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Standard Reference Materials:

Feasibility Study for the Development of Standards Using Differential Scanning Calorimetry

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

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Preface

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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:

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Contents

List of Tables

List of Figures

Feasibility Study for the Development of Standards Using Differential Scanning Calorimetry

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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

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[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

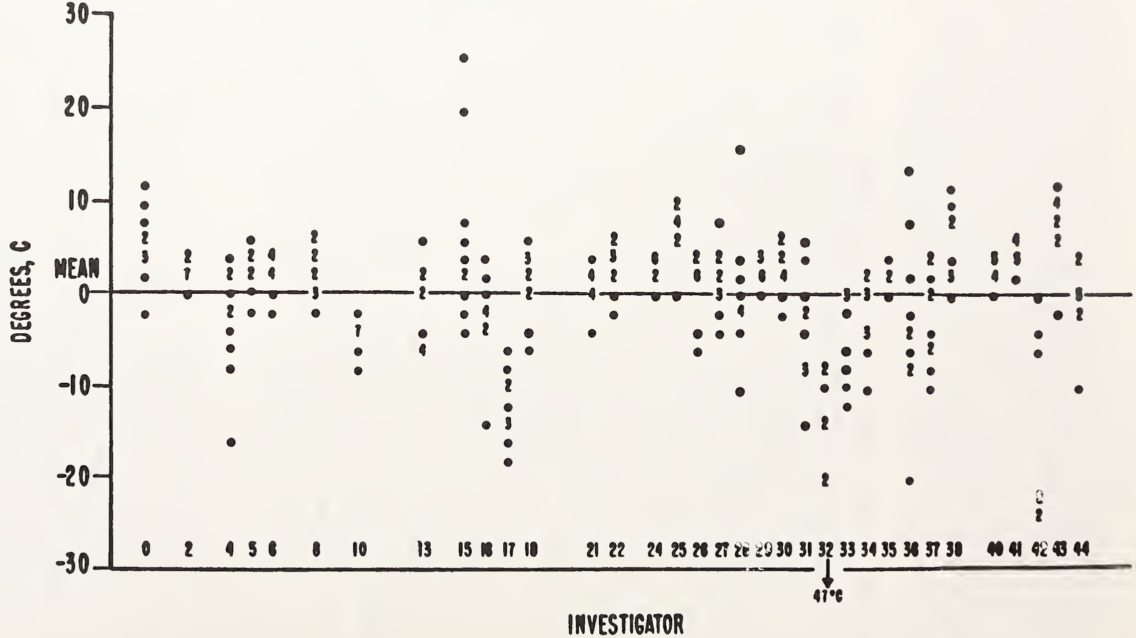

Figure 1. Deviations from the mean value as reported by the 34 investigators (submitted to the Standards Committee of ICTA).[3]

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.

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[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 remounted 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 $\pm$ 0.002[a] mg
	49.972 $\pm$ 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 $\pm$ 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 $\pm$ 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)

Operator 1

	T(K)	Enthalpy (J/g)
	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

	T(K)	Enthalpy (J/g)
	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)			Enthalpy (J/g)		Degrees of Freedom
Range	Variance	---	Variance	Range	
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,

$$T = (T_0 \times S) + I, \qquad (2)$$

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).

$$S = (TS_1 - TS_2)/(TO_1 - TO_2) \qquad (3)$$

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

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$\pm$0.2[11]	456.24
2-Chloroanthraquinone		482.75$\pm$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}),

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

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

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

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

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

The $\Delta H(act)$ 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. 31	32	33	34	35	Mean	Standard Deviation
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. 21	22	23	24	25	Mean	Standard Deviation
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. 11	12	13	14	15	Mean	Standard Deviation
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. 31	32	33	34	35	Mean	Standard Deviation
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. 21	22	23	24	25	Mean	Standard Deviation
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. 11	12	13	14	15	Mean	Standard Deviation
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. 1	2	3	4	5	Mean	Std.Dev.	Full Correction Mean	Full Correction Std.Dev.	Fusion Correction Mean	Fusion Correction 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.

