Certificate

ICTA Certified Reference Materials

For Measurements Below 350 K

Certified by the

International Confederation for Thermal Analysis

and

Distributed by the

United States National Bureau of Standards

as

GM-757

These Certified Reference Materials are certified for measurement by differential thermal analysis or differential scanning calorimetry at temperatures below 350 K for calibration under dynamic temperature change and for interlaboratory comparison of data.

The National Bureau of Standards distributes a number of materials certified by recognized standards organizations, professional societies, or other government agencies.

The National Bureau of Standards has ascertained that the certifying organization is a recognized non-profit professional society one of whose objectives is to improve the reliability of measurements. The sponsoring organization is solely responsible for the quality of the material and for the accuracy of the statements and data related to this certified reference material.

Certificate

ICTA Certified Reference Materials (CRM)
for differential thermal analysis, differential scanning calorimetry,
and related techniques below 350 K

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INTERNATIONAL CONFEDERATION FOR THERMAL ANALYSIS

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GM-757

The CRM provides:

(1) a homogeneous batch of the specified material;

(2) the mean values of the defined points shown in Table II, Page 12;

(3) the mean values listed according to the type of cell arrangement and sensor location, Tables III-VII;

(4) work sheets for comparisons of users instrument with the comparable arrangement in Item (3) and for logging instrument behavior; and

(5) a description of the Committee's method and rationale for evaluating the data as well as other background information.

The certificate was prepared for the ICTA by
PAUL D. GARN and OSCAR MENIS
of the
Committee on Standardization
International Confederation for Thermal Analysis

Members of the Committee are:

Paul D. Garn	R. C. Mackenzie	Takeo Ozawa
R. P. Graham	H. G. McAdie	F. Paulik
K. Heide	O. Menis	J. P. Redfern
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I. INTRODUCTION

In this certificate information is presented to enable the user of the ICTA's Certified Reference Materials to obtain optimum accuracy in measurement of dynamic thermal systems. It is a continuation of the effort of the Standards Committee of ICTA to provide dynamic temperature standards needed in several fields of thermal analysis. These vary in character and cover a wide temperature range.

A dynamic temperature standard differs from an equilibrium temperature standard in that, based on empirical studies, it exhibits the following characteristics: (a) it has an easily detected and reproducible thermal effect (i.e., provides an easily measureable and sensitive signal); (b) undergoes its thermal change rapidly enough to be measured in commercially available dynamic instruments; (c) is stable enough to permit its convenient use under the normal operating conditions of the instrument. These materials are not intended and may not meet the criteria for equilibrium temperature standards. Their values are based on dynamic measurements and incorporate the errors associated with them.

The need for dynamic temperature standards for differential thermal analysis (DTA) had been recognized by a number of agencies, but no substantial effort to provide these standards was made prior to the formation of the Committee on Standardization of the International Confederation for Thermal Analysis (ICTA). That Committee began an intensive study of the problems in 1966. The National Bureau of Standards participated in the planning and implementation of a test program designed to screen proposed standards. The Committee members provided liaison with related organizations in other countries.

By 1967, priorities has been established and a number of materials were tested within the scope of the highest priority, viz. inorganic specimens within the ambient to 1000°C temperature range. Choice of material was restricted

to those having first-order-solid state phase changes in the appropriate temperature ranges. Melting points were excluded because several types of specimen holders in common use could not retain liquids and decomposition processes were considered to be unsuitable because the atmosphere could not be controlled in many apparatuses. It was clearly defined that these standards are intended for calibration of the temperature scale under the conditions of the experiment; any modification of the experimental conditions to facilitate the testing of the reference materials would defeat the purpose.

During the preparation and testing of the first sets of reference materials, plans to meet other needs were made by the same committee. Subsequently, the present program was initiated because of requests for low temperature reference materials for organic materials in the 20-200°C range. The decision was based on responses to questionnaires by members of the International Confederation of Thermal Analysis, and also from a suggestion by the Commission I.4 of the International Union for Pure and Applied Chemistry.

The testing leading to the certification of the low temperature materials was designated as the Third International Test Program (Third ITP). Data were sent to the Chairman for preparation for computation. The computations were carried out by the Vice Chairman in the same manner as for the Second ITP. See APPENDICES A & B.

II. THE THIRD INTERNATIONAL TEST PROGRAM

The Third ITP was carried out to provide experimental data for certification of the particular lots of potential DTA temperature standards from which the samples were taken. On the basis of data obtained from the Third International Test Program, and the recommendation of its Committee on

Standardization, the International Confederation for Thermal Analysis issues these specimens as Certified Reference Materials for measurements in the region below 350 K.

III. MATERIALS

A. Criteria

The need for $Solid_1$ - $Solid_2$ transitions did not appear to be important in the temperature range projected for coverage. Both the preponderance of literature on materials which are liquid at ambient temperature and the absence of significant numbers of low-temperature DTA apparatus which could not contain liquids militated against such a restriction. Hence, melting points were selected on these bases:

1. More information was available on more materials than for $Solid_1$ - $Solid_2$ transitions. Selection of materials would be easier.

2. The large number of acceptable materials indicated that availability would not present a problem.

3. The magnitude of the thermal effect is generally much greater for a Solid - Liquid than for a $Solid_1$ - $Solid_2$ transition.

4. Homogeneity of a batch of liquid is more easily achieved than for a solid.

It was reconized that the effect of impurities upon the measured temperature may be greater for Solid - Liquid than for $Solid_1$ - $Solid_2$ transitions, the selected batch of material is therefore intended for interlaboratory comparison and not as an absolute thermo-dynamic standard. This is not an important issue because it is not specific <u>materials</u> which are being certified, but <u>particular batches</u> of these materials.

One material, cyclohexane, was selected in part because it has also a well defined $Solid_1$ - $Solid_2$ transition.

B. Selected Materials

From the criteria above, studies of the literature, and preliminary testing, preselected batches of the materials listed below were chosen:

Material	Source
1.2 Dichlorethane	Baker Reagent Grade
Cyclohexane	Baker Reagent Grade
Phenylether	Baker Reagent Grade
o-Terphenyl	Eastman

Because their use is as a common reference material, only the material purchased and tested is certified and it is not the intent of this committee that the data be considered normative for the chemical species. For this reason, any attempt to relate the data to equilibrium values is neither necessary nor appropriate. See APPENDIX C.

IV. INVESTIGATORS AND EQUIPMENT

Table I lists the investigator, country, and type of equipment.

