Giarratano, P. J., Standard Reference Materials: Thermal Conductivity and Electrical Resistivity Standard Reference Materials: Austenitic Stainless Steel, SRM's 735 and 798, from 4 to 1200 K, NBS Spec. Publ. 260-46 (March 1975). SN003-003-01278-5*

Hust, J. G., Standard Reference Materials: Electrical Resistivity of Electrolytic Iron, SRM 797, and Austenitic Stainless Steel, SRM 798, from 5 to 280 K, NBS Spec. Publ. 260-47 (February 1974). COM74-50176**

Mangum, B. W., and Wise, J. A., Standard Reference Materials: Description and Use of Precision Thermometers for the Clinical Laboratory, SRM 933 and SRM 934, NBS Spec. Publ. 260-48 (May 1974). 60 cents* SN003-003-01278-5

Carpenter, B. S., and Reimer, G. M., Standard Reference Materials: Calibrated Glass Standards for Fission Track Use, NBS Spec. Publ. 260-49 (November 1974). COM74-51185

Hust, J. G., and Giarratano, P. J., Standard Reference Materials: Thermal Conductivity and Electrical Resistivity Standard Reference Materials: Electrolytic Iron, SRM's 734 and 797 from 4 to 1000 K, NBS Spec. Publ. 260-50 (June 1975). $1.00* SN003-003-01425-7

Mavrodineanu, R., and Baldwin, J. R., Standard Reference Materials: Glass Filters As a Standard Reference Material for Spectrophotometry; Selection; Preparation; Certification; Use-SRM 930, NBS Spec. Publ. 260-51 (November 1975). $1.90* SN003-003-01481-8

Hust, J. G., and Giarratano, P. J., Standard Reference Materials: Thermal Conductivity and Electrical Resistivity Standard Reference Materials 730 and 799, from 4 to 3000 K, NBS Spec. Publ. 260-52 (September 1975). $1.05* SN003-003-01464-8

Durst, R. A., Standard Reference Materials: Standardization of pH Measurements, NBS Spec. Publ. 260-53 (December 1975, Revised). $1.05 SN003-003-01551-2

Burke, R. W., and Mavrodineanu, R., Standard Reference Materials: Certification and Use of Acidic Potassium Dichromate Solutions as an Ultraviolet Absorbance Standard, NBS Spec. Publ. 260-54 (August 1977). $3.00* SN003-003-01828-7

Ditmars, D. A., Cezairliyan, A., Ishihara, S., and Douglas, T. B., Standard Reference Materials: Enthalpy and Heat Capacity; Molybdenum SRM 781, from 273 to 2800 K, NBS Spec. Publ. 260-55 (September 1977). $2.20* SN003-003-01836-8

Powell, R. L., Sparks, L. L., and Hust, J. G., Standard Reference Materials: Standard Thermocouple Materials, Pt.67: SRM 1967, NBS Spec. Publ. 260-56 (February 1978). $2.20* SN003-003-018864

Cali, J. P. and Plebanski, T., Guide to United States Reference Materials, NBS Spec. Publ. 260-57 (February 1978). $2.20* PB 277173

Barnes, J. D., and Martin, G. M., Standard Reference Materials: Polyester Film for Oxygen Gas Transmission Measurements SRM 1470, NBS Spec. Publ. 260-58 (June 1979) $2.00* SN003-003-02077

Chang, T., and Kahn, A. H. Standard Reference Materials: Electron Paramagnetic Resonance Intensity Standard; SRM 2601, NBS Spec. Publ. 260-59 (August 1978) $2.30* SN003-003-01975-5

Velapoldi, R. A., Paule, R. C., Schaffer, R., Mandel, J., and Moody, J. R., Standard Reference Materials: A Reference Method for the Determination of Sodium in Serum, NBS Spec. Publ. 260-60 (August 1978). $3.00* SN003-003 01978-0

Verdier, P. H., and Wagner. H. L., Standard Reference Materials: The Characterization of Linear Polyethylene (SRM 1482, 1483, 1484), NBS Spec. Publ. 260-61 (December 1978). $1.70* SN003-003-02006-1

Soulen, R. J., and Dove, R. B., Standard Reference Materials: Temperature Reference Standard for Use Below 0.5 K (SRM 768). NBS Spec. Publ. 260-62 (April 1979). $2.30* SN003-003-02047-8

Velapoldi, R. A., Paule, R. C., Schaffer, R. Mandel, J., Machlan, L. A., and Gramlich, J. W., Standard Reference Materials: A Reference Method for the Determination of Potassium in Serum. NBS Spec. Publ. 260-63 (May 1979). $3.75* SN003-003-02068

Velapoldi, R. A., and Mielenz, K. D., Standard Reference Materials: A Fluorescence Standard Reference Material Quinine Sulfate Dihydrate (SRM 936), NBS Spec. Publ. 260-64 (January 1980). $4.25* SN003-003-02148-2

Marinenko, R. B., Heinrich, K. F. J., and Ruegg, F. C., Standard Reference Materials: Micro-Homogeneity Studies of NBS Standard Reference Materials, NBS Research Materials, and Other Related Samples. NBS Spec. Publ. 260-65 (September 1979). $3.50* SN003-003-02114-1

Venable, W. H., Jr., and Eckerle, K. L., Standard Reference Materials: Didymium Glass Filters for Calibrating the Wavelength Scale of Spectrophotometers (SRM 2009, 2010, 2013). NBS Spec. Publ. 260-66 (October 1979). $3.50* SN003-003-02127-0

Velapoldi, R. A., Paule, R. C., Schaffer, R., Mandel, J., Murphy, T. J., and Gramlich, J. W., Standard Reference Materials: A Reference Method for the Determination of Chloride in Serum, NBS Spec. Publ. 260-67 (November 1979). $3.75* SN003-003-02136-9

Mavrodineanu, R. and Baldwin, J. R., Standard Reference Materials: Metal-On-Quartz Filters as a Standard Reference Material for Spectrophotometry-SRM 2031, NBS Spec. Publ. 260-68 (April 1980). $4.25* SN003-003-02167-9

Velapoldi, R. A., Paule, R. C., Schaffer, R., Mandel, J., Machlan, L. A., Garner, E. L., and Rains, T. C., Standard Reference Materials: A Reference Method for the Determination of Lithium in Serum, NBS Spec. Publ. 260-69 (July) 1980). $4.25* SN003-003-02214-4

Marinenko, R. B., Biancaniello, F., Boyer, P. A., Ruff, A. W., DeRobertis, L., Standard Reference Materials: Preparation and Characterization of an Iron-Chromium-Nickel Alloy for Microanalysis, NBS Spec. Publ. 260-70 (May 1981). $2.50* SN003-003-02328-1

Seward, R. W., and Mavrodineanu, R., Standard Reference Materials: Summary of the Clinical Laboratory Standards Issued by the National Bureau of Standards, NBS Spec. Publ. 260-71 (November 1981). $6.50* SN003-003-02381-7

Reeder, D.J., Coxon, B., Enagonio, D., Christensen, R. G., Schaffer, R., Howell, B. F., Paule, R. C., Mandel, J., Standard Reference Materials: SRM 900, Antiepilepsy Drug Level Assay Standard, NBS Spec. Publ. 260-72 (June 1981). $4.25* SN003-003-02329-9

Interrante, C. G., and Hicho, G. E., Standard Reference Materials: A Standard Reference Material Containing Nominally Fifteen Percent Austenite (SRM 486), NBS Spec. Publ. 260-73 (January 1982). $2.75* SN003-003-02386-8

Marinenko, R. B., Standard Reference Materials: Preparation and Characterization of K-411 and K-414 Mineral Glasses for Microanalysis: SRM 470. NBS Spec. Publ. 260-74 (April 1982). $3.50 SN003-003-023-95-7

Weidner, V. R., and Hsia, J. J., Standard Reference Materials: Preparation and Calibration of First Surface Aluminum Mirror Specular Reflectance Standards (SRM 2003a), NBS Spec. Publ. 260-75 (May 1982). $3.75 SN003-003-023-99-0

Hicho, G. E. and Eaton, E. E., Standard Reference Materials: A Standard Reference Material Containing Nominally Five Percent Austenite (SRM 485a), NBS Spec. Publ. 260-76 (August 1982). $3.50 SN003-003-024-33-3

Furukawa, G. T., Riddle, J. L., Bigge, W. G., and Pfieffer, E. R., Standard Reference Materials: Application of Some Metal SRM's as Thermometric Fixed Points, NBS Spec. Publ. 260-77 (August 1982). $6.00 SN003-003-024-34-1

Hicho, G. E. and Eaton, E. E., Standard Reference Materials: Standard Reference Material Containing Nominally Thirty Percent Austenite (SRM 487), NBS Spec. Publ. 260-78 (September 1982). $3.75* SN003-003-024-35-0

Richmond, J. C., Hsia, J. J. Weidner, V. R., and Wilmering, D. B., Standard Reference Materials: Second Surface Mirror Standards of Specular Spectral Reflectance (SRM's 2023, 2024, 2025), NBS Spec. Publ. 260-79 (October 1982). $4.50* SN003-003-024-47-3

Schaffer, R., Mandel, J., Sun, T., Cohen, A., and Hertz, H. S., Standard Reference Materials: Evaluation by an ID/MS Method of the AACC Reference Method for Serum Glucose, NBS Spec. Publ. 260-80 (October 1982). $4.75* SN003-003-024-43-1

Burke, R. W., and Mavrodineanu, R. (NBS retired), Standard Reference Materials: Accuracy in Analytical Spectrophotometry, NBS Spec. Publ. 260-81 (April 1983). $6.00* SN003-003-024-8

Weidner, V. R., Standard Reference Materials: White Opal Glass Diffuse Spectral Reflectance Standards for the Visible Spectrum (SRM's 2015 and 2016). NBS Spec. Publ. 260-82 (April 1983). $3.75* SN003-003-024-89-9**

Bowers, G. N., Jr., Alvarez, R., Cali, J. P. (NBS retired), Eberhardt, K. R., Reeder, D. J., Schaffer, R., Uriano, G. A., Standard Reference Materials: The Measurement of the Catalytic (Activity) Concentration of Seven Enzymes in NBS Human Serum SRM 909, NBS Spec. Publ. 260-83 (June 1983). $4.50* SN003-003-024-99-6

Gills, T. E., Seward, R. W., Collins, R. J., and Webster, W. C., Standard Reference Materials: Sampling, Materials Handling, Processing, and Packaging of NBS Sulfur in Coal Standard Reference Materials, 2682, 2683, 2684, and 2685, NBS Spec. Publ. 260-84 (August 1983). $4.50* SN003-003-025-20-8

Swyt, D. A., Standard Reference Materials: A Look at Techniques for the Dimensional Calibration of Standard Microscopic Particles, NBS Spec. Publ. 260-85 (September 1983). $5.50* SN003-003-025-21-6

Hicho, G. E. and Eaton, E. E., Standard Reference Materials: A Standard Reference Material Containing Two and One-Half Percent Austenite, SRM 488, NBS Spec. Publ. 260-86 (December 1983). $1.75* SN003-003-025-41-1

Mangum, B. W., Standard Reference Materials: SRM 1969: Rubidium Triple-Point - A Temperature Reference Standard Near 39.30 °C, NBS Spec. Publ. 260-87 (December 1983). $2.25* SN003-003-025-44-5

Gladney, E. S., Burns, C. E., Perrin, D. R., Roelandts, I., and Gills, T. E., Standard Reference Materials: 1982 Compilation of Elemental Concentration Data for NBS Biological, Geological, and Environmental Standard Reference Materials. Spec. Publ. 260-88 (March 1984). $7.00* SN003-003-02565-8

Hust, J. G., Standard Reference Materials: A Fine-Grained, Isotropic Graphite for Use as NBS Thermophysical Property RM's from 5 to 2500 K, NBS Spec. Publ. 260-89 (September 1984). $4.50* SN003-003-02608-5

Hust, J. G., and Lankford, A. B., Standard Reference Materials: Update of Thermal Conductivity and Electrical Resistivity of Electrolytic Iron, Tungsten, and Stainless Steel, NBS Spec. Publ. 260-90 (September 1984). $3.00* SN003-003-02609-3

Goodrich, L. F., Vecchia, D. F., Pittman, E. S., Ekin, J. W., and Clark, A. F., Standard Reference Materials: Critical Current Measurements on an NbTi Superconducting Wire Standard Reference Material, NBS Spec. Publ. 260-91 (September 1984). $2.75* SN003-003-02614-0

Carpenter, B. S., Standard Reference Materials: Calibrated Glass Standards for Fission Track Use (Supplement to NBS Spec. 260-49). NBS Spec. Publ.. 260-92 (September 1984). $1.50* SN003-003-02610-7

Ehrstein, J., Preparation and Certification of Standard Reference Materials for Calibration of Spreading Resistance Probes, NBS Spec. Publ. 260-93 (January 1985).