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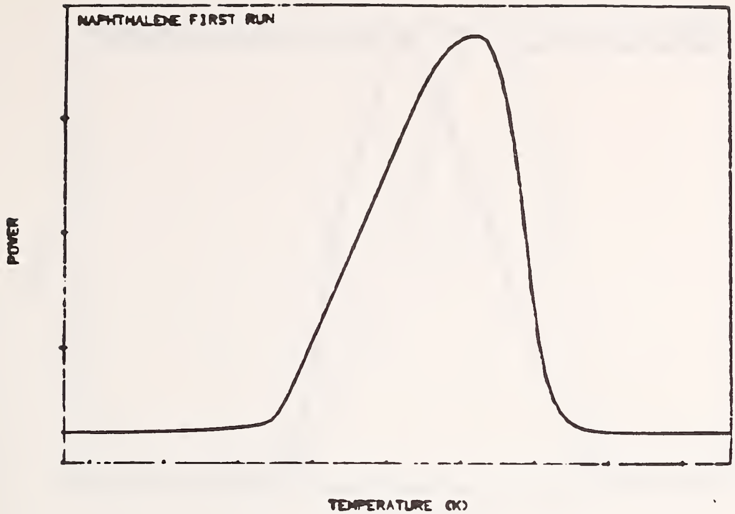
[2]Recent work with a new lot of anisic acid has shown that the acid contains impurities which make it unsuitable for use as a standard. This fact reinforces the need to use certified materials as calibrants.



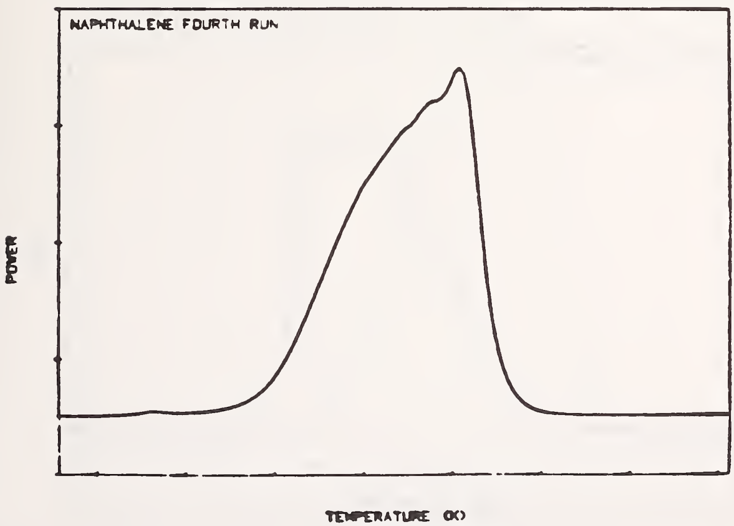
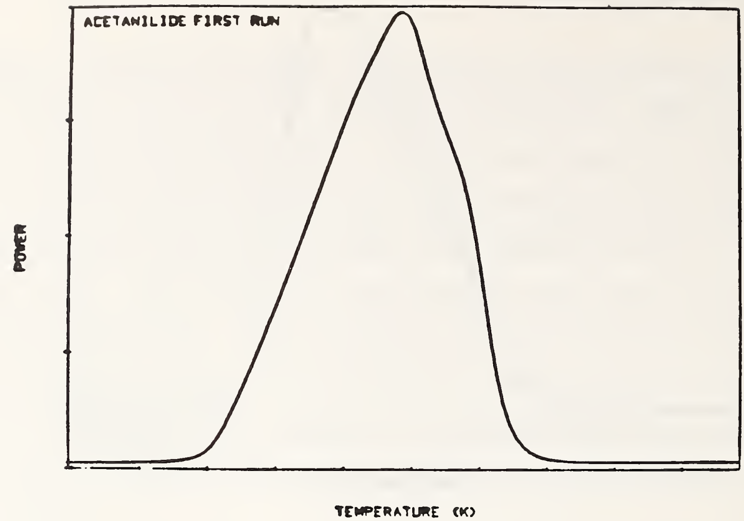


Figure 2. Initial and Final Runs for Naphthalene.