TABLE I

PARTICIPANTS AND APPARATUS USED IN THIRD INTERNATIONAL TEST PROGRAM

Investigator and Country	Apparatus
Dr. Kirsten Aas/ Dr. Karsten Gamlem (Norway)	DuPont 900 Thermal Analyzer
Mr. A. Bernard (France)	Bureau de Liaison Model M4
Dr. R. L. Bohon (USA)	DuPont 900 Thermal Analyzer
Dr. B. Bolin/ Dr. B. O. Haglund (Sweden)	Mettler TA 1
Dr. H. Flammersheim (DDR)	Perkin-Elmer, DSC-1B
Dr. M. Harmelin (France)	Bureau de Liaison Model M4
Mrs. C. W. Huffman (USA)	DuPont 900 Thermal Analyzer
Mr. T. Koide (Japan)	Own design
Mr. E. A. Lewis (USA)	DuPont 920 Thermal Analyzer

Investigator and Country	Apparatus
Dr. E. E. Marti (Switzerland)	Perkin-Elmer Corp. DSC-2
Dr. O. Menis/ Mr. B. I. Diamondstone (USA)	DuPont 900 Thermal Analyzer
Prof. H. R. Oswald (Switzerland)	Mettler Instruments Recording Vacuum Thermoanalyzer
Mr. T. Ozawa (Japan)	Rigaku Denki Co. Ltd. DSC, Model 8057
Mr. R. Yokota/ Prof. H. Kambe (Japan)	Perkin-Elmer Model DSC-1

V. PROCEDURE

The instructions given to the participants in this test program are presented below with explanatory statements.

1. The operating conditions of each instrument should be those normally employed.

   In all cases, it is the instrument's response to the thermal event which is under test--not the event itself. Hence, the conditions should not differ from those used for other samples.

2. The accuracy of the temperature-measuring thermocouple should be known. If calibration is required, the Committee prefers use of recognized melting point standards. Distilled water and triple distilled mercury are satisfactory.

   The accuracy of thermocouples can be tested independently; for example, external to the furnace assembly by standard techniques. If an equilibrium test cannot be made, use of a large sample and low heating or cooling rates will give the optimum approach to equilibrium.

3. All temperature data should be reported to the nearest 1°C.

   Even though some instruments can be read to the nearest 0.1°C, most instruments used in this temperature

range can be read only to the nearest degree. The data show that there is no gain in requesting greater precision.

4. A time-temperature curve from the temperature-sensor should be included. If the temperature is measured in the sample cell, this record should be obtained using hexane in the reference cell.

   The time-temperature plot yields a measure of the uniformity of the heating rate. Whereas slow changes are seldom serious, a discontinuity may produce an artifact in the curve and a substantial change will result in varying resolution in different temperature ranges.

5. Each sample should be examined at one heating rate in the range of 4-10°C $min.^{-1}$.

   This range is typical and neither the transition point nor the meltings will vary with heating rate. The apparent variation for any particular instrument is small. See Section VIII. B.

6. Both programmed heating and cooling should be employed if the apparatus permits. If cooling runs are made, the rate of cooling should approximate the rate of heating.

   The cooling data provide a measure of the supercooling of the materials. The ability to detect supercooling varies from instrument to instrument.

7. One curve of the reference material against the reference material should be supplied, using the maximum ΔT sensitivity employed with the test materials.

   A substantial baseline drift will impair resolution of the peak and, of course, the measured points.

8. Samples should not be diluted or otherwise pretreated.

Any contamination by dilution is certain to change the measured temperatures. Any pretreatment will render the sample different from the material to be certified.

9. Maximum sample size should be less than 300 mg.

The test program is most useful if it is related to commonly used commercial instruments. These generally accommodate 3-250 mg. of typical liquids.

10. At least two curves should be run on each material. If more than two curves are run and any rejected, the rejected data should be forwarded with the other data, together with the reason for rejection.

A measure of the reproducibility of the individual instrument is an important part of the test. Rejected runs, which are insignificant individually, may disclose a behavior pattern.

11. The sample atmosphere should be oxygen-free nitrogen at 1 atm. pressure dried over $MgClO_4$ or its equivalent.

Water is a serious contaminant and therefore presents a particular problem but oxidation is avoided as a matter of good technique.

12. Where possible the same sample holder or container should be used for the entire series of tests.

Substitution of another sample vessel may change the response slightly.

13. Conditions of packing of the sample within the sample holder should be specified.

This applies only to the solid o-terphenyl in this study.

14. The Committee would appreciate receiving a measurement of each peak area as defined in the accompanying figure, expressed in the units, °C. sec. mg^{-1}.

The data will be examined for the possibility of quantitative calibration.

15. Results should be reported according to the recommendations for good practice published by the Committee.

These recommendations have been published in Analytical Chemistry, Vol. 39, 543 (1967). The reporting form precludes most error in transmission of data.

16. The Committee would appreciate samples being examined in the randomized order provided to eliminate systematic bias.

Systematic testing from the lowest to the highest temperatures or highest to lowest temperatures may set up a temperature distribution within the furnace assembly which would not be reproduced in a single run. Randomizing the samples approaches most closely the ordinary conditions of operation.

VI. DATA HANDLING

A. Data Preparation

From descriptions submitted by each investigator, appropriate code designations for pertinent instrumental parameters were selected jointly by P. D. Garn and H. G. McAdie. In cases where an investigator employed different instrumental parameters for different materials care was taken to separate data from these experiments. These were, where possible, identical to the coding for the Second International Test Program (Certified Reference Materials listed by the U. S. National Bureau of Standards as GM 758-759-760). The parameters are shown in Figure 1.

Temperature and area data from each experiment were coded from the values supplied by each investigator. An "experiment" was defined as including the heating and cooling modes if both were carred out. No attempt was made to