Gills, T. E., Koch, W. F. Stolz, J. W., Kelly, W. R., Paulsen, P. J., Colbert, J. C. Kirklin, D. R., Pei, P.T.S., Weeks, S., Lindstrom, R. M. Fleming, R. F., Greenberg, R. R., and Paule, R. C., Methods and Procedures Used at the National Bureau of Standards to Certify Sulfur in Coal SRM's for Sulfur Content, Calorific Value, Ash Content, NBS Spec. Publ. 260-94 (December 1984).

Mulholland, G. W., Hartman, A. W., Hembree, G. G., Marx, E., and Lettieri, T. R., Standard Reference Materials: Development of a 1 μm Diameter Particle Size Standard, SRM 1690, NBS Spec. Publ. 260-95 (May 1985).

Carpenter, B. S., Gramlich, J. W., Greenberg, R. R., and Machlan, L. A., Standard Reference Materials: Uranium-235 Isotopic Abundance Standard Reference Materials for Gamma Spectrometry Measurements, NBS Spec. Publ. 260-96 (In Press).

Mavrodineanu, R. and Gills, T. E., Standard Reference Materials: Summary of the Coal, Ore, Mineral, Rock, and Refractory Standards Issued by the National Bureau of Standards, NBS Spec. Publ. 260-97 (In Press).

Hust, J. G., Standard Reference Materials: Glass Fiberboard SRM for Thermal Resistance, NBS Spec. Publ. 260-98 (In Press).

Callanan, J. E., Sullivan, S. A., and Vecchia, D. F., Standard Reference Materials: Feasibility Study for the Development of Standards Using Differential Scanning Calorimetry, NBS Spec. Publ. 260-99 (In Press).

* Send order with remittance to Superintendent of Documents, US Government Printing Office Washington, DC 20402. Remittance from foreign countries should include an additional one-fourth of the purchase price for postage.

** May be ordered from: National Technical Information Services (NTIS). Springfield Virginia 22161.

Contents

List of Tables

List of Figures

Feasibility Study for the Development of Standards Using Differential Scanning Calorimetry

Jane E. Callanan,[a] Sandra A. Sullivan,[a] and Dominic F. Vecchia[b]

Center for Chemical Engineering[a]

Center for Applied Mathematics[b]
National Engineering Laboratory
National Bureau of Standards
Boulder, Colorado 80303

The tremendous increase in the use of differential scanning calorimetry, coupled with the decrease in the capability for conventional precision calorimetry, has created a need for more and better thermal standards for use with scanning calorimeters and other thermal instruments currently available, such as thermomechanical analyzers. The development of these standards by methods such as adiabatic or drop calorimetry is impractical because of the number and variety of standards required, the associated expense, and the lack of facilities and personnel to do the certification. A two-part study was designed to evaluate the capability of a differential scanning calorimeter for developing temperature and enthalpy of fusion standards. Part I evaluated the variability of the differential scanning calorimeter (DSC) and factors which affected it; Part II applied American Society for Testing and Materials (ASTM) procedures for the temperature and heat flow calibration. The study shows that fusion standards can be developed with a differential scanning calorimeter.

Key words: differential scanning calorimetry; enthalpy; fusion; pilot study; standards; temperature; thermal analysis

I. Introduction and Rationale for Study

The last decade has seen a tremendous increase in the number of differential scanning calorimeters (DSC)[1] in use. During this same decade, the number of

---

[1] The acronym DSC refers to an instrument; d.s.c. refers to the calorimetric technique.

adiabatic calorimeters available has declined alarmingly. Because of this decline many investigators are constrained to use DSCs, but require the maximum accuracy and precision possible. A paper to be published shortly in the open literature outlines the prescriptions for use found satisfactory in our laboratory [1].

Adiabatic (precision) calorimeters use measurements of time, voltage and current, the latter two obtained by use of a calibrated standard cell and calibrated standard resistor. Construction details and a system of shields largely eliminate heat transfer to the environment. The quantities required for the determination of the heat capacity are measured with great accuracy.

A differential scanning calorimeter consists of twin cups (calorimeters), circuitry that can produce a linear increase or decrease in temperature of both cups, and a differential circuit that either keeps both cups at the same temperature or evaluates the temperature difference between them. It does not have an electrical calibration heater nor the means to measure (and/or design to minimize) differences in heat leaks between calibration and "unknown" experiments. As the heat leak is large and somewhat dependent on the environment, standards must be run repeatedly with those scanning calorimeters classified as power-compensated, Boersma differential thermal analyzers (DTA) or DTA instruments.

The DSC is not an absolute measuring instrument; standards must be used as calibrants each time measurements are made. The validity of the results obtained is dependent on the calibration. Instrumental controls may be adjusted to give the correct value for the calibrant or the data may be corrected as required by the calibration results. Because of the inherent day-to-day instrumental variability and the time that may be required for instrument adjustment, the most satisfactory procedure is occassionally to set controls on the instrument to give values close to those in the literature and then to correct data as indicated by daily calibration checks.

The reference materials most generally used for differential scanning calorimeters (DSC) are the Special Reference Materials (GM) distributed by the Office of Standard Reference Materials (OSRM) as GM 754 and 757-60 [2]. These materials were developed by the International Conference on Thermal Analysis (ICTA) in the late 1960's to allow for comparison among results obtained with instruments of widely-different design; often these were non-commercial, uniquely- constructed instruments. The materials were not intended to be standard reference materials in the strict sense. The temperature variations noted in the ICTA certificate which accompanies GM 758-60, shown in figure 1, are an order of magnitude greater than those that would be obtained with modern instrumentation [3].

When the DSC is used in the scanning mode, as it is generally, standards become particularly important. Compensation for thermal lag is not automatic in the scanning mode, as it is when enthalpic procedures are used [4,5,6]. Therefore it is desirable to have a standard that is similar in nature to the sample being tested, i.e., that will have similar thermal lag. Metallic standards are preferred for studies of metals, organic materials for organics, powdered standards or crystalline standards for corresponding materials, etc. In addition, the excellent calibration methods established by the American Society for Testing and Materials (ASTM) work best when calibrants available are about 50 K apart [7,8].

Several factors led us to attempt to develop new Standard Reference Materials (SRM's) for d.s.c. Instruments commercially available today readily give an order of magnitude improved precision over the instruments used for the ICTA standards. There has been an explosion in the use of differential scanning calorimetry; thus needs for standards are greater. Present day energy costs require improved thermal property data. Facilities for obtaining very accurate and

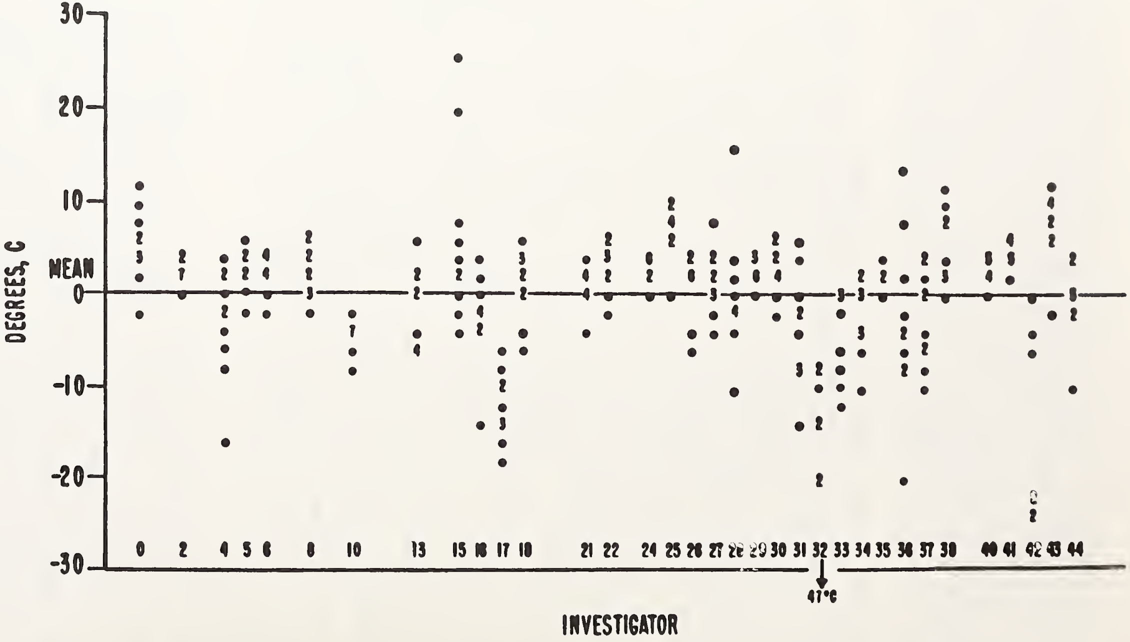


Figure 1. Deviations from the mean value as reported by the 34 investigators (submitted to the Standards Committee of ICTA).[3]

precise calorimetric data are few and far between, and becoming more so [9]. In addition, the cost associated with these measurements is high. For many purposes industry does not need data of the accuracy provided by methods comparable to adiabatic calorimetry. For all these reasons it seemed worthwhile to attempt the relatively inexpensive certification of materials, using d.s.c., which do relate to thermodynamic equilibrium values.

II. Outline of Study

The first part of the study was intended to determine whether a differential scanning calorimeter could be used to develop standards for d.s.c. In certifying standards the usual practice is to develop the standard with a different method, preferably an absolute measuring one, such as adiabatic or drop calorimetry. If only one or two standards were required, precision calorimetry would be feasible, but expensive and difficult. The facilities for making such measurements in the temperature range needed most (300 - 1000 K) are virtually nonexistent or unavailable in the United States. Therefore we designed a study of indium fusion to evaluate the variability inherent in the DSC and our procedures for working with it, and thus the suitability of a DSC for the development of standards. The judgement regarding suitability was to be based on a statistical analysis of the experimental results; this analysis would consider both total variability and the effects of instrumental and manipulative factors on this variability.

The second part of the study, which will be described in more detail later, applied ASTM calibration procedures to a selected group of substances. Substances 1 and 3 were used, as bracketing substances, to calibrate the DSC and the transition properties of substance 2 obtained. Then substances 2 and 4 were used for bracketing and the properties of substance 3 obtained. This procedure, followed through the selected list, would allow us to determine 1) whether the DSC would produce the accepted temperatures satisfactorily and 2) what error is to be expected in various temperature ranges.