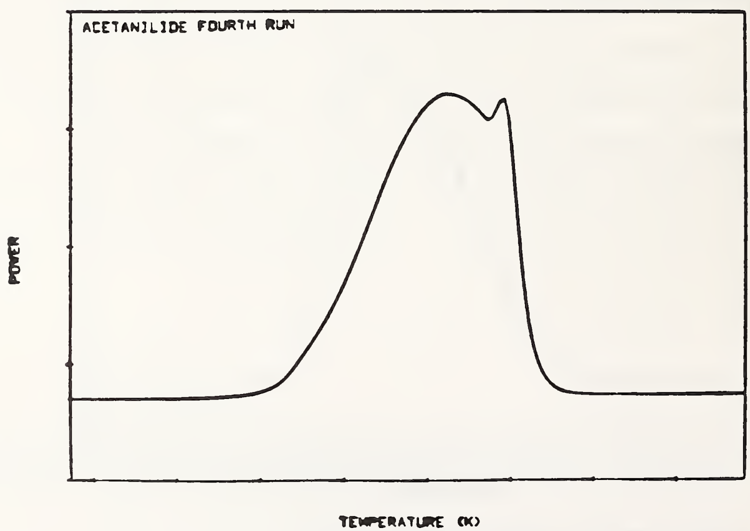
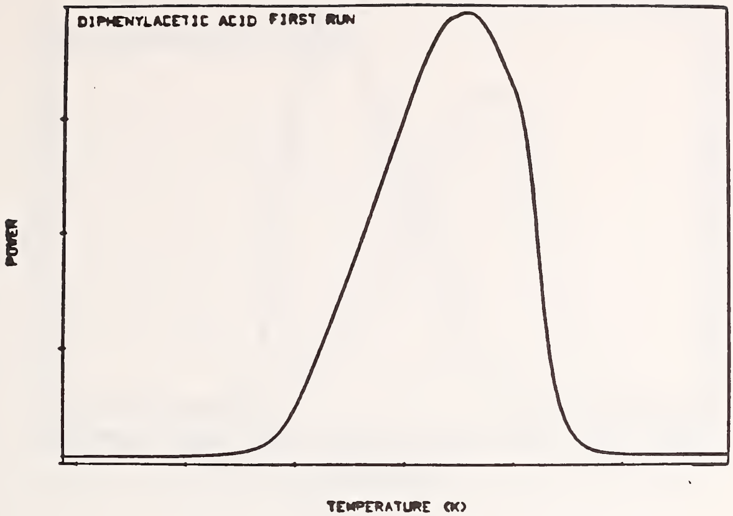


Figure 3. Initial and Final Runs for Acetanilide.



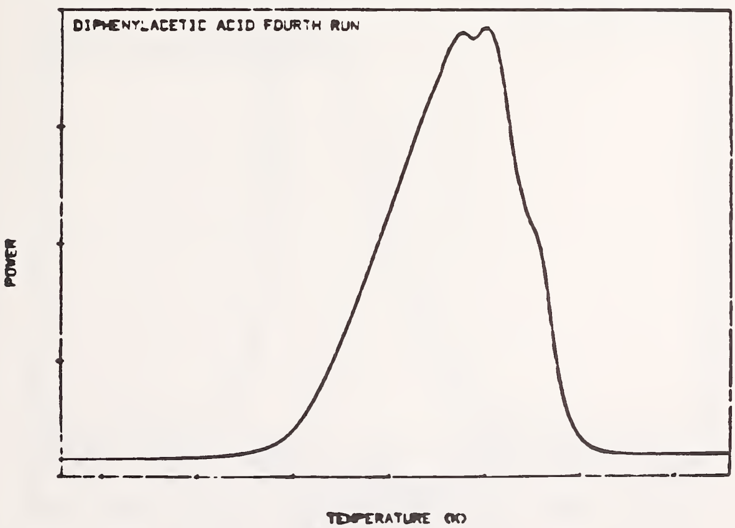
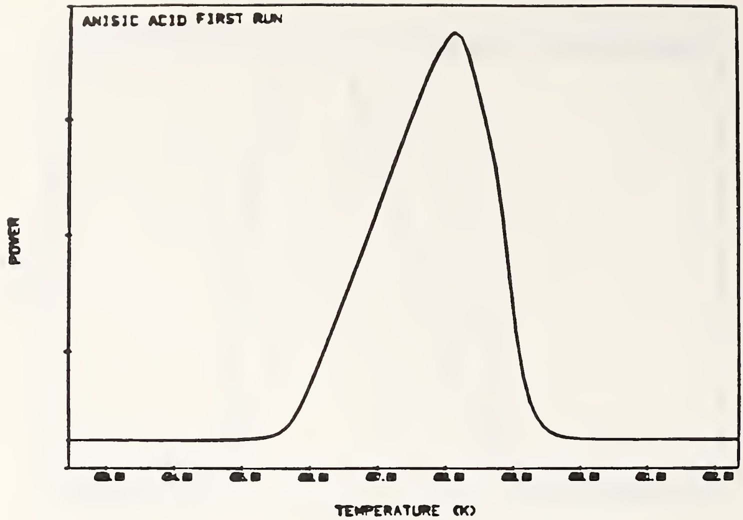