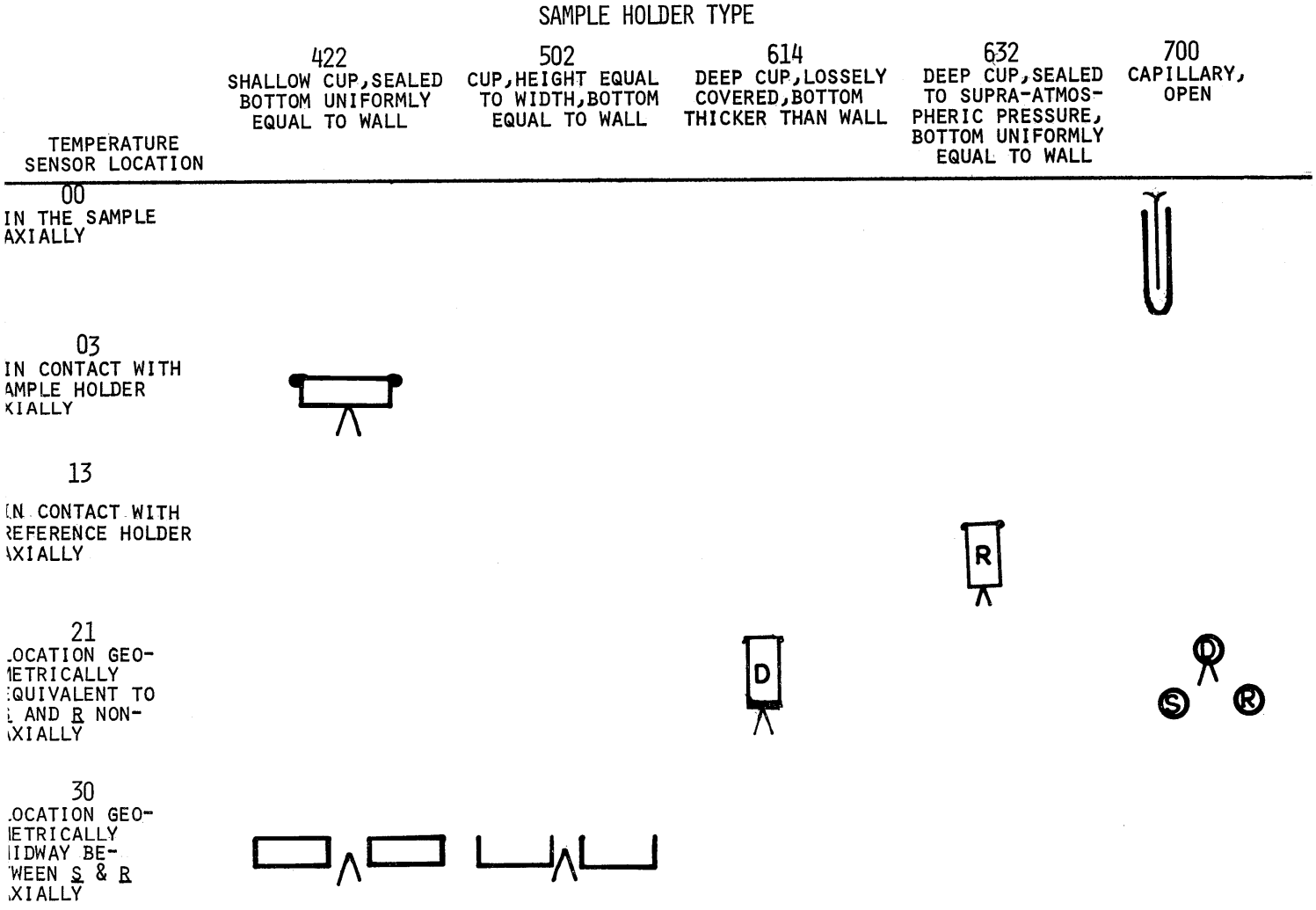


FIGURE 1

The Physical Relationships between Sample Holder and Temperature Sensor in the Experimental Arrangements Used in the Third International Test Program

measure, review, check, or correct these data; however, each chart record was examined in relation to the data being coded to reduce transcription errors and avoid misinterpretation. In cases where obvious discrepancies appeared, or where further information regarding instrumentation was required, details were obtained by correspondence.

A number of conventions were adopted:

1. Extrapolated onset temperature was defined as the intersection of the forward-extrapolated baseline with the backward-extrapolated initial side of the peak, as shown in Figure 2. The term "onset temperature" throughout this report refers to that point.

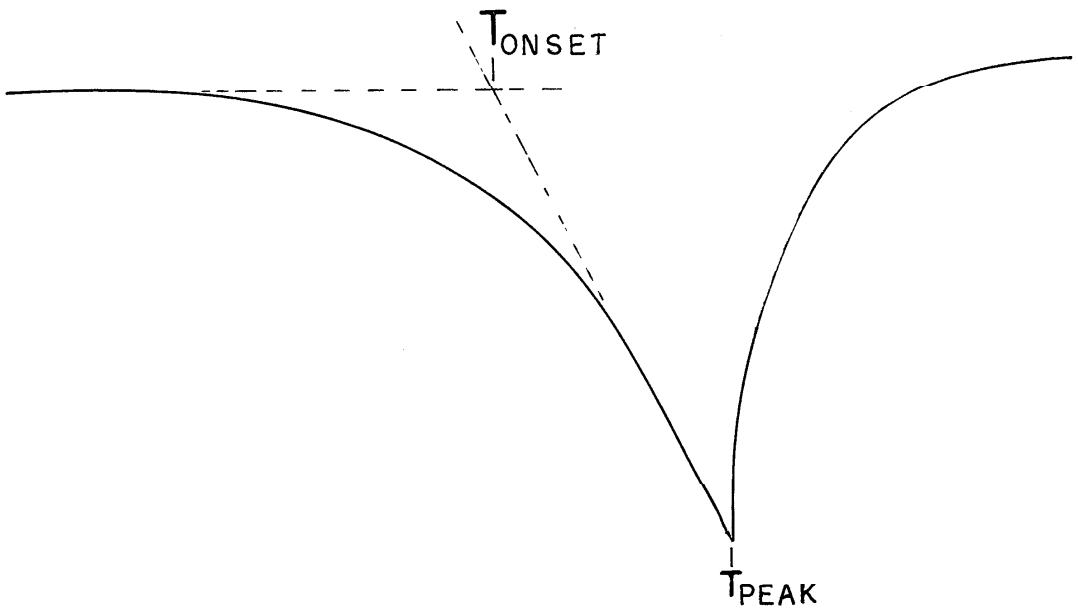


FIGURE 2

Representative DTA Peak Showing Defined Points

2. Where samples were cycled, only the first cycle data were coded.
3. Replicate experiments from some investigators were made with identical sample weights. Where information to the contrary was lacking, these were treated as individual loadings of the sample holder, although it is possible that in a few cases only one loading was made and the sample merely cycled.
4. Sample weights $\geq$ 1000 mg were coded as 999.99 mg.

5. In cases where information recorded on the experimental charts differed from that in tables, or other typed summaries, the chart information was used.

Data Processing

The data processing proceeded in a manner very similar to that of the Second ITP. The information was coded by H. G. McAdie using the same format and forwarded to P. D. Garn. Computer cards were punched and verified in the usual manner. Test runs were then made to detect inconsistent values; outlying data were hand-checked.

The basic computer program has been revised in format to minimize machine time and to keep abreast of the machine and administrative languages. The content remains unchanged except that the data were introduced in degrees Kelvin to avoid negative values.

The cards were machine-sorted and manually arranged into the selected subsets; for example, all data from a given sample holder type. The printout listed the data in the subset, then these listed tabulations and computations:

Mean
Standard deviation
Minimum observation in that set
Maximum observation in that set
Number of observation in that set for the
Heating onset
Heating peak
Cooling onset
Cooling peak

The sequence of steps following the 1973 meeting of the Committee on Standardization was as follows:

1. The data were submitted to H. G. McAdie, who prepared a preliminary set of means from the data available.

2. An ad hoc committee comprising P. D. Garn, H. Kambe, H. G. McAdie, O. Menis, and T. Ozawa met in Akron to study the Data. From this study and the experience of the Second ITP, they concluded that a search for systematic deviation comparable to that for the Second ITP would not be needed.

The use of (principally) liquid samples and the need for cooling well below ambient temperatures had led to a greater degree of similarity of sample holders.

3. The data were coded by H. G. McAdie according to the format of the Second ITP, with extensions or modifications made in consultation with P. D. Garn.