III. Part I. Variability Study

A. Procedures

The protocol to be followed was discussed with Karen Kafadar, formerly of the Statistical Engineering Division (714) of the Center for Applied Mathematics, Gaithersburg [10].

Three forms of indium which were readily available (rod, granules, foil) were used to conduct a five-specimen, four-replicate analysis of the temperature and enthalpy of transition. Information about the three forms of indium used for the study is given in table 1. In-laboratory measurements of the purity qualitatively reinforced the nominal values.

Table 1. Indium properties

Form	Nominal purity (percent)
Granular	99.999
Rod	99.9999
Foil (0.076 mm thick)	99.999

The sixty replicate runs were made in random order. Since it was possible that variations in mains voltage could affect the results, some samples were run during the normal working day, some during start up and shut down periods, some in the evening and on weekends. In addition to these sixty measurements, three-replicate measurements were made on six specimens without any operator interference (leaving the specimens in place and rerunning them.) These allowed for the estimation of variability due to the instrument itself. On examination of the results after completion of this work, two short studies were added. One of these was designed to help us separate remount variations from specimen variations; the other allowed for comparison between two experienced operators.

Variations introduced by weighing procedures and in the data analysis program were evaluated separately.

The accuracy and precision of the weighing procedure were estimated from ten replicate measurements of the NBS-calibrated 50 mg Class M weight; this weight was chosen as it is close to the mass of the specimens used. All mass determinations were made on a microbalance capable of weighing to tenths of a microgram. The usual weighing procedure in this laboratory always involves duplicate weighings. If these agree within 5 micrograms, no further weighings are made. A change of 5 μg in specimen mass results in a 0.05% change in the heat capacity of sapphire; a change of 50 μg affects the heat capacity by 0.58%. If there is an unusual variation, which may result from environmental factors, repeated measurements are made until reproducible results are obtained.

The automated data acquisition/reduction system uses a Simpson's rule integration routine for determining the area under the peak, i.e., the enthalpy of fusion. Before the integration routine is called for in the data reduction scheme, the operator must decide, from the scan, where the transition begins and ends, and set cursors accordingly. Cursor judgement variations were determined as follows. The same scan was used by three observers, each of whom made three evaluations; these evaluations were made at widely-spaced time intervals to attempt to rule out bias caused by operator memory.

In attempting to assign relative variances in this study, as initially devised, it became obvious that we had no way to separate the variance due to remounting the specimen in the DSC from that due to the specimen itself. For this reason a single specimen was remounted five times. This operation was repeated by a second experienced operator.

For the temperature calibration the instrument was first linearized over the temperature range of the fusion standards by adjustment of appropriate circuitry incorporated into the instrument. Then, again by adjusting additional controls, the observed onset temperature of fusion was matched to the literature value for that standard. The enthalpy calibration of the instrument was based on an enthalpic heat capacity determination with sapphire. Temperature and enthalpy measurements for the specimens were corrected from day to day as indicated by the fusion standards, which were checked several times during each day of the study.

Our instrument was calibrated with an existing indium rod and a new tin standard. On only one day were significant variations in the standard noted; corrections for that day were made on the basis of the time of the calibration and the experimental run. Because the corrected means obtained for the indium specimens do not agree with the accepted values, it is obvious that the indium fusion standard needed replacement. But, since the purpose of this work was to study the consistency of results with the calorimeter on a number of specimens, preparation of a new standard was not considered necessary at the time.

The analysis in this report, coupled with information generated in our laboratory, allowed for the determination of the significant variables and the magnitude of their effects. Results of the analysis are discussed below. An explanation of the methods used to account for specimen variability can be found in an appendix to this report.

B. Results and discussion

Table 2 shows the estimated temperature and enthalpy of fusion for each form of indium. Each estimate is the sample mean of 20 measurements (four repeats from each of five specimens). The standard error of the mean[2] is also included in table 2. Estimated standard errors were computed based on a statistical model that accounts for possible specimen-to-specimen variability. An explanation of the methods that were used to obtain the standard errors and their associated degrees of freedom can be found in the appendix. For reference the simple standard deviation of each set of 20 measurements, which ignores the grouping of repeat measurements by specimen, is also given in table 2.

---

[2] Standard error of the mean is synonymous with standard deviation of the mean.

Table 2. Means obtained in indium variability study

	Mean	N	Standard Error of Mean*	Degrees of Freedom	Standard Deviation
			Temperature		
	K		K		K
Grand Mean	429.558	60			
Granular	429.565	20	.083	4	0.216
Rod	429.509	20	.038	19	0.164
Foil	429.602	20	.036	19	0.159
			Enthalpy		
	J/g		J/g		J/g
Grand Mean	28.773	60			
Granular	28.623	20	.089	4	0.293
Rod	28.761	20	.105	4	0.322
Foil	28.936	20	.055	4	0.172

*See appendix

Though the DSC reads only to two decimals, a third is retained in reporting derived results because of information that can sometimes be obtained from it. Tables 3 and 4 list the original temperatures and enthalpies from which table 2 was derived. A five-specimen sampling, used to ensure the proper separation of variables for comparisons made later in this paper, was selected at random from values given for each form in tables 3 and 4. The mean, standard deviation and variance for a five-specimen sampling are shown in these tables also.

The variations given in table 2 show the present data to be more precise, by 1-2 orders of magnitude, than the data shown in figure 1. Thus, these results indicate that we can establish the temperature and enthalpy of fusion satisfactorily for use with differential scanning calorimeters.

Replicate measurements made without operator interference showed a standard deviation considerably smaller than that noted with operator interference. The results of these replicate runs are shown in table 5. In this table, three decimals are retained, as earlier, for statistical purposes. The original data appear in table 6. The variance associated with these measurements is referred to as instrument variance in later portions of this paper.

Table 3. Fusion temperatures for indium specimens (K)

	Granular		Rod		Foil
I1	429.63	I6	429.50	I11	429.71*
	429.96		429.39*		429.60
	430.01*		429.40		429.74
	429.62		429.58		429.67
I2	429.63	I7	429.38*	I12	429.53
	429.34		429.31		429.72
	429.72		429.65		429.83
	429.32*		429.60		429.45*
I3	429.48	I8	429.84	I13	429.53
	429.49		429.46		429.50*
	429.41*		429.33*		429.48
	429.36		429.30		429.75
I4	429.35	I9	429.78	I14	429.34
	429.33		429.37*		429.67
	429.38*		429.75		429.72*
	429.41		429.67		429.45
I5	429.64	I10	429.56	I15	429.81
	429.61		429.52*		429.74
	429.92*		429.36		429.25*
	429.68		429.43		429.54

*Results used for estimation of specimen variance.

Five-Specimen Results

Mean ± Standard Deviation	429.608 ± 0.329	429.552 ± 0.220	429.526 ± 0.196
Variance	0.108	0.048	0.038

Table 4. Enthalpies of fusion for indium specimens (J/g)

	Granular		Rod		Foil
I1	28.70	I6	29.20	I11	29.08
	28.12*		29.12*		29.04
	28.79		28.91		28.91
	27.82		28.87		29.00*
I2	28.49	I7	29.16*	I12	29.04
	28.91		29.04		28.74*
	28.62		28.66		28.83
	28.54*		28.70		29.04
I3	29.00	I8	29.04	I13	29.08
	28.83*		28.91		29.12
	28.95		28.20*		28.95*
	28.87		28.95		28.87
I4	28.74	I9	28.74*	I14	29.29*
	28.49		28.91		28.83
	28.58*		28.20		28.83
	28.79		28.95		29.16
I5	28.79	I10	28.45	I15	28.79
	28.70		28.41*		28.62
	28.45*		28.28		28.87*
	28.28		28.45		28.66

*Results used for estimation of specimen variance.

Five-Specimen Results

Mean ± Standard Deviation	28.504 ± 0.257	28.726 ± 0.424	28.970 ± 0.204
Variance	0.066	0.180	0.042

Table 5. Mean and standard deviation for replicate runs, in succession, with no disturbance of the specimen

Specimen	Temperature Mean K	Temperature Standard Deviation K	Enthalpy Mean J/g	Enthalpy Standard Deviation J/g	Degrees of Freedom
Granular					
Mean[a]	429.565	0.148	28.623	0.256	15
I4	429.415	0.026	28.480	0.088	3
I5	429.653	0.038	28.702	0.031	2
Rod					
Mean[a]	429.509	0.168	28.761	0.270	15
I6	429.42	0.020	28.815	0.088	2
I7	429.337	0.025	29.121	0.109	2
Foil					
Mean[a]	429.602	0.170	28.937	0.148	15
I12	429.847	0.015	28.732	0.088	2
I13	429.505	0.007	29.142	0.029	1
I14	429.740	0.020	29.066	0.025	2

[a] These means + deviations refer to procedures in which the specimen was re-mounted in the calorimeter for each measurement. The standard deviations have been corrected for specimen-to-specimen variability. See table 3 in appendix.

Table 6. Original data for replicate runs, in succession, with no disturbance of the specimen

		Temperature (K)	Enthalpy (J/g)
Granular	(I4)	429.38	28.58
		429.41	28.45
		429.43	28.41
		429.44	28.54
	(I5)	429.61	28.70
		429.67	28.74
		429.68	28.66
Rod	(I6)	429.40	28.91
		429.42	28.74
		429.44	28.79
	(I7)	429.31	29.04
		429.34	29.08
		429.36	29.25
Foil	(I12)	429.83	28.83
		429.85	28.66
		429.86	28.70
	(I13)	429.50	29.12
		429.51	29.16
	(I14)	429.72	29.04
		429.74	29.08
		429.76	29.08

The results of the evaluation of the weighing procedures, table 7, show that no significant error is introduced by these procedures.

Table 7. Weighing procedure evaluation

Calibration value of mass	49.966 mg
Experimental value	49.973 ± 0.002[a] mg
	49.972 ± 0.001[b] mg

[a] Includes all ten measurements.

[b] Excludes two measurements outside of our acceptable range. This result follows from our normal weighing procedure.

> NOTE: The difference between the calibration mass of the 50 mg weight and the average value obtained here is insignificant when the combined uncertainties in the calibration weights and the standard deviation of the instrument are considered. For a weighing-by-difference procedure such as used in this work, it is customary to use the combined uncertainties (0.0022 μg) plus three times the standard deviation.

The reproducibility of the computer analysis procedure, reflected as analytical variance in table 10, was evaluated by having three operators evaluate a single experimental run three times. These analyses were done relatively far apart in time to reduce operator bias introduced by memory. There was no variation in the temperature of transition as a result of cursor settings; the same value, 429.87 K, was obtained in all nine evaluations. For the enthalpy evaluation, the average value for all nine trials was 28.414 ± 0.046 J/g, which corresponds to a variability of 0.16%. Two of the operators always obtained the same value. The third obtained different values which average to 28.380 ± 0.063 J/g; this corresponds to a variability of 0.22%.

However, this evaluation was in a sense unnecessary as the calibration routine used in this laboratory cancels out systematic error involved in the integration. The random error associated with the integration arises from the same sources as the random error associated with the instrument variation in this study. The resulting contribution to the error of the measurements, therefore, is considered to be included in the instrument error.

The results for the remount and operator study are shown in table 8. The data on which these are based are shown in table 9.

Table 8. Remount and operator study

Operator	T(K)	Enthalpy (J/g)
1*	429.098 ± 0.144	28.420 ± 0.106
2	429.088 ± 0.134	28.608 ± 0.106

*Primary operator for experimental work in this report.