Figure 4. Initial and Final Runs for Diphenylacetic Acid.



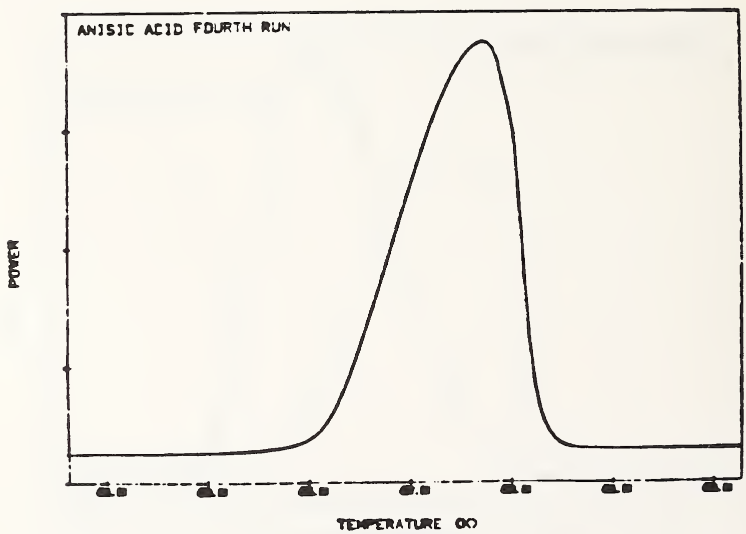
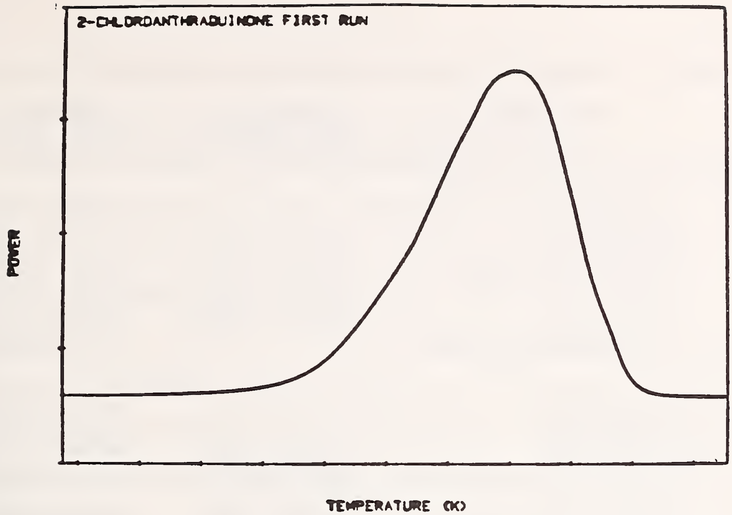


Figure 5. Initial and Final Runs for Anisic Acid.