4. The coded data were forwarded to The University of Akron. Those data received were processed for reporting and certification at Fourth ICTA.

5. Subsequently, all data were processed to ascertain the overall means and to examine the effects of sample holder configuration and of thermocouple placement.

VII. RESULTS - TEMPERATURE DATA

A. Examination for Systematic Bias

The extensive formal testing for systematic bias which was undertaken for the Second International Test Program was judged to be unwarranted for the Third ITP. The relatively good agreement arises in part from the lesser diversity of apparatus types. The testing was limited to the effects of sample holder type and sensor location with the exception of one set of data. This participant submitted four sets of data at each of two heating rates, 4 and 8°/min. The mean values for either the onset or peak temperatures generally differed by less than the larger of the two standard deviations and always by less than their sum. There was not even an invariant trend for either heating rate to yield higher or lower values than the other. From this experiment it can be concluded that the heating rate does not contribute a significant difference.

TABLE II - Mean Values of Laboratory Data in Degrees Kelvin

The means and standard deviations were calculated treating the average data of each laboratory as equivalent in weight to all others. The order of listing is randomized and is not related to the order given in Table I.

	1,2-Dichloroethane		Cyclohexane				Phenyl Ether		o-Terphenyl	
	Melting		Transition		Melting		Melting		Melting	
	ExOn	Peak	ExOn	Peak	ExOn	Peak	ExOn	Peak	ExOn	Peak
Mean	237.3	241.6	187.1	190.9	278.0	280.2	298.6	301.9	328.2	331.1
S. D.	2.0	4.3	3.5	4.0	1.1	1.9	2.2	2.3	2.2	3.1
Laboratory										
1	242.5	247.2	192.2	196.3	279.5	282.1	299.4	303.6	324.6	327.1
2	237.6	237.8			278.8	279.7	299.2	300.3	329.2	329.1
3	235	242	184	192	278	282	297	304	326	332
4	238	242	190	193	278	279	298	303	328	330
5	236.2	238.7			277.3	278.6	297.3	300.2	326.1	328.6
6	238	252			276	282	303		331	339
7	237.1	241.5			278.2	280.4	298.3	303.5	329.6	330.7
8	235	242			277	282	293	300	326	334
9	239.0	243.8	188.2	192.5	279.1	282.6	300.2	306.5	331.9	334.5
10	237.4	239.6			279.2	281.0	301.1	303.4	329.4	330.8
11	235	236	187	185	278	279	298	299	328	329
12	235.9	237.9	184.9	186.0	276.1	276.3	298.0	300.7	329.4	330.1
13	239	242			277	280	300	301	329	333
14		240.0		191.7		279.2		298.9		327.1

B. Examination for Random Error or Bias

The laboratory means were tested against the unweighted means by accepted statistical methods. In one case, the laboratory mean was different from the unweighted mean by more than three standard deviations. This datum was discarded.

With the above exception, there were six cases in which a laboratory mean differed by as much as two standard deviations from the unweighted mean. Two laboratories each provided two of these and two other laboratories one each.

One investigator, who submitted four sets of data for the cyclohexane melting, reported a temperature substantially different for one data set from the others. From the Q-test (at 90% confidence), the extrapolated onset could be rejected even though the peak temperature could not. This accounts for the range of peak temperatures for sample holder 700 and sensor location 00 extending to lower temperature values than the corresponding extrapolated onset; see Figures 3 and 4.

C. Mean Temperature Data

The unweighted means for all laboratories are given in Table II. The presence or absence of a decimal place indicates the precision reported by the individual laboratories.

D. Inherent Bias

These data retain an inherent bias due to the greater numbers of some particular types of sample holders. Of the 13 participants, six used devices classed as 422 in the sample holder code and five of these devices had their temperature sensors in the 03 position. The next largest group was SH 700; two of the three members of this group had sensors in the 00 position, one in the 21.

Because the several types which was used in this test program are not equally represented, no statistical significance ought to be imputed to the variations in data. These variations may still be compared qualitatively. It must be noted that a proper statistical treatment is economically infeasible.

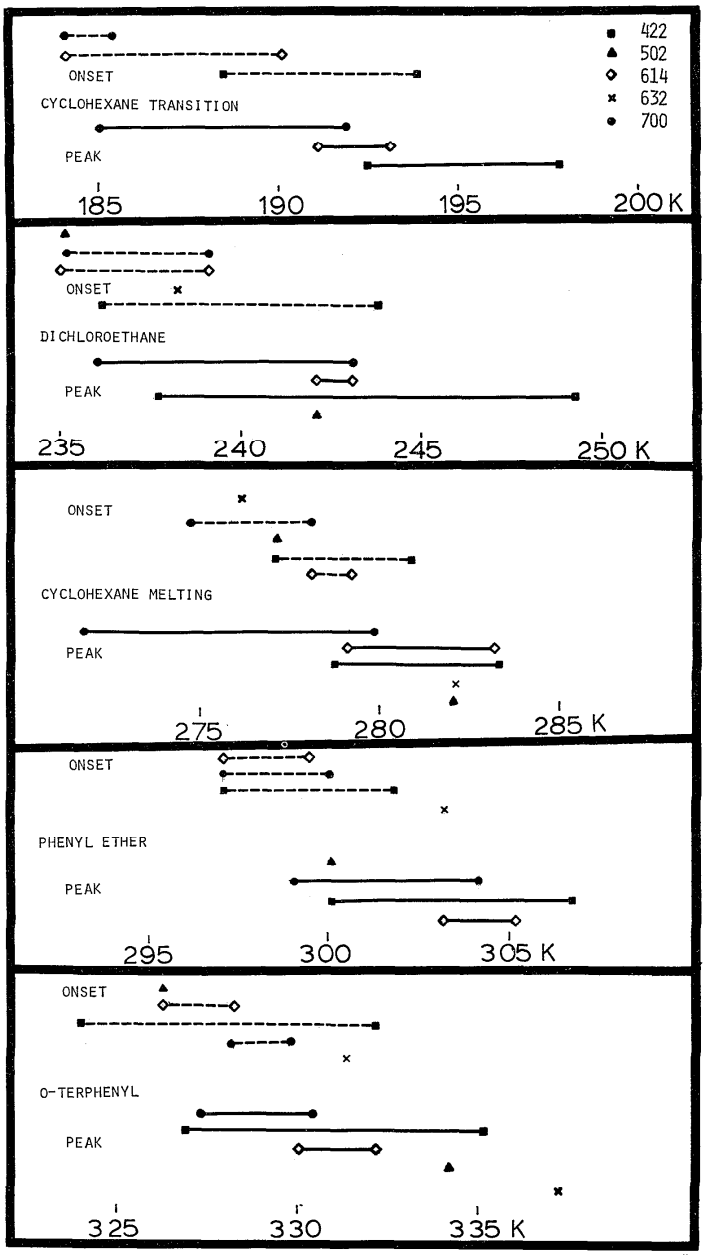


FIGURE 3

Range of Data for Each Sample Holder Type for Each Material in the Third International Test Program

The data are given in degrees K for the raw data. Where a single mark appears, single or duplicate values were reported. The data are in the order of mean values from Tables III-VII, the lowest temperature being at the top.