Table 9. Results for repeat runs with specimens remounted (I12)

	T(K)	Enthalpy (J/g)
	Operator 1	
	428.99	28.41
	429.14	28.24
	429.14	28.28
	429.15	28.28
	428.82	28.49
Mean	429.048	28.340
Standard Deviation	0.144	0.106
Mean corrected for daily calibration	429.098 ± 0.144	28.420 ± 0.106
	Operator 2	
	429.79	28.19
	429.01	28.41
	428.65	28.16
	428.88	28.15
	429.89	28.23
Mean	428.844	28.228
Standard Deviation	0.134	0.106
Mean corrected for daily calibration	429.088 ± 0.134	28.608 ± 0.106

In order to determine whether time of run or mass of specimen affected the measurements, the temperatures and enthalpies of transition were plotted as a function of these two variables.

The time at which the runs were made, either day of the week or time of day, had no correlation with the results. Thus variations in mains voltage do not appear to be affecting instrument behavior. Specimen masses varied from 0.93 - 3.49 mg. No correlation between specimen mass and either temperature or enthalpy of fusion was observed.

The statistical analysis indicated that somewhat "tighter" results were obtained with the foil. In addition, auxilliary information showed that the most serious variations appeared to exist among specimens of the same form, the within-form variations.

In order to get an idea of the contribution of specimen inhomogeneity to the variance, an analysis of the contributions to the variance, as shown in table 10, was carried out. The range for each variable is also given. For the evaluation of the analytical variability an existing indium scan was used. All the other variables given in table 10 refer to foil specimens. Specimen I12 was used for remount and operator variability tests. Five results each, both temperature and enthalpy, were selected at random from the results for foil shown in tables 11 and 12 and used to obtain the estimate of total variance for a population of five in table 10. (The value given in table 2 is for a population of 20.) The (1) and (2) associated with remount variance refer to two different operators.

The total variability had contributions from the instrument itself, S_i, the remounting operation, S_r, and the specimen, S_s.

$$S_t^2 = S_s^2 + S_r^2 + S_i^2 \qquad (1)$$

Table 10. Contributions to variance; range (foil)

Temperature (K) Range	Temperature (K) Variance	---	Enthalpy (J/g) Variance	Enthalpy (J/g) Range	Degrees of Freedom
0.00	$(0.00)^2$	mass	$(0.00)^2$	0.00	9
0.00	$(0.00)^2$	analytical procedure	$(0.055)^2$	0.03	8
.03	$(0.015)^2$	instrument	$(0.088)^2$	0.17	2
0.33	(1)$(0.144)^2$ (2)$(0.134)^2$	remount	$(0.106)^2$	0.25	4
0.01	$(0.00)^2$	operator	$(0.00)^2$	---	
0.58	$(0.196)^2$	TOTAL	$(0.204)^2$	0.27	4
---	$(0.133)^2$	specimen	$(0.172)^2$	---	

S_t is the standard deviation for five starred measurements, shown in table 3. The magnitude of S_i can be determined from results in table 5, repeat runs in place. Results for remounting the same specimen give $S_r^2 + S_i^2$, table 9. The estimate of specimen variance given in table 10 was obtained by

$$S_t^2 - (S_r^2 + S_i^2) = S_s^2.$$

For this estimate the remount results for the primary operator were used and the operator variance omitted. The contribution to the variance from the analytical procedure is included in the other contributions and was not subtracted separately.

The estimate of specimen variability for enthalpy using this approach differs from that given in table 3 of the appendix, which was obtained using an alternate procedure. This difference, 0.02 J, is insignificant for a DSC.

C. Summary

In summary, the total uncertainty in enthalpy, as calculated for the five-specimen results for foil given in tables 3 and 4, was 0.7%; in temperature, 0.05%. Thus, unquestionably, satisfactory values for SRM's for d.s.c. and other thermal analysis techniques can be obtained using a DSC in its most precise modes of operation. Also, metallic samples in foil form gave slightly better uniformity than rod; foil appears to be significantly better than granular specimens. If, then, materials of equal purity are available for standards development, foil is the preferable form.

IV. Part II. Calibration Study

A. Procedures

1. General

The second part of this study called for an evaluation of the ASTM calibration procedures when used with suitable materials [7,8].

The test materials selected were from the group of melting point standards certified by the National Physical Laboratory (NPL) and marketed in the United States through OSRM. The materials used and their reference temperatures are given in Table 11.

Table 11. Melting points of test materials (K)

Substance	NPL Certificate Values [13]	Literature Values
Naphthalene	353.37	353.37 [11]
Acetanilide	387.51	387.51 [11]
Diphenylacetic acid	420.41	420.41 [11]
Anisic acid	456.45	456.14 [12]
2-Chloroanthraquinone	482.75	482.20 [12]

The certificates for these materials indicate that these reference temperatures refer to a specific heating regime, heating at 2 K/min with the specimen contained in a glass capillary tube. Where other definitive work has been done, the values are listed in column 3 of table 11.

We chose to use five specimens of each of these materials and run a four-replicate analysis. This choice was based on the results of the indium study.

The specimen sets were randomly selected; within these sets, however, the specimens were run in the order of increasing melting points. The two-point temperature calibration procedure recommended by ASTM was followed [7].

The protocol for temperature calibration calls for bracketing the temperature of interest with two known standards and then following the calculations outlined below.

The experimental procedure involved running an indium standard before and after the unknown runs, as well as at intervals in between. The actual number of indium checks depended on the number of sets of samples run on any specific day. In fact, the calibration checks were not necessary as the differences between observed and literature values are incorporated into the equations. However, as the indium runs are part of our normal procedures, they were made. Enthalpic measurements of sapphire over the pertinent temperature ranges were made so that the ASTM procedures for enthalpy calibration could be applied.

2. Temperature calibration

The calculation of the observed transition temperature was obtained from eq (1) of the temperature calibration protocol,

$$T = (T_0 \times S) + I, \tag{2}$$

where T is the actual specimen temperature, T_0 is the observed temperature, S is the slope and I, the intercept. The slope and intercept are calculated from eqs (3) and (4).

$$S = (TS_1 - TS_2)/(TO_1 - TO_2) \tag{3}$$

$$I = [(TO_1 \times TS_2) - (TS_1 \times TO_2)]/(TO_1 - TO_2). \tag{4}$$

A preliminary evaluation of the method was based on results for metallic specimens chosen at random from existing calibration logs. These results, as well as those from a preliminary study of some organic NPL standards, are shown in table 12.

Table 12. Results obtained in preliminary evaluation of the two-point temperature calibration

		Fusion Temperature (K)	
		Literature	Observed
Indium		429.784[13]	429.71
Tin		505.118[14]	504.87
Lead		600.58[15]	600.08
Zinc		692.73[14]	692.83
	*Calculated		
In,Pb	Sn	505.13	
In,Zn	Sn,Pb	504.88, 600.02	
Indium		429.784[13]	430.07
Anisic Acid		456.45±0.2[11]	456.24
2-Chloroanthraquinone		482.75±0.3[11]	481.83
Tin		505.118[14]	505.74
	*Calculated		
In,Sn	AA,2-CL	455.86, 481.83	
In,2-CL	AA	456.30	
AA,Sn	2-CL	482.34	

*The values cited as calculated in this table have been obtained using the two substances in the first column as bracketing substances. The materials for which calculated values were obtained are shown in the second column. The calculated temperatures are shown in the third column.

3. Enthalpy calibration

The enthalpies of transition were determined from the scans by an automated protocol which was evaluated in the indium study discussed earlier in this report. Corrections to the enthalpy were made as recommended in the ASTM Heat Flow Protocol, E968 [8]. This protocol calls for determination of the melting isotherm for one standard material to obtain its enthalpy of fusion.

A calibration coefficient at the fusion temperature is determined from a comparison of the observed enthalpy of fusion with the literature value. This calibration is extended to other temperatures by factors derived from determinations of the heat capacity of sapphire (or another heat capacity standard) at the reference temperature and temperature(s) of interest.

A few changes were made in the recommended protocol. It was not necessary for us to make a preliminary run as specified in Note 2 [8] as the automated system is capable of adjusting for deflection. We used a heating rate of 5 K/min rather than 10 K/min as, in our experience, accuracy is improved at lower scan rates. The enthalpic method was used, rather than a scanning method, to determine the heat capacities for extension of the calibration to other temperatures. All specimens were run under identical conditions. Argon was used as purge gas, set at 137.9 kPa gauge (20 psig). The specimen holders were hermetically sealed aluminum pans. Masses were determined on an electronic microbalance accurate to better than 2 μg. For our purpose the peak melting temperature was not necessary; for the equipment and program used, the onset temperature is considered to be the fusion temperature.

Indium foil (99.999% pure) was used as the fusion standard and Calorimetry Conference sapphire for the specific heat capacity measurements. The latter measurements were made by the enthalpic method over a temperature interval chosen so that the temperature of interest was at the midpoint of the run [4-6]. Since our measurement system is automated, the equations specified in the ASTM protocol were not applicable [8]. The equations substituted follow.

The calibration coefficient (E) is obtained from the ratio of the literature value of the enthalpy of transition (ΔH_{lit}) to the observed value (ΔH_{obs}),

$$E = \Delta H(\mathrm{lit})/\Delta H(\mathrm{obs}). \tag{5}$$

Then the true enthalpy of fusion (ΔH_{act}) of measured specimens is obtained from

$$\Delta H(\mathrm{act}) = E \times \Delta H(\mathrm{meas}), \tag{6}$$

where $\Delta H(\mathrm{meas})$ is the measured enthalpy of fusion for that specimen. For extension to other temperatures a correction factor, F, is obtained from the sapphire results:

$$F = C_p(\mathrm{lit})/C_p(\mathrm{obs}). \tag{7}$$

The $\Delta H(\mathrm{act})$ from eq (6) is multiplied by the ratio of the F-factor at the temperature of interest to the F-factor at the reference temperature. The F-factor normally changes somewhat with temperature; for that reason an F-factor specific to the temperature of interest is used.

B. Results and discussion

Results for the temperature calibration study are shown in table 13 for the initial heating only. Results for repeat meaurements are given in table 14. The results for initial runs show the calculated temperatures in line 1. As the procedure calls for bracketing the temperature of interest, naphthalene and diphenylacetic acid were used to determine the values for acetanilide, which has an intermediate melting temperature. Then acetanilide and anisic acid were used to bracket diphenylacetic acid, etc. The raw data used in the calculations are shown in table 13. In all cases the results of this study for initial runs agree with the certificate values. Though the standard deviations are greater than

Table 13a. Transition temperatures (K) - acetanilide (initial run)

Substance	Specimen No.					Mean	Standard Deviation
	31	32	33	34	35		
Acetanilide	387.357	387.467	387.466	387.602	386.880	387.354	0.279
Naphthalene*	353.51	353.51	353.41	353.85	353.81	353.62	0.198
Diphenylacetic Acid*	419.89	419.99	420.07	419.79	418.37	419.62	0.708
Acetanilide*	387.03	387.19	387.18	387.39	385.95	386.95	0.572

experimental transition temperature: 387.35 ± 0.28
certificate transition temperature: 387.51 ± 0.05 [11]

Table 13b. Transition temperatures (K) - diphenylacetic acid (initial run)

Substance	Specimen No.					Mean	Standard Deviation
	21	22	23	24	25		
Diphenylacetic Acid	420.156	420.106	420.050	420.383	420.394	420.218	0.160
Acetanilide*	387.19	387.39	385.95	387.03	387.18	386.95	0.572
Anisic Acid*	456.30	455.76	454.48	455.79	455.98	455.66	0.695
Diphenylacetic Acid*	419.99	419.79	418.37	419.89	420.07	419.62	0.708

experimental transition temperature: 420.22 ± 0.16
certificate transition temperature: 420.41 ± 0.05 [11]

Table 13c. Transition temperatures (K) - anisic acid (initial run)

Substance	Specimen No.					Mean	Standard Deviation
	11	12	13	14	15		
Anisic Acid	456.644	456.092	455.694	456.552	455.910	456.180	0.409
Diphenylacetic Acid*	419.99	419.89	419.79	420.07	418.37	419.62	0.708
2-chloroanthraquinone*	482.36	482.51	483.24	481.91	481.68	482.34	0.604
Anisic Acid*	456.30	455.79	455.76	455.98	454.48	455.66	0.695

experimental transition temperature: 456.18 ± 0.41
certificate transition temperature: 456.45 ± 0.20 [11]

*Uncorrected data from which corrected values were obtained utilizing the procedure outlined in the text.