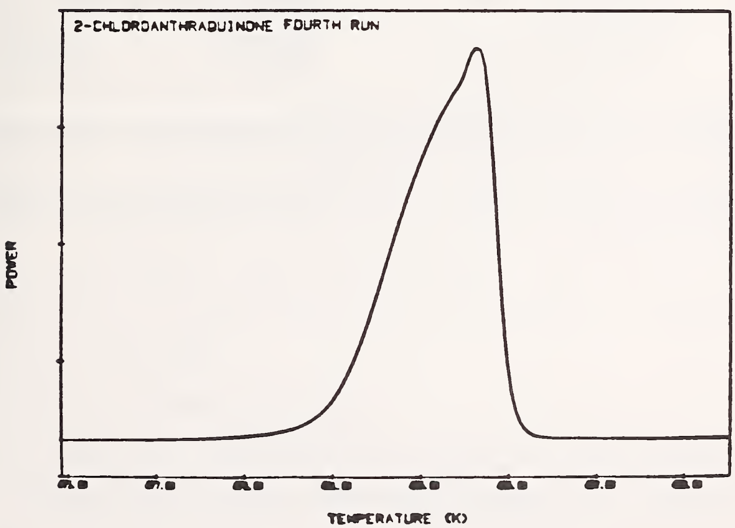


Figure 6. Initial and Final Runs for 2-Chloroanthraquinone.

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.

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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

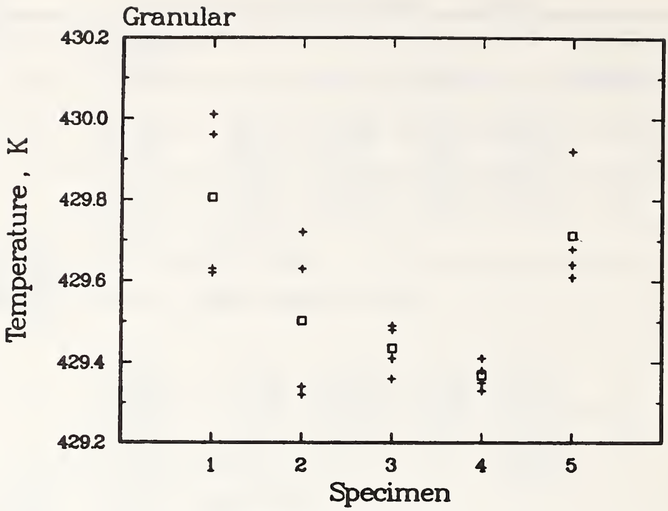

Figure 1a. Fusion temperature measurements for indium granules. (□ indicates specimen mean)

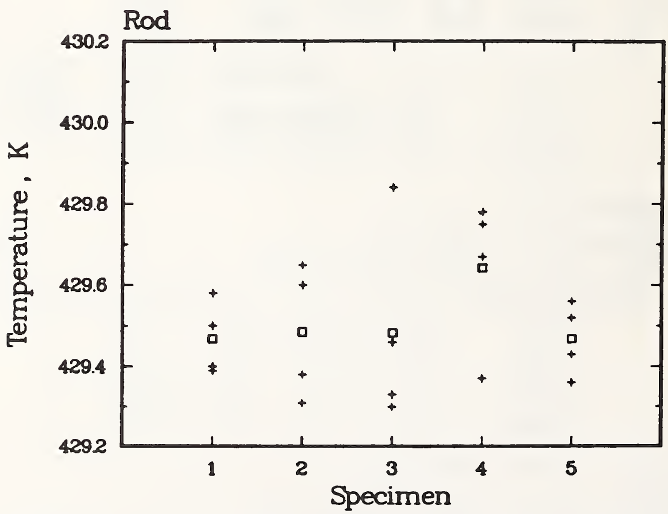

Figure 1b. Fusion temperature measurements for indium rod. (□ indicates specimen mean)

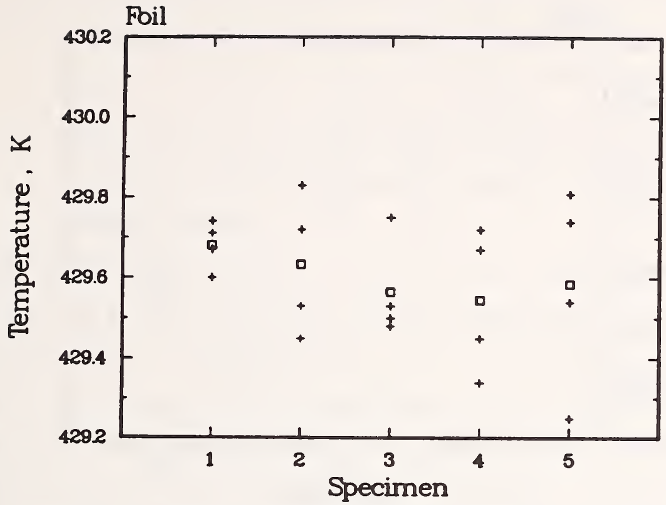

Figure 1c. Fusion temperature measurements for indium foil.
(□ indicates specimen mean)