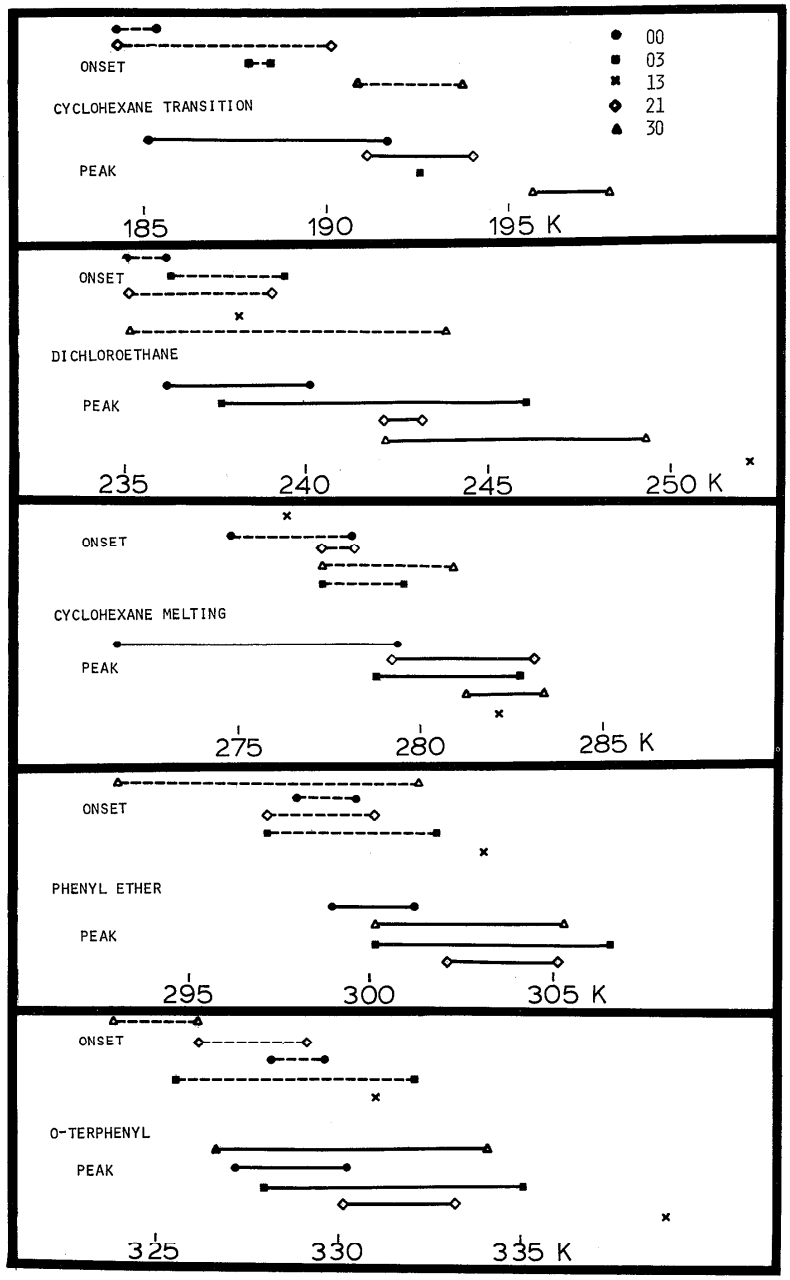


FIGURE 4

Range of Data for Each Sensor Location Type for Each Material in the Third International Test Program

The data are given in degrees K for the raw data. Where a single mark appears, single or duplicate values were reported. The data are in the order of mean values from Tables III-VII, the lowest temperature being at the top.

VIII. DATA INTERPRETATION

A. General

Even though the variations in experimental results are smaller than in the Second International Test Program (inorganic solids) the differences are large enough to warrant relating them to the major parameters -- the sample holder type and the location of the sensor. The reason for the variations is principally the positions of the sensor with relation to the heat path. This relation is described more fully in Section VIII. C. The two parameters are interdependent in part because the choice of sample holder limits per se the available choices of sensor location. For example, putting a sensor in the center, axially, of a shallow pan sample holder is impracticable. In many cases, the means of data from other types fall outside the experimental range of the data from the predominant types. To the extent that these variations are consistent, they can be inferred to be systematic, arising from the differences in instruments.

The data for the several materials, arranged by sample holder type and sensor location, are given in Tables III - VII. This mean for ALL DATA in each table is that from Table II and is included for convenient reference.

B. Comparison by Sample Holder and Sensor Location Types

Systematic tests for variations in the behavior of instrument types were carried out in two ways; the difference between the means in Tables III - VII were tabulated in Table VIII and the spans of raw data were plotted for each material for each parameter in Figures 3 and 4. The use of whole numbers in Table VIII allows ready discernment of trends.

Sample holders 422, 614 and 700 were used by more than one laboratory, as were sensor locations 00, 03, 21 and 30 (See Figure 2); discussion of trends will be limited to these. The data 614 and 700 showed no trend, but 700 has a predominantly negative deviation. This too is influenced by sensor location differences.

TABLE III

Effect of the type of sample holder and the location of the temperature measuring transducer on the measured extrapolated onset and peak for the phase transition in cyclohexane.

	Extrapolated Onset	Peak
All data	187.1 ± 3.5	190.9 ± 4.0
Sample Holder Code		
422	190	194
614	187	192
700	186	187.3 ± 2.4
Thermocouple Location Code		
00	186	187.7 ± 3.6
03	188	192
21	187	192
30	192	196

TABLE IV

Effect of the type of sample holder and the location of the temperature measuring transducer on the measured extrapolated onset and peak for the melting of 1,2-dichloroethane.

	Extrapolated Onset	Peak
All data	237.3 ± 2.0	241.6 ± 4.3
Sample Holder Code		
422	238.3 ± 1.6	241.4 ± 3.5
502	235	242
614	237	241
632	238	252
700	236.7 ± 2.1	239.0 ± 2.6
Thermocouple Location Code		
00	235	238.0 ± 2.0
03	237.5 ± 1.0	240.3 ± 2.4
13	238	252
21	237.5 ± 2.2	241.2 ± 1.4
30	239	245

TABLE V

Effect of the type of sample holder and the location of the temperature measuring transducer on the measured extrapolated onset and peak for the melting of cyclohexane.

	Extrapolated Onset	Peak
All data	278.0 1.1	280.2 1.9
Sample Holder Code		
422	278.7 0.8	280.8 1.5
502	277	282
614	278	280
632	276	282
700	277.0 2.4	278.0 2.0
Thermocouple Location Code		
00	276	277.7 1.1
03	278.4 ± 0.7	280.6 ± 1.5
13	276	282
21	277.7 ± 0.6	280.3 ± 1.5
30	278	282

TABLE VI

Effect of the type of sample holder and the location of the temperature measuring transducer on the measured extrapolated onset and peak for the melting of phenyl ether.