Table 14a. Transition temperatures (K) - acetanilide (repeat runs)

Run No.	Specimen No.					Mean	Standard Deviation
	31	32	33	34	35		
2	386.530	387.394	387.510	386.935	387.320	387.138	0.402
3	387.125	387.723	387.211	387.988	387.882	387.586	0.394
4	387.085	387.342	387.231	387.756	387.895	387.462	0.348

Grand Mean (20)	Standard Deviation
387.385	0.370

Table 14b. Transition temperatures (K) - diphenylacetic acid (repeat runs)

Run No.	Specimen No.					Mean	Standard Deviation
	21	22	23	24	25		
2	420.159	420.162	421.157	420.168	421.104	420.550	0.530
3	419.746	419.905	420.334	419.781	420.464	420.046	0.331
4	419.768	420.409	420.323	420.274	419.677	420.090	0.341

Grand Mean (20)	Standard Deviation
420.226	0.391

Table 14c. Transition temperatures (K) - anisic acid (repeat runs)

Run No.	Specimen No.					Mean	Standard Deviation
	11	12	13	14	15		
2	456.810	456.331	455.777	457.088	455.853	456.372	0.577
3	456.575	456.697	456.383	456.826	457.139	456.724	0.284
4	456.666	456.425	456.663	457.004	456.774	456.706	0.210

Grand Mean (20)	Standard Deviation
456.495	0.433

those shown on the certificate, they are in line with those obtained in the indium study. The calculated values for repeat runs are shown in table 14.

The results, shown in table 13, indicate that the ASTM two-point calibration procedure can be used to establish suitable temperature calibration standards for d.s.c. They also indicate that the substances used in this study are useful calibrants.

The results for the enthalpy measurements are shown in table 15. Columns 1-5 refer to the replicate specimens. Rows 1-4 contain the data for the initial and three subsequent runs. The columns under full correction refer to the ASTM method using the results for sapphire in addition to those for indium, as described earlier in the paper. The columns headed fusion correction refer to the more commonly used method of correcting enthalpy by a factor obtained from an experimental indium scan compared to its accepted value without any extension to other temperatures. Though the full correction is recommended by ASTM, results for the fusion only method are listed both because this method represents the most widely used method of making corrections and because a comparison of the two methods is desirable.

The enthalpies obtained with the full correction differ significantly from those with only the indium fusion correction for naphthalene, acetanilide and 2-chloroanthraquinone. The results using only the indium correction generally agree with literature values within experimental error; results using the full correction do not. Attempts are being made to resolve this difficulty through communication with ASTM Committee E-37 (Thermal Methods) and by continued investigation in this laboratory.

Another concern in the study of these materials was their stability: Is it possible to reuse a specimen for repeated calibrations? The shape of the scans obtained with the five test materials sometimes varied with repeated use.

Table 15. Enthalpies of fusion (J/g)

Substance	Run No.	Specimen No.							Full Correction		Fusion Correction	
		1	2	3	4	5	Mean	Std.Dev.	Mean	Std.Dev.	Mean	Std.Dev.
Naphthalene	1	149.54	149.12	146.90	147.90	147.82	148.67	1.246	152.67	0.869	149.35	0.850
	2	148.57	149.28	147.19	148.07	147.53	148.13	0.833	152.72	0.470	149.66	0.624
	3	148.24	148.49	147.95	144.56	147.95	147.44	1.625	150.37	1.515	148.14	1.474
	4	147.95	145.10	146.73	146.98	147.36	146.82	1.066	149.58	3.053	148.88	1.304
Acetanilide	1	161.42	163.38	162.63	163.97	161.12	162.51	1.226	165.97	1.063	163.65	1.264
	2	161.08	160.54	162.55	161.67	161.38	161.44	0.745	166.11	0.611	163.07	0.577
	3	160.50	161.17	162.30	161.71	162.09	161.55	0.728	162.99	1.929	162.31	0.849
	4	159.70	162.30	162.17	163.18	161.04	161.68	1.339	163.32	2.201	164.55	1.602
Diphenylacetic Acid	1	146.36	147.32	148.45	149.37	147.74	147.84	1.139	149.70	1.232	148.67	1.315
	2	146.06	147.23	145.69	145.90	146.15	146.20	0.602	147.95	0.672	147.64	0.540
	3	144.68	146.52	147.28	148.07	146.90	146.69	1.260	147.57	1.577	147.47	1.362
	4	145.94	145.94	145.94	149.24	146.56	146.72	1.434	148.99	1.534	148.83	1.436
Anisic Acid*	1		194.35	195.52	193.76	193.38	194.25	0.932	194.18	1.232	195.49	1.112
	2		192.63	195.64	192.76	192.30	193.33	1.553	194.30	1.782	195.42	1.978
	3		194.22	196.27	193.51	191.92	193.98	1.805	194.60	1.779	195.00	2.080
	4		191.75	194.85	193.26	192.04	192.98	1.408	194.43	1.603	195.35	1.409
2-chloroanthraquinone	1	147.44	147.23	147.78	147.44	147.32	147.44	0.209	145.06	0.779	148.15	0.758
	2	145.44	144.14	145.73	145.23	144.52	145.01	0.661	143.84	1.860	146.38	0.395
	3	145.10	142.80	146.86	145.85	144.81	145.08	1.503	144.26	3.258	145.99	1.235
	4	141.25	143.84	146.48	146.31	144.93	144.56	2.143	147.36	1.938	146.72	1.143

Anisic acid, specimen 1, was discarded because the sample pan was not sealed properly, therefore the specimen lost mass.

Examples of original and subsequent fusion scans for the test materials are shown in figures 2-6. Anisic acid was remarkable for stability.[2] Though the enthalpy of many of the substances does not differ significantly in repeat runs from that of the initial runs the shapes of the curves were often distorted. The automated program could not deal properly with temperature onset for these distorted curves. This fault is not in the procedure itself but in the logic of the commercial program used. In such instances, the onset temperature was satisfactorily evaluated manually. As far as use as standards is concerned, the deterioration of a material is not a problem. In instances in which such deterioration takes place, it would be necessary to stipulate that fresh specimens be prepared when needed.

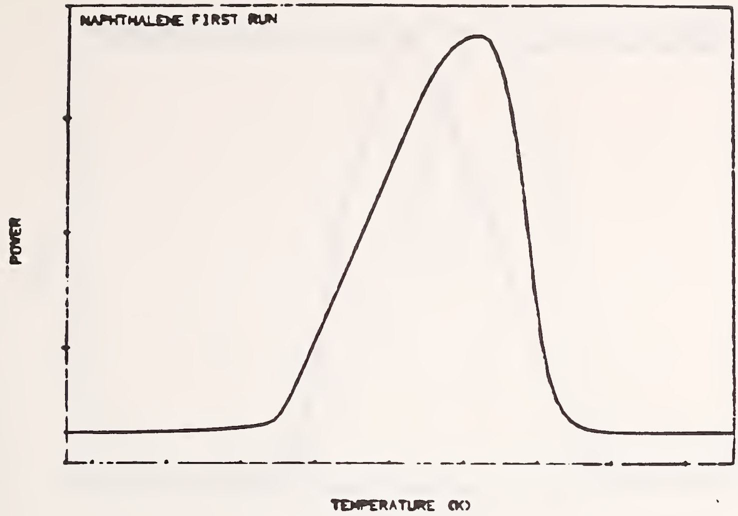
Table 16 summarizes the results obtained in the calibration study and gives available literature values for comparison.

C. Summary

The temperature and enthalpy of transition certified for fusion standards can be improved by more than an order of magnitude by use of the ASTM Recommended Practice [7,8]. The best results are obtained when like substances are used for the calibrations and when the temperature difference between calibrants is about 50 K. No blanket statement can be made about reusing standard specimens. If the curves are not distorted, the specimen may be used again; if the curves are misshapen, the specimen may not be reused.

---

[2] Recent work with a new lot of anisic acid has shown that the acid contains impurities which make it unsuitable for use as a standard. This fact reinforces the need to use certified materials as calibrants.



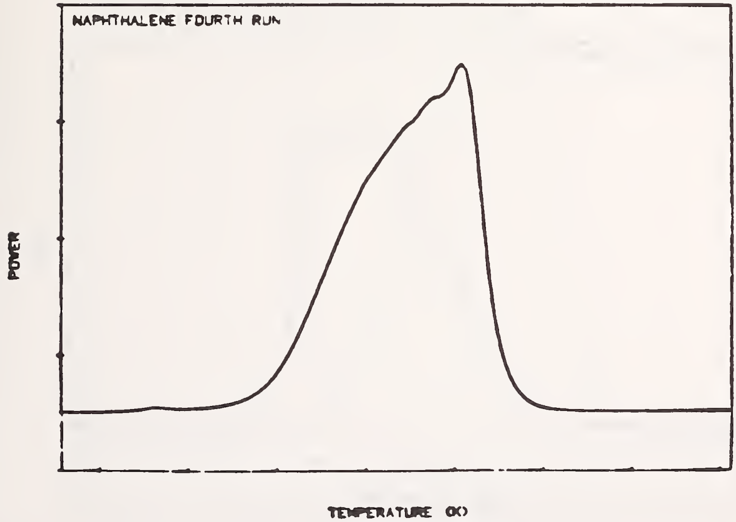
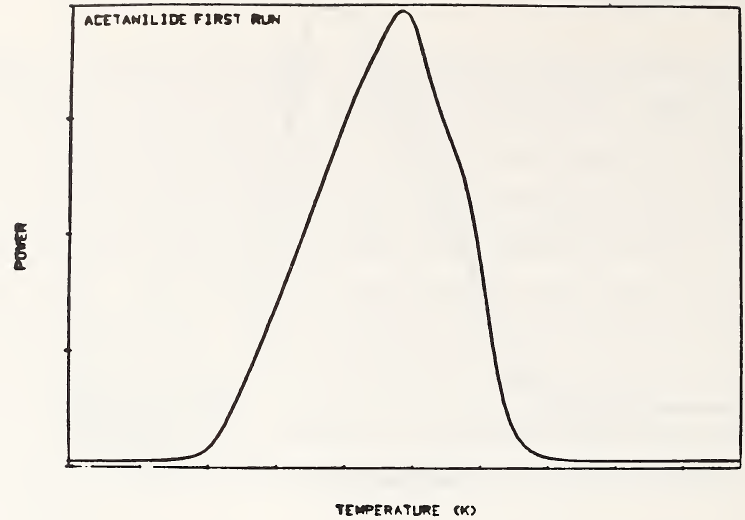


Figure 2. Initial and Final Runs for Naphthalene.