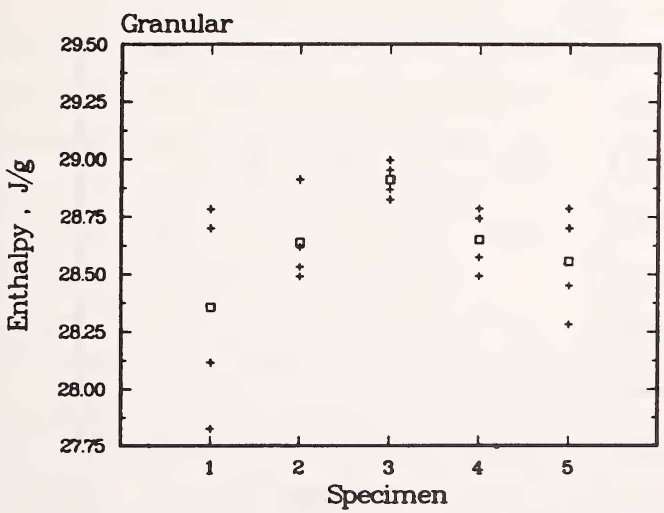

Figure 2a. Enthalpy measurements for indium granules.
(□ indicates specimen mean)

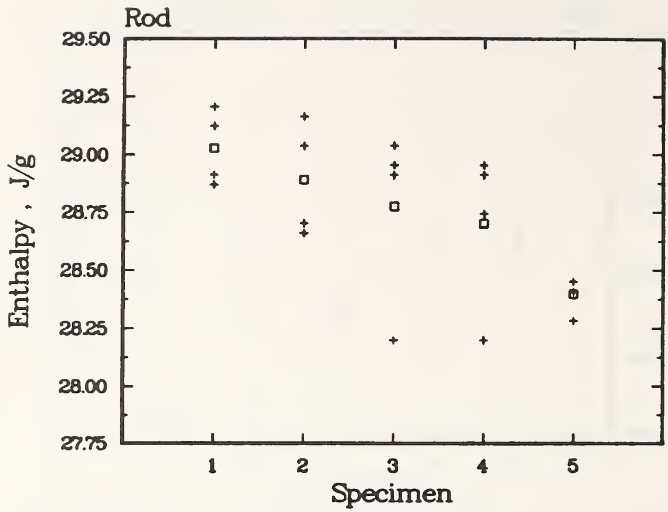

Figure 2b. Enthalpy measurements for indium rod.
(□ indicates specimen mean)

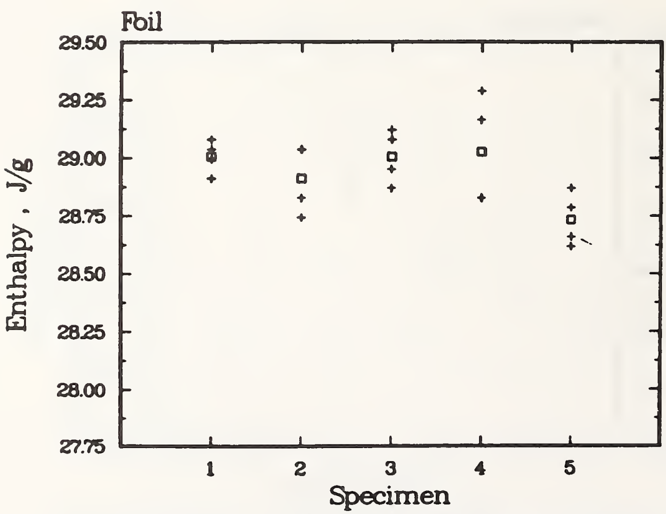

Figure 2c. Enthalpy measurements for indium foil.
(□ indicates specimen mean)

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.

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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

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