	Extrapolated Onset	Peak
All data	298.6 ± 2.2	301.9 ± 2.3
Sample Holder Code		
422	299.0 ± 1.4	302.7 ± 2.4
502	293	300
614	298	304
632	303	
700	298.7 ± 1.2	300.5 ± 1.9
Thermocouple Location Code		
00	298	299.3 ± 0.6
03	299.0 ± 1.5	302.8 ± 2.6
13	303	
21	298.3 ± 1.9	303.3 ± 0.6
30	296	302

TABLE VII

Effect of the type of sample holder and the location of the temperature measuring transducer on the measured extrapolated onset and peak for the melting of o-Terphenyl.

	Extrapolated Onset	Peak
All data	328.2 ± 2.2	331.1 ± 3.1
Sample Holder Code		
422	328.5 ± 2.6	330.2 ± 2.7
502	326	334
614	327	331
632	331	339
700	328.8 ± 0.7	329.8 ± 1.7
Thermocouple Location Code		
00	328.8 ± 1.0	329.5 ± 0.6
03	329.3 ± 2.1	330.8 ± 2.3
13	331	339
21	327.7 ± 1.2	331.5 ± 1.4
30	324.9 ± 1.0	328.6 ± 2.3

TABLE VIII

Deviations of Sample Holder and Sensor Location Temperatures from Mean Values

Sample Holder

MATERIAL	422 Onset	422 Peak	502 Onset	502 Peak	614 Onset	614 Peak	632 Onset	632 Peak	700 Onset	700 Peak
CYCLOHEXANE TRANSITION	+3	+3			0	+1			-1	0
1,2 DICHLOROETHANE	+1	0	-1	0	0	-1	+1	+10	-1	-3
CYCLOHEXANE MELTING	+1	0	-1	+2	0	0	-2	+2	-1	-2
PHENYL ETHER	0	0	-6	-3	-1	+1	+4		0	-3
O-TERPHENYL	0	-1	-2	+3	-1	0	+3	+8	0	-1

Sensor Location

	00 Onset	00 Peak	03 Onset	03 Peak	13 Onset	13 Peak	21 Onset	21 Peak	30 Onset	30 Peak
CYCLOHEXANE TRANSITION	-1	-3	+1	+1			0	+1	+5	+5
1,2 DICHLOROETHANE	-2	-4	0	-1	+1	+10	0	0	+2	+3
CYCLOHEXANE MELTING	-2	-3	+1	0	-2	+2	0	0	0	+2
PHENYL ETHER	-1	-4	0	0	3	0	0	0	-3	-1
O-TERPHENYL	0	-2	+1	0	+3	+8	-1	0	-3	-2

The wide range of values (Figure 3) noted in Type 422 sample holder (the most common type reported in this program) can be attributed in part to the fact that they represent data from five different instruments in six laboratories. Five of these had Type 03 sensor location. In Figure 4 the range is noticeably reduced because all of the instruments have both 422 sample holder and 03 sensor locations.

Examination of the deviations due to the sensor location discloses that the 00 location used by most of the 700 instruments has a very clear negative deviation from the mean and that the difference is greater for the Peak than for the Onset. The reason is straightforward; the heat which is necessary to raise the thermocouple temperature must first pass through the sample. Therefore, the thermocouple temperature cannot exceed the sample temperature. On the other hand, each of the other types has the sensor either in the heat path (see Section VIII. C.), for example in contact with the sample holder, or isolated even more from the sample. It follows that the temperature of the sensor is rising continuously, the rate of rise being influenced in part by the heat demand of the sample for most configurations. Therefore the spread of temperature between the Onset and the Peak is typically greater for the other location types than for 00, and, because of the near-constant temperature in 00, the already negative deviation in the Onset values becomes accentuated in the Peak.

The most significant trend of the data is for sensor location 30. The vary distinct trend from higher-than-mean to lower-than-mean values arises from the continuously varying ease of heat transfer from the source to the sample and/or sensor. For this configuration, the sensor is isolated and is therefore unaffected by the heat capacity of the holder and sample. At very low temperatures, at which heat transfer is almost entirely by convection, the low heat capacity of the isolated thermocouple and its support enables an upward progress of temperature independent of events in the sample

holder. In this case, the need for even a small quantity of extra heat to carry out the transition or melting leads to a time lag for the sample holder whereas the measured temperature moves steadily upward.

At higher temperatures, the increasing kinetic energy of the gas in the assembly tends to equalize temperatures more rapidly, hence the effect diminishes.

One may also raise the hypothesis that if the recording system is not purely potentiometric -- and therefore draws current -- the passage of this electric current will have a small heating effect. This too would diminish as the temperature approached the ambient.

C. Physical Principles Delineating the Influence of Sample Holder and Sensor Location Types

In the analysis of data from the Second International Test Program it was shown that the measured temperature in a DTA apparatus was influenced substantially by the comparative position of the sample and the measuring point within the field of thermal flux. When the temperature measuring point was in intimate contact with the sample, the temperature interval during which the transition took place was smaller. Heating and cooling temperatures were in better agreement and the spread of data was smaller than for other arrangements. These other arrangements are more susceptible to error because there is no way to place the measuring point so that it will have the same temperature as the specimen itself both

1. during steady state heating and
2. during a thermal event in which the specimen is absorbing energy in the process of changing its state.

The same sources of error are operative in this program.

Figure 1 shows general relationships used by the particpants in this program. They typify the conventional apparatus commonly used for these measurements. They also show significant differences in the comparative positions of the

measuring point and the sample holder with respect of the heat path.

The influence of position can best be understood by looking in more detail at a generalized view (Figure 5) of the path of heat from the source to the specimen and to the measuring point, remembering that our goal is to measure at Point M (in Figure 5) the temperature at which an event actually occurs in Area S. These illustrations are incomplete in that Type A would ordinarily be radially symmetric about the measuring point, for example, a thermocouple on the axis of a cylindrical sample; Type B may be radially symmetric about the sample; Type D may have the sample at any position including in part directly over the measuring

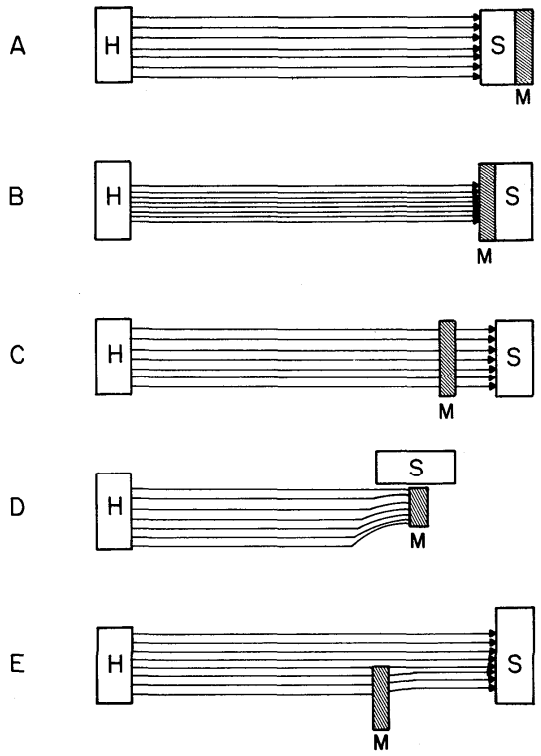


FIGURE 5

Representations of Typical Relationships of the Measuring Point to the Heat Source and the Sample

point and including then the possibility of radial symmetry. Discussion of all possible combinations would be too lengthy and involved to be productive.