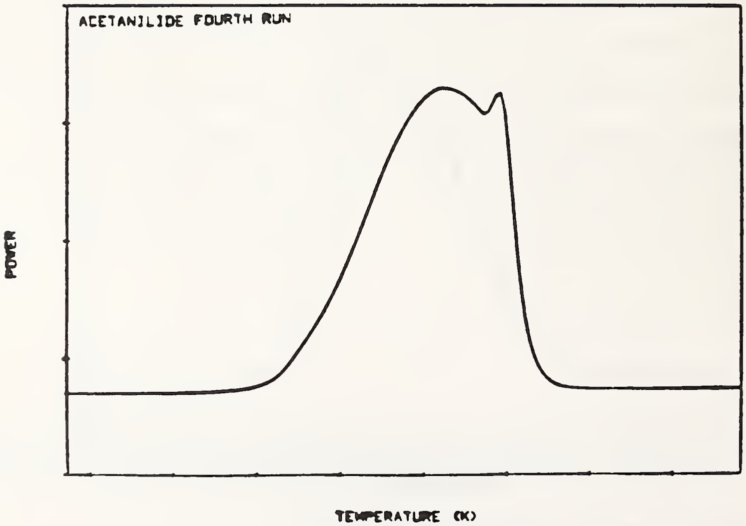


Figure 3. Initial and Final Runs for Acetanilide.

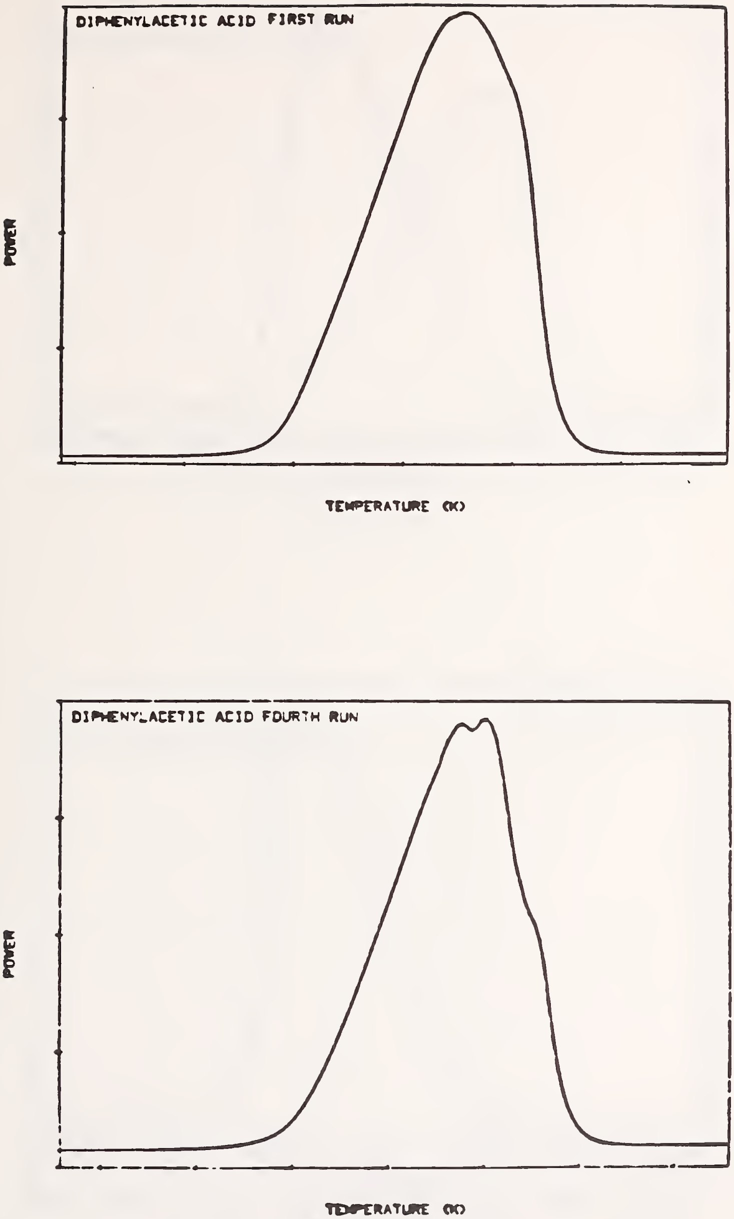


Figure 4. Initial and Final Runs for Diphenylacetic Acid.

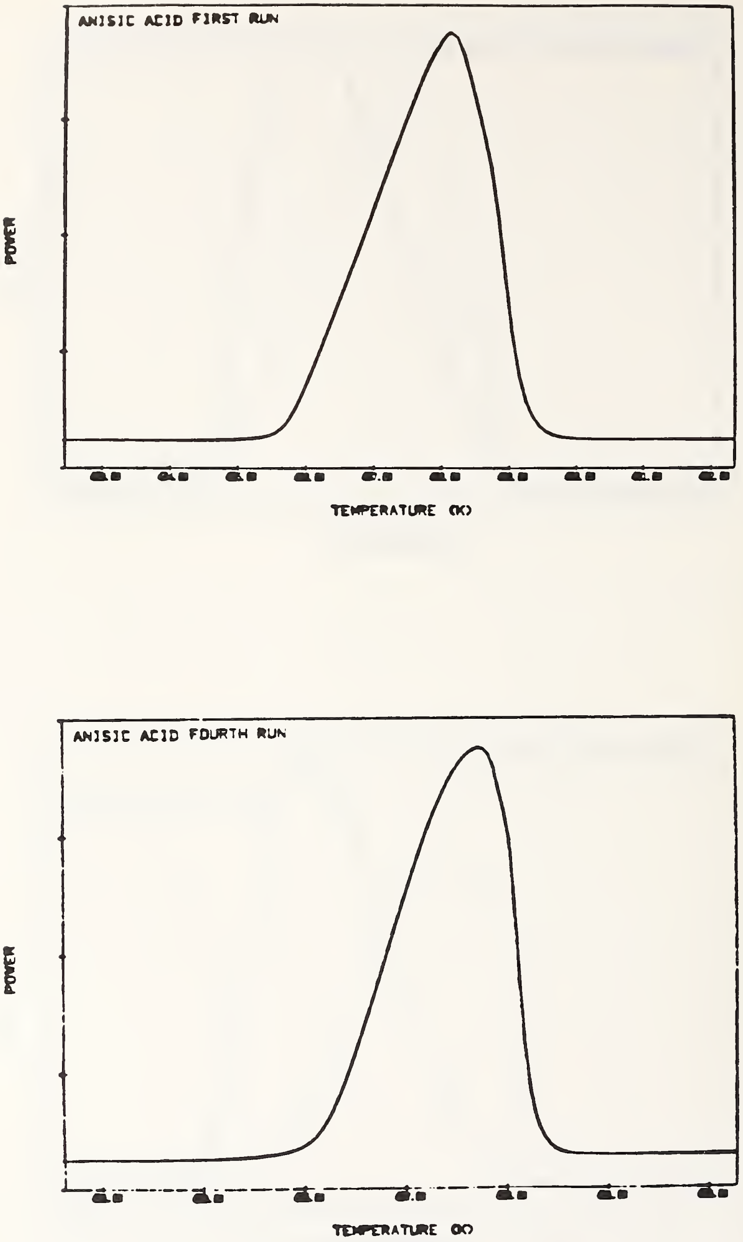


Figure 5. Initial and Final Runs for Anisic Acid.

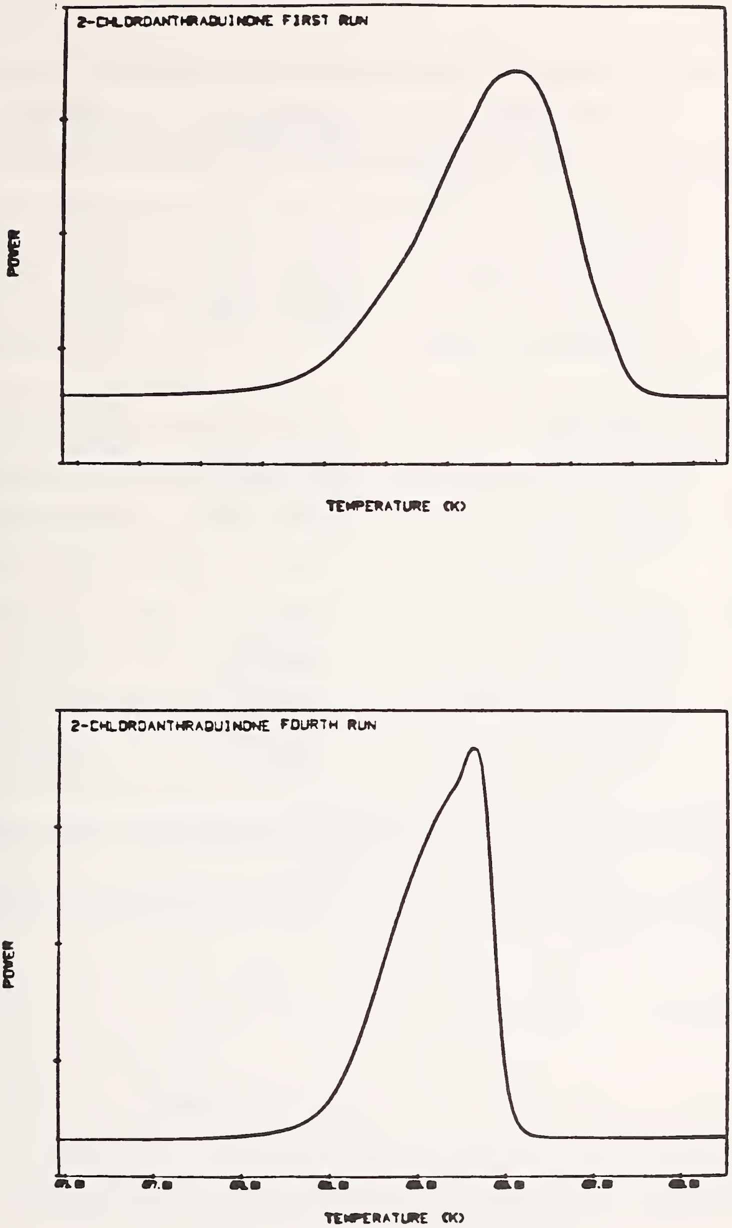


Figure 6. Initial and Final Runs for 2-Chloroanthraquinone.

Table 16. Summary of transition temperatures and enthalpies

	Substance	Transition Temperature (K)	Enthalpy of Transition (J/g)*
INITIAL RUN			
	Naphthalene		149.35 ± 0.85
	Acetanilide	387.35 ± 0.28	163.65 ± 1.26
	Diphenylacetic Acid	420.22 ± 0.16	148.67 ± 1.32
	Anisic Acid	456.18 ± 0.41	195.49 ± 1.11
	2-Chloroanthraquinone		148.15 ± 0.76
ALL RUNS			
	Naphthalene		149.01 ± 1.18
	Acetanilide	387.38 ± 0.37	163.40 ± 1.343
	Diphenylacetic Acid	420.23 ± 0.39	148.16 ± 1.28
	Anisic Acid	456.50 ± 0.43	195.31 ± 1.53
	2-Chloroanthraquinone		146.81 ± 1.20
LITERATURE			
	Naphthalene	353.37[16]	148.6[16]
	Acetanilide	387.51[16]	160.2[16]
	Diphenylacetic Acid	420.41[16]	147.3[16]
	Anisic Acid	456.14[12]	207.91[12]
	2-Chloroanthraquinone	482.20[12]	135.35[12]

NOTE: Naphthalene and 2-chloroanthraquinone have no temperatures listed since they were the outer bracketing substances.

*The enthalpies of transition given are those that have been corrected by the fusion correction only.

References

1. Callanan, J. E.; Sullivan, S. A. to be published.
2. Hudson, C. H., editor. NBS Standard Reference Materials Catalog 1984-5, Nat. Bur. Stand. (U.S.) Spec. Publ. 260; 1984 February. 174 pp.
3. Garn, P. D.; Menis, P. Certificate for ICTA Certified Reference Materials for Differential Analysis from 125-940 °C. 1971.
4. Brennan, W. P.; Gray, A. P. The calorimetric precision and accuracy of a scanning calorimeter. Paper presented at the Pittsburgh Conference, March 1973. Reprint available from Perkin-Elmer Corporation, Instrument Division, Norwalk, Connecticut, USA 06856 as Thermal Analysis Application Study 9.
5. Richardson, M. J.; Burrington, P. Thermal gradients in differential scanning calorimetry. Journal of Therm. Anal. 6: 345-354; 1974.
6. Mraw, S. C.; Naas, D. F. The measurement of accurate heat capacities by differential scanning calorimetry. Comparison of results on pyrite (100-800 K) with literature values from precision adiabatic calorimetry. J. Chem. Thermodynamics. 11: 567-584; 1979.
7. ASTM Standard Practice for temperature calibration of differential scanning calorimeters and differential thermal analyzers E967-83. Annual Book of Standards. 14.02: 782-787; 1984.
8. ASTM Standard Practice for heat flow calibration of differential scanning calorimeters E968-83. Annual Book of Standards. 14.02: 788-794; 1984.
9. McGlashan, M. L. Current trends in precise calorimetry. Thermochemica Acta 72: 55-70; 1984.
10. Kafadar, K. Private communication.
11. NPL Certificate of measurement CRM No. M14-11. Set of ten melting point standards. National Physical Laboratory, Teddington, U.K.; 1980 November.

12. Pella, E.; Nebuloni, M. Temperature measurements with a differential calorimeter. Journal of Therm. Anal. 3: 229-246; 1971.

13. Andon, R. J. L.; Connett, J. E.; Martin, J. F. The enthalpy of fusion of indium; certification of a sample for use as a CRM. NPL Report Chem. 101; 1979 July.

14. The international practical temperature scale of 1968 amended edition of 1975. Metrologia 12: 7-17; 1976.

15. McLaren, E. H.; Murdoch, E. G. The freezing points of high purity metals as precision temperature standards (lead). Can. J. Phys. 38: 577; 1960.

16. Andon, R. J. L.; Connett, J. E. Calibrants for thermal analysis. Measurement of their enthalpies of fusion by adiabatic calorimetry. Thermochemica Acta 42: 241-247; 1980.

Appendix

To judge the suitability of a DSC for the development of standards, it is necessary to identify and evaluate the various sources of experimental variability in temperature and enthalpy measurements. In general, such variability could arise from the DSC, from the procedures and laboratory conditions for working with the DSC, or from inhomogeneity among specimens of the reference material. This appendix describes results of a study that was designed to identify and quantify some of the sources of variation in the DSC procedure and the potential reference materials.

Temperature and enthalpy of transition were measured four times on each of five specimens from three forms of indium (granules, rod, foil). Each of the specimens was remounted in the calorimeter between repeat measurements. It should be noted that the latter protocol means that these data cannot provide distinct estimates of remount variability and variation due to the instrument itself. However, a measure of variability (inhomogeneity) among specimens for each form of indium can be obtained from the analysis.

A statistical analysis of variance shows that specimen-to-specimen variation in enthalpy measurements is potentially significant for all three forms of indium. Evidence of inhomogeneity in melting points was found only for granular indium.

Sample Data

The data and summary statistics from this study are displayed in table 1 and table 2. Figures 1a-c and 2a-c illustrate the specimen-to-specimen (and within-specimen) variability that were observed in the data for temperature and enthalpy of transition, respectively. Specimen-to-specimen variation in temperature is clearly significant for granular indium, but no inhomogeneity is apparent for the other forms of indium. For enthalpy measurements, specimen-to-specimen variation is barely discernible for all three forms of indium.

Table 1. Fusion Temperature of Indium

Form	Specimen	Temperature, K				Specimen Mean		Within Specimen Std. Dev.
Granular	1	429.63	429.96	430.01	429.62	429.81		0.21
	2	429.63	429.34	429.72	429.32	429.50		0.20
	3	429.48	429.49	429.41	429.36	429.44		0.06
	4	429.35	429.33	429.38	429.41	429.37		0.04
	5	429.64	429.61	429.92	429.68	429.71		0.14
					Grand Mean	429.56	Pooled Within-Specimen SD	0.15
					SD of Specimen Means	0.19		
Rod	1	429.50	429.39	430.40	429.58	429.47		0.09
	2	429.38	429.31	429.65	429.60	429.49		0.17
	3	429.84	429.46	429.33	429.30	429.48		0.25
	4	429.78	429.37	429.75	429.67	429.64		0.19
	5	429.56	429.52	429.36	429.43	429.47		0.09
					Grand Mean	429.51	Pooled Within-Specimen SD	0.17
					SD of Specimen Means	0.08		
Foil	1	429.71	429.60	429.74	429.67	429.68		0.06
	2	429.53	429.72	429.83	429.45	429.63		0.17
	3	429.53	429.50	429.48	429.75	429.57		0.13
	4	429.34	429.67	429.72	429.45	429.55		0.18
	5	429.81	429.74	429.25	429.54	429.59		0.25
					Grand Mean	429.60	Pooled Within-Specimen SD	0.17
					SD of Specimen Means	0.15		

Table 2. Enthalpy of Fusion of Indium

Form	Specimen	Enthalpy, J/g				Specimen Mean		Within-Specimen Std. Dev.
Granular	1	28.70	28.12	28.79	27.82	28.36		0.46
	2	28.49	28.91	28.62	28.53	28.64		0.19
	3	29.00	28.83	28.95	28.87	28.91		0.08
	4	28.74	28.49	28.58	28.79	28.65		0.14
	5	28.79	28.70	28.45	28.28	28.56		0.23
					Grand Mean	28.62	Pooled Within-Specimen SD	0.26
					SD of Specimen Means	0.20		
Rod	1	29.20	29.12	28.91	28.87	29.03		0.16
	2	29.16	29.04	28.66	28.70	28.89		0.25
	3	29.04	28.91	28.20	28.95	28.78		0.39
	4	28.74	28.91	28.20	28.95	28.70		0.35
	5	28.45	28.41	28.28	28.45	28.40		0.08
					Grand Mean	28.76	Pooled Within-Specimen SD	0.27
					SD of Specimen Means	0.24		
Foil	1	29.08	29.04	28.91	29.00	29.01		0.07
	2	29.04	28.74	28.83	29.04	28.91		0.15
	3	29.08	29.12	28.95	28.87	29.01		0.12
	4	29.29	28.83	28.83	29.16	29.03		0.24
	5	28.79	28.62	28.87	28.66	28.73		0.12
					Grand Mean	28.94	Pooled Within-Specimen SD	0.15
					SD of Specimen Means	0.12		

Statistical Analysis

For measurements on a given form of indium, a useful model to describe both the within- and among-specimen variation can be represented as follows:

$$X_{ij} = \mu + \delta_i + \epsilon_{ij}, \qquad (1)$$

where

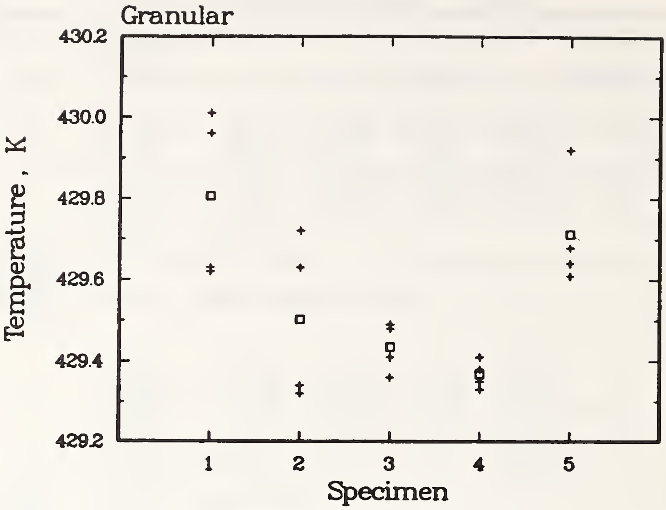


Figure 1a. Fusion temperature measurements for indium granules. (□ indicates specimen mean)

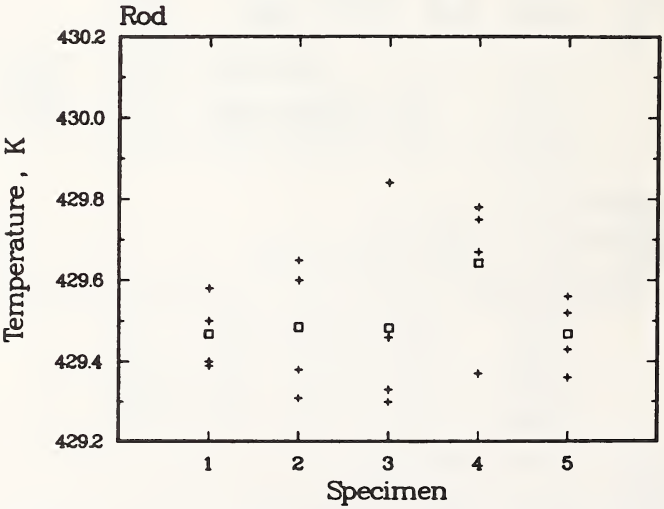


Figure 1b. Fusion temperature measurements for indium rod. (□ indicates specimen mean)

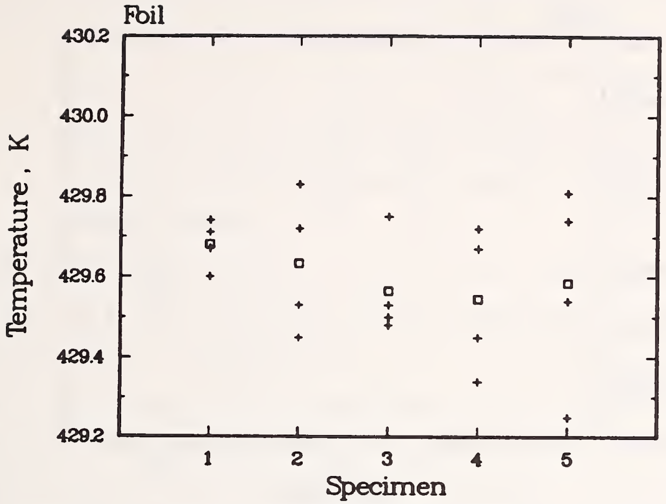


Figure 1c. Fusion temperature measurements for indium foil.
(□ indicates specimen mean)

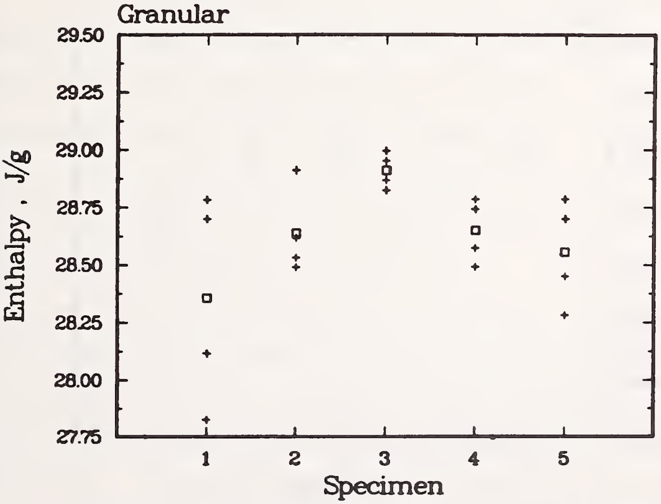


Figure 2a. Enthalpy measurements for indium granules.
(□ indicates specimen mean)