The path of heat is through materials which display both a heat capacity and a thermal resistance; consequently, there will be a temperature gradient in the system--positive toward the heat source. Types A and B, in which M is in direct contact with S, will yield the closest relationship of the measured temperature to the sample temperature because there is no intervening gradient. Type C, with its spearation and intervening heat flux, will show an apparent temperature dependence because the need to convey a greater quantity of heat at the higher rates requires a larger gradient between the measuring point and the sample. For either D or E, the heat flux will tend to heat the measuring point more or less independently of the sample, yielding a less clearly defined relationship between the sample temperature and the measured temperature. In steady state heating, the two temperatures may be very close, but during extra absorption of heat by the sample, or even during a discontinuous increase of heat capacity, this relationship will necessarily change.

The choice of commercial apparatus very often dictates the location of the sensor. Reconciliation of data between these and other instruments is made easier by knowing the relative values obtained with the different furnace and sample assemblies. Equally important, in those instruments in which there is an option, the choice can be made to best advantage -- either to obtain the best data on the material or to approximate as closely as possible another type of apparatus for comparison of data. For this reason, the data on these Certified Reference Materials can be of great assistance.

IX. CONCLUSIONS

A. The Utility of These Certified Reference Materials

The data from the individual investigators show good reproducibility. The materials are each known to be homogeneous stable at ambient temperatures and each is from a single homogeneous batch. The peaks are readily discernible and measurable. They are, therefore, useful as reference materials.

B. Variations in Instruments

The variations which appear in the measured temperatures are relatable to differences in instrument design. For this reason, data on some other material which have been obtained on different instruments in different laboratories can be related through the differences observed by running these reference materials in the same instruments. The availability to all laboratories of Certified Reference Materials from a known common source assures the users that the comparison is valid.

This test program suffered from a relative paucity of data from any but the most popular instrument types. Continued improvement in reference materials will require the participation of a substantial number of competent workers. Any suggestions or constructive criticism may be addressed to the Committee on Standardization of the ICTA. The mailing address of the present chairman is Professor Paul Garn, The University of Akron, Akron, Ohio 44325, U.S.A.

C. The Significance of Variation from the Mean Temperatures

In any given apparatus, the measured temperatures of the onset and peak for the Certified Reference Material may differ from the mean values by reason of difference in temperature sensor location or type of sample holder from the most common form. The existence of a significant difference does not, of itself, imply any untoward measuring error.

Furthermore, the existence of a significant difference does not vitiate the utility of the Certified Reference Materials as a means for intercomparison of data. The mean values are the composite values from a range of instrument types. Therefore these values may differ measurably from those obtained on any specific instrument. However, based on the analysis of data in this report, the user should be able to interpret his results, evaluate the performance of his instrument, and compare his data with other results. A work sheet is provided (Appendix D) to enable the user to maintain a performance record for the instrument used.

X. SUMMARY

The testing and evaluation program leading to the certification of selected batches of cyclohexane, 1,2 dichloroethane, phenyl ether, and o-terphenyl as Certified Reference Material set GM 757 is described. The defined points, the onset and peak temperatures, are highly reproducible within a laboratory and on similar instruments.

Separation by sample holder location and by sensor location discloses variations which are related to instrument design. Use of these reference materials enables investigators to reconcile differences in measured temperatures on other materials and to compare their instruments with others of that type.

XI. ACKNOWLEDGEMENTS

The material contained in this report represents the labors of persons in 14 laboratories, named in Appendix A, each of whom volunteered time and effort to participate in this Third International Test Program. The committee on Standardization is grateful to them and their supporting organizations.

The invaluable help of J. P. Cali and R. K. Kirby, of the NBS Office of Standard Reference Materials, in preparing for certification and distribution is gratefully acknowledged.

For the special support of one of us (PDG) in his participation in planning and in computation of data, the authors are grateful to The University of Akron.

APPENDIX A

INSTRUCTIONS AND REPORTING FORMAT

INTERNATIONAL CONFEDERATION FOR THERMAL ANALYSIS
COMMITTEE ON STANDARDIZATION

INSTRUMENT DESCRIPTION
Third International Test Programme
DTA Temperature Standards <100°C

Investigator .....

Instrument Manufacturer .....

Instrument Model No. .....

ΔT Thermocouple Material .....

ΔT Thermocouple Wire Diameter (mm.) .....

T Thermocouple Material .....

T Thermocouple Reference Temp. (°C) .....

Was T Thermocouple Calibrated? Yes ..... No .... If yes, how? .....

.....

Location of T Thermocouple .....

Method of T Measurement .....

Sample holder material .....

Description of sample holder size and shape .....

Sample atmosphere flow pattern .....

Sample atmosphere flow rate ($cc.min.^{-1}$) .....

Please supply a small drawing or photograph of the sample holder.

INTERNATIONAL CONFEDERATION FOR THERMAL ANALYSIS
COMMITTEE ON STANDARDIZATION

PROCEDURES
Third International Test Programme
DTA Temperature Standards <100°C

1. The operating conditions of each instrument should be those normally employed.

2. The accuracy of the temperature-measuring thermocouple should be known. If calibration is required, the Committee prefers use of recognized melting point standards. Distilled water and triple distilled mercury are satisfactory.

   The accuracy of thermocouples can be tested independently; for example, external to the furnace assembly by standard techniques. If an equilibrium test cannot be made, use of a large sample and low heating or cooling rates will give the optimum approach to equilibrium.

3. All temperature data should be reported to the nearest 1°C.

4. A time-temperature curve from the temperature-sensor should be included. If the temperature is measured in the sample cell, this record should be obtained using hexane in the reference cell.

5. Each sample should be examined at one heating rate in the range of 4-10°C $min.^{-1}$.

6. Both programmed heating and cooling should be employed if the apparatus permits. If cooling runs are made, the rate of cooling should approximate the rate of heating.

   One curve of the reference material against the reference material should be supplied, using the maximum ΔT sensitivity employed with the test materials.

8. Samples should not be diluted or otherwise pretreated.

9. Maximum sample size should be less than 300 mg.

10. At least two curves should be run on each material. If more than two curves are run and any rejected, the rejected data should be forwarded with the other data, together with the reason for rejection.

11. The sample atmosphere should be oxygen-free nitrogen at 1 atm. pressure dried over $MgClO_4$ or its equivalent.

12. Where possible the same sample holder or container should be used for the entire series of tests.

13. Conditions of packing of the sample within the sample holder should be specified.

14. The Committee would appreciate receiving a measurement of each peak area as defined in the accompanying figure, expressed in the units, °C. sec. mg^{-1}.

15. Results should be reported according to the recommendations for good practice published by the Committee.

16. The Committee would appreciate samples being examined in the randomized order provided to eliminate systematic bias.

INTERNATIONAL CONFEDERATION FOR THERMAL ANALYSIS

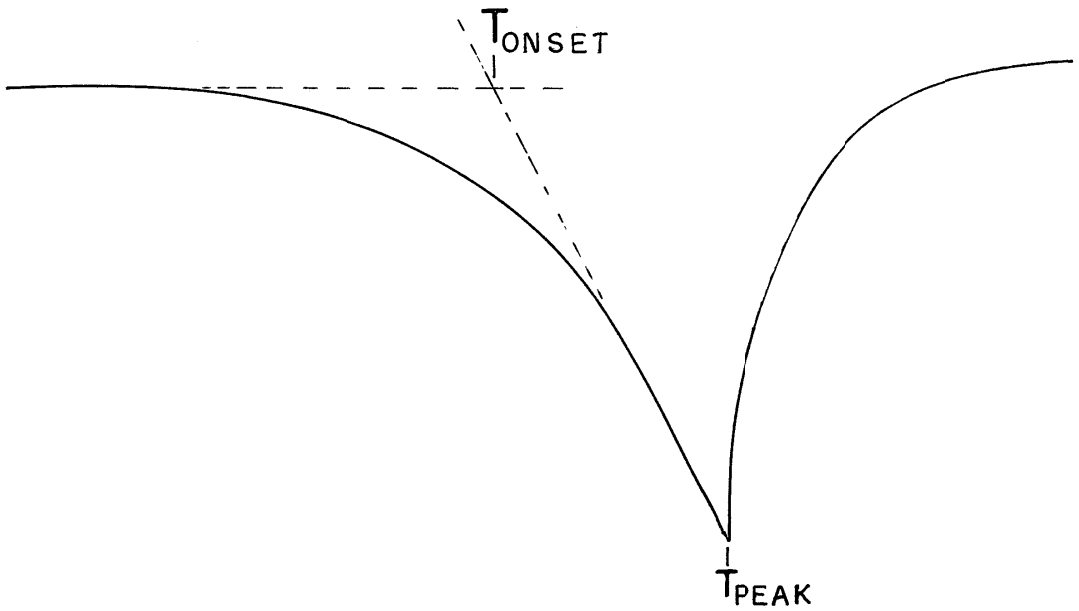
COMMITTEE ON STANDARDIZATION

DATA REPORT

Third International Test Programme

DTA Temperature Standards <100°C

Sample	Run No.	Sample Weight (mg.)	ΔT Sensitivity at peak temp. (°C.cm.$^{-1}$)	Chart Speed (cm.min.$^{-1}$)	Heating Rate (°C.min.$^{-1}$)	Temperature (°C.) Ext. Onset	Peak	Peak Area (°C.sec.mg.$^{-1}$)



APPENDIX B

COMMITTEE MEMBERSHIP DURING SELECTION OF MATERIALS AND PREPARATION FOR DATA GATHERING

International Confederation for Thermal Analysis
Committee on Standardization: (1971-74)

Chairman		(Canada)	H. G. McAdie
Vice-Chairman		(U.S.A.)	P. D. Garn
Secretary		(U.K.)	R. C. Mackenzie
National Delegates*		(France)	M. Harmelin
		(Germany)	K. Heide
		(Hungary)	F. Paulik
		(Japan)	H. Kambe
		(Scandinavia)	G. Roed
		(Switzerland)	H. G. Wiedemann
		(U.K.)	F. P. Wilburn
		(U.S.A.)	O. Menis
		(Italy)	G. Lombardi
Representative Delegates	ASTM	(U.S.A.)	P. D. Garn
	IUPAC		R. P. Graham
	NBS	(U.S.A.)	O. Menis
	Soc. Anal. Chem.	(U.K.)	C. J. Keattch
	SAMA	(U.S.A.)	A. P. Gray
Ex-Officio Delegates	ICTA	(Switzerland)	H. R. Oswald
		(U.K.)	R. C. Mackenzie
		(U.K.)	J. P. Redfern

*The "National Delegates" were selected and invited to function both as active workers on the Committee and as liaison to and from national and regional organizations. The category was dropped in 1975. Responsibility for liaison falls to members of ICTA Council chosen by national/regional groups.

APPENDIX C

REPORTED EQUILIBRIUM TEMPERATURE VALUES FOR THE MATERIALS SELECTED

Thermodynamic equilibrium temperature values for the compounds selected have been measured by other workers. The agreement of measured points on the DTA-DSC curve with the thermodynamic values depends upon such diverse variables as sample holder type and the magnitude of the temperature. Exact correspondence should not be expected whereas close agreement is a reasonable expectation. The reported values are presented below for reference only and without criticism of the experimentation.

Compound	Phase Change	Equilibrium Temperature	References
Cyclohexane	Transition	186.3	1,2,3
"	Melting	279.9	4
1,2-Dichloroethane	Melting	237.5	4
Phenyl ether	Melting	300.1	5
o-Terphenyl	Melting	329.4	6

References:

1. R. S. Ruhrwein and H. M. Huffman, J. Am. Chem. Soc. 65, 1620 (1943)
2. W. T. Ziegler and D. H. Andrews, J. Am. Chem. Soc. 64, 2482 (1942)
3. J. G. Aston, G. J. Szasz and H. L. Fink, J. Am. Chem. Soc. 65, 1135 (1943)
4. "Selected Values of Chemical Thermodynamic Properties", NBS Circular 500 (1952)
5. J. Timmermans, "Physicochemical Constants of Pure Organic Compounds"
6. S. S. Chang and A. B. Bestul, J. Phys. Chem. 56, 503 (1972)

APPENDIX D

WORK SHEET

Instrument Make ______________________________

Sample Holder ______________ Sensor Location ______________

Table Means	Cyclohexane Transition Onset	Cyclohexane Transition Peak	1,2-Dichloroethane Onset	1,2-Dichloroethane Peak	Cyclohexane Melting Onset	Cyclohexane Melting Peak	Phenyl Ether Onset	Phenyl Ether Peak	O-Terphenyl Onset	O-Terphenyl Peak
Sample Holder ____	____K	____K	____K	____K	____K	____K	____K	____K	____K	____K
Sensor Location ____	____	____	____	____	____	____	____	____	____	____

Experimental Data

Date										
________	____	____	____	____	____	____	____	____	____	____
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