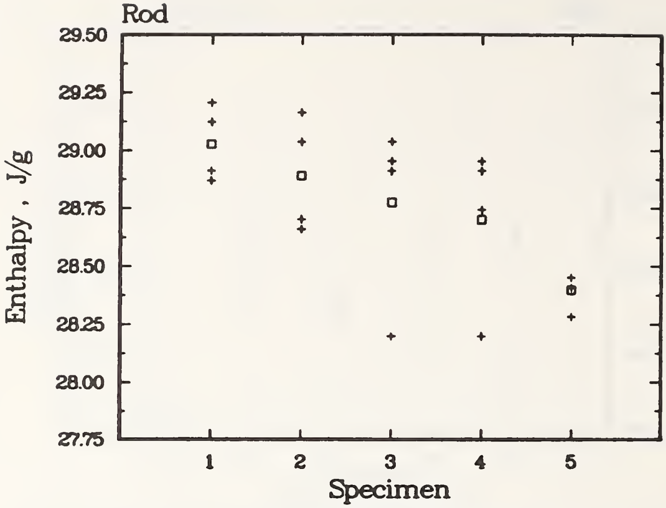


Figure 2b. Enthalpy measurements for indium rod.
(□ indicates specimen mean)

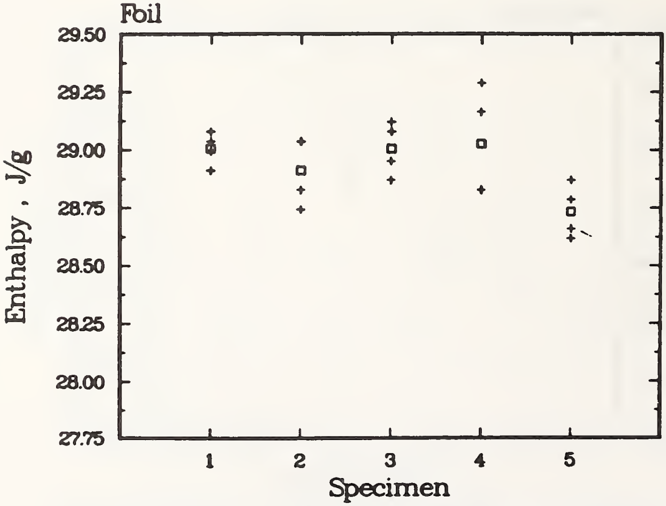


Figure 2c. Enthalpy measurements for indium foil.
(□ indicates specimen mean)

X_{ij} = measured temperature (enthalpy) for repeat run j on specimen i

μ = "true" temperature (enthalpy) for the indium form

δ_i = deviation of specimen i from the true temperature (enthalpy)

ϵ_{ij} = "measurement" error for repeat run j on specimen i (includes effects of remounting, operating procedures, ambient conditions, as well as instrument error).

For each form of indium, the index i runs from 1 to 5 = the number of specimens, and j runs from 1 to 4 = the number of repeated measurements on each specimen. The inhomogeneity, δ_i, and measurement error, ϵ_{ij}, are assumed to have probability distributions that are approximately Gaussian with zero means and standard deviations σ_δ and σ, respectively. Thus, for the indium data, the model represents variability in the data arising in two stages. First, all four measurements receive a common "among-specimen" deviation, δ_i. Then each measurement gets its own within-specimen error, ϵ_{ij}.

The components of variance associated with differences between specimens (σ_δ^2) is a measure of inhomogeneity in the reference material samples. The within-specimen variance (σ^2) comprises other relevant contributions to overall variability that arise because of the chosen experimental protocol.

A statistical analysis of variance corresponding to the model (1) was done (separately) on both temperature and enthalpy data for each form of indium. Estimates of specimen-to-specimen variation and "measurement" error variation that were obtained from the analysis are shown in table 3. Significance levels for the hypothesis of no specimen-to-specimen variation are also given in table 3. The significance levels that were attained show a strong indication of variation in melting temperatures between specimens of granular indium, but no evidence of significant variation for either rod or foil. However, all three forms of indium exhibited possibly inhomogeneous enthalpies of transition among specimens.

Because the results suggest that the magnitude of among-specimen or within-specimen variations may depend on the form of indium, a more general analysis (combining data from all forms) was not conducted.

Table 3. Estimated Specimen-to-Specimen and Within-Specimen Variation

	Temperature			Enthalpy		
	Among Repeats $\hat{\sigma}^2$	Specimen-to-Specimen $\hat{\sigma}_\delta^2$	Significance Level, Test $\sigma_\delta = 0$	Among Repeats $\hat{\sigma}^2$	Specimen-to-Specimen $\hat{\sigma}_\delta^2$	Significance Level, Test $\sigma_\delta = 0$
Granular	$(0.148)^2$	$(0.171)^2$	.0034	$(0.256)^2$	$(0.153)^2$	.0937
Rod	$(0.168)^2$	0	.5419	$(0.270)^2$	$(0.193)^2$	.0502
Foil	$(0.170)^2$	0	.7977	$(0.148)^2$	$(0.097)^2$	.0692

In order to evaluate the uncertainty of the grand mean of all measurements on a given form, a proper estimate of the standard error is obtained by combining both specimen-to-specimen variation (where applicable) and the experimental error variance. Statistical theory [1] gives the following formula for the true standard error of the grand mean of 20 form measurements under model (1):

$$SE(\overline{X}) = \left(\frac{\sigma^2 + 4\sigma_\delta^2}{20}\right)^{1/2} .$$

The usual formula for the standard error of the mean, based on the simple (ungrouped) standard deviation of all 20 measurements, is not useful to estimate this standard error.

Estimates of average melting point and enthalpy of transition for indium forms are given in table 4, along with standard errors that allow for specimen-to-specimen variation where appropriate. Simple standard deviations of the data were used to compute uncertainties of rod and foil melting points (based on the results of the significance tests shown in table 3).

Table 4. Estimated Fusion Temperatures, Enthalpies, and Standard Errors

	Mean Temperature (K)	Standard Error of Mean (K)	Degrees of Freedom	Mean Enthalpy (J/g)	Standard Error of Mean (J/g)	Degrees of Freedom
Granular	429.57	0.08	4	28.62	0.09	4
Rod	429.51	0.04*	19	28.76	0.11	4
Foil	429.60	0.04*	19	28.94	0.06	4

*Computed assuming homogeneous specimens.

Reference

[1] Box, G. E. P., Hunter, W. G., and Hunter, J. S. (1978). Statistics for Experimenters, John Wiley, New York, pp. 571-583.

NBS-114A (REV. 2-80)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** *(See instructions)*	1. PUBLICATION OR REPORT NO. NBS/SP-260/99	2. Performing Organ. Report No.	3. Publication Date August 1985

4. TITLE AND SUBTITLE

Standard Reference Materials:

Feasibility Study for the Development of Standards Using Differential Scanning Calorimetry

5. AUTHOR(S)

J. E. Callanan, S. A. Sullivan, and D. F. Vecchia

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
U.S. DEPARTMENT OF COMMERCE
GAITHERSBURG, MD 20899

7. Contract/Grant No.

8. Type of Report & Period Covered

Final

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

Same as item 6.

10. SUPPLEMENTARY NOTES

Library of Congress Catalog Card No.: 85-600567

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

The tremendous increase in the use of differential scanning calorimetry, coupled with the decrease in the capability for conventional precision calorimetry, has created a need for more and better thermal standards for use with scanning calorimeters and other thermal instruments currently available, such as thermomechanical analyzers. The development of these standards by methods such as adiabatic or drop calorimetry is impractical because of the number and variety of standards required, the associated expense, and the lack of facilities and personnel to do the certification. A two-part study was designed to evaluate the capability of a differential scanning calorimeter for developing temperature and enthalpy of fusion standards. Part I evaluated the variability of the differential scanning calorimeter (DSC) and factors which affected it; Part II applied American Society of Testing Materials (ASTM) procedures for the temperature and heat flow calibration. The study shows that fusion standards can be developed with a differential scanning calorimeter.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

differential scanning calorimetry; enthalpy; fusion; pilot study; standards; temperature; thermal analysis

13. AVAILABILITY

☒ Unlimited
☐ For Official Distribution. Do Not Release to NTIS
☒ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.
☐ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

14. NO. OF PRINTED PAGES

55

15. Price

USCOMM-DC 6043-P80

NBS Technical Publications

Periodical

Journal of Research—The Journal of Research of the National Bureau of Standards reports NBS research and development in those disciplines of the physical and engineering sciences in which the Bureau is active. These include physics, chemistry, engineering, mathematics, and computer sciences. Papers cover a broad range of subjects, with major emphasis on measurement methodology and the basic technology underlying standardization. Also included from time to time are survey articles on topics closely related to the Bureau's technical and scientific programs. Issued six times a year.

Nonperiodicals

Monographs—Major contributions to the technical literature on various subjects related to the Bureau's scientific and technical activities.

Handbooks—Recommended codes of engineering and industrial practice (including safety codes) developed in cooperation with interested industries, professional organizations, and regulatory bodies.

Special Publications—Include proceedings of conferences sponsored by NBS, NBS annual reports, and other special publications appropriate to this grouping such as wall charts, pocket cards, and bibliographies.

Applied Mathematics Series—Mathematical tables, manuals, and studies of special interest to physicists, engineers, chemists, biologists, mathematicians, computer programmers, and others engaged in scientific and technical work.

National Standard Reference Data Series—Provides quantitative data on the physical and chemical properties of materials, compiled from the world's literature and critically evaluated. Developed under a worldwide program coordinated by NBS under the authority of the National Standard Data Act (Public Law 90-396). NOTE: The Journal of Physical and Chemical Reference Data (JPCRD) is published quarterly for NBS by the American Chemical Society (ACS) and the American Institute of Physics (AIP). Subscriptions, reprints, and supplements are available from ACS, 1155 Sixteenth St., NW, Washington, DC 20056.

Building Science Series—Disseminates technical information developed at the Bureau on building materials, components, systems, and whole structures. The series presents research results, test methods, and performance criteria related to the structural and environmental functions and the durability and safety characteristics of building elements and systems.

Technical Notes—Studies or reports which are complete in themselves but restrictive in their treatment of a subject. Analogous to monographs but not so comprehensive in scope or definitive in treatment of the subject area. Often serve as a vehicle for final reports of work performed at NBS under the sponsorship of other government agencies.

Voluntary Product Standards—Developed under procedures published by the Department of Commerce in Part 10, Title 15, of the Code of Federal Regulations. The standards establish nationally recognized requirements for products, and provide all concerned interests with a basis for common understanding of the characteristics of the products. NBS administers this program as a supplement to the activities of the private sector standardizing organizations.

Consumer Information Series—Practical information, based on NBS research and experience, covering areas of interest to the consumer. Easily understandable language and illustrations provide useful background knowledge for shopping in today's technological marketplace.

Order the **above** *NBS publications from: Superintendent of Documents, Government Printing Office, Washington, DC 20402.*

Order the **following** *NBS publications—FIPS and NBSIR's—from the National Technical Information Service, Springfield, VA 22161.*

Federal Information Processing Standards Publications (FIPS PUB)—Publications in this series collectively constitute the Federal Information Processing Standards Register. The Register serves as the official source of information in the Federal Government regarding standards issued by NBS pursuant to the Federal Property and Administrative Services Act of 1949 as amended, Public Law 89-306 (79 Stat. 1127), and as implemented by Executive Order 11717 (38 FR 12315, dated May 11, 1973) and Part 6 of Title 15 CFR (Code of Federal Regulations).

NBS Interagency Reports (NBSIR)—A special series of interim or final reports on work performed by NBS for outside sponsors (both government and non-government). In general, initial distribution is handled by the sponsor; public distribution is by the National Technical Information Service, Springfield, VA 22161, in paper copy or microfiche form.

U.S. Department of Commerce
National Bureau of Standards
Gaithersburg, MD 20899