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# ICTA CERTIFIED REFERENCE MATERIALS FOR LOW TEMPERATURE *

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## ABSTRACT

The standardization program for ICTA certified reference materials for measurement below 350 K disclosed variations which are clearly attributable to differences between instruments. The variations are related to the types of sample holder and to the location of the temperature sensor. The existence of these variations shows clearly the need for use of certified reference materials when interlaboratory comparison of data is to be made.

## INTRODUCTION

The utility of reference materials from a single source is well known in many areas of chemical or physical measurement. The importance of such materials is not quite so apparent in dynamic thermal methods as it is in others because the temperature sensor can be independently calibrated, separately from the sample and heat source. The responses of sensors are well established. It is easy to overlook the fact that the sensor provides a measure only of its own temperature. Only by inference do we obtain a measure of the temperature of the specimen under study. This becomes important when data must be compared between laboratories, particularly when different instruments are used. To enable these interlaboratory comparisons, the International Confederation for Thermal Analysis (ICTA) has undertaken the task of providing reference materials for various uses. These are first tested for suitability, a formal test program is carried out on specific batches of the selected materials, the material and a certificcate describing the test program are delivered to the U.S. National Bureau of Standards (NBS) and the materials are distributed under the NBS Special Materials program.

ICTA certified reference materials for measurements below 350 K, which

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are described herein, comprise four materials of which the NBS has stocks sufficient to issue many sets. In addition to their meltings, one of these undergoes a crystallographic phase transition. The test program is described in detail in the certificate accompanying the certified reference material (CRM), which is marketed under the catalog listing GM-757.

## MATERIALS

After committee testing, batches of the listed materials were obtained for the test program and distribution.

| Material | Source |
|---|---|
| 1,2-Dichloroethane | Baker reagent grade |
| Cyclohexane | Baker reagent grade |
| Phenyl ether | Baker reagent grade |
| *o*-Terphenyl | Eastman |

## PROCEDURE

Samples of each material were distributed to the test program participants listed in Table 1 with a protocol for the measurement and reporting.

The data and the instrument descriptions were sent to the erstwhile chairman, H.G. McAdie. An ad hoc committee from the Committee on Standardization (P.D. Garn, D. Menis, H.G. McAdie, H. Kambe and T. Ozawa) studied

TABLE 1

List of participants and apparatus

| 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 (U.S.A.) | DuPont 900 Thermal Analyzer |
| Dr. B. Bolin/Dr. B.O. Haglund (Sweden) | Mettler TA1 |
| Dr. H. Flammersheim (D.D.R.) | Perkin-Elmer, DSC-1B |
| Dr. M. Harmelin (France) | Bureau de Liaison Model M4 |
| Mrs. C.W. Huffman (U.S.A.) | DuPont 900 Thermal Analyzer |
| Mr. T. Koide (Japan) | Own design |
| Mr. E.A. Lewis (U.S.A.) | DuPont 920 Thermal Analyzer |
| Dr. E.E. Marti (Switzerland) | Perkin-Elmer Corp. DSC-2 |
| Dr. O. Menis/Mr. B.I. Diamondstone (U.S.A.) | DuPont 900 Thermal Analyzer |
| Prof. H.R. Oswald (Switzerland) | Mettler Instruments Recording Vacuum Thermoanalyzer |
| Mr. R. Yokota/Prof. H. Kambe (Japan) | Perkin-Elmer Model DSC-1 |
| Mr. T. Ozawa (Japan) | Rigaku Denki Co. Ltd. DSC, Model 8057 |

the data and concluded that an intensive search for systematic deviation, such as was carried out for the CRM for the 125—940°C range, would not be needed. The data were processed to ascertain the overall means and standard deviations and to examine the effects of sample holder configuration and of temperature sensor placement.

Examination for random error led to the discarding of one laboratory mean (deviation >3 std. dev.) and one laboratory datum (Q-test at 90% confidence). Laboratory means were used in computations to provide *unweighted* means.

## REPORTED DATA

Fourteen laboratories (seven countries, nine instrument models) reported data. Half of them could not reach the cyclohexane transition ca. 190 K. After the preliminary evaluation, the laboratory means were sorted by instrument parameters. The sample holder types with concomitant sensor locations reported in this study are shown in Fig. 1. The number code had been assembled for the earlier test program. The overall means with the sample holder and sensor location means are given in Tables 2—6. These data are for the heating mode only.

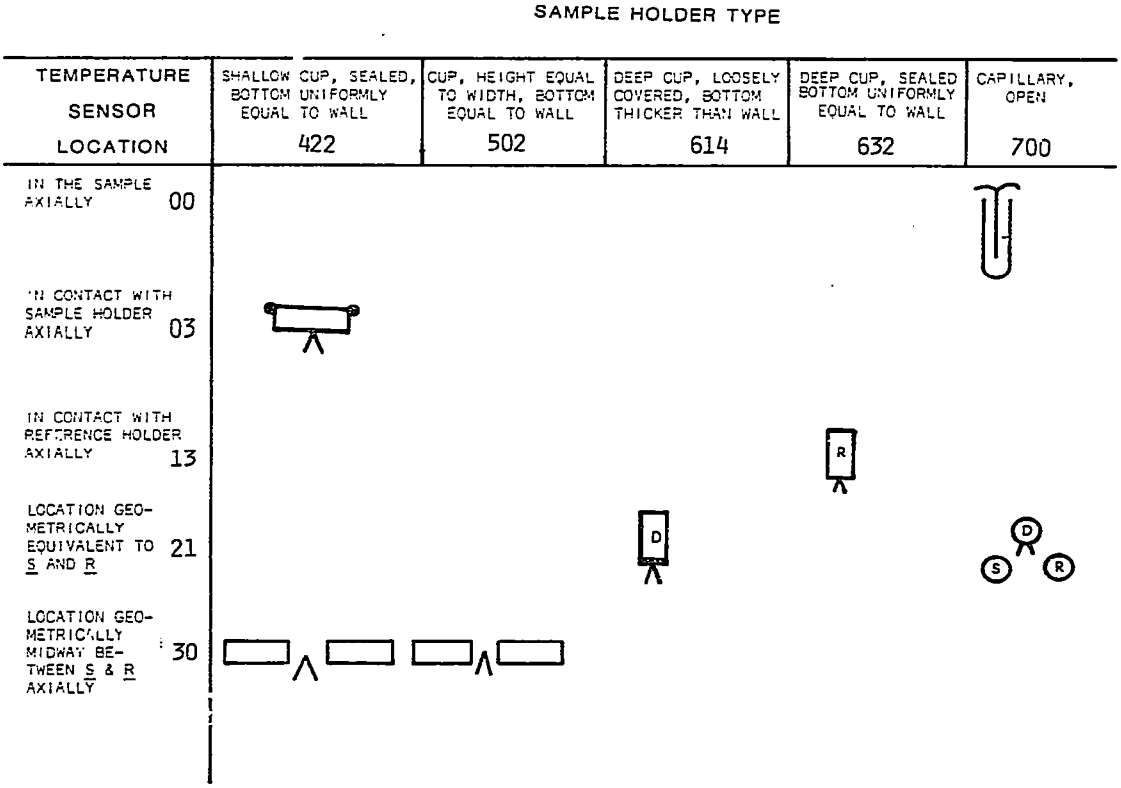

Fig. 1. The physical relationships between sample holder and temperature sensor in the experimental arrangements used in the third international test program.

TABLE 2

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

| | Sample holder code | Thermocouple location code | Extrapolated onset | Peak |
|---|---|---|---|---|
| All data | | | 187.1 ± 3.5 | 190.9 ± 4.0 |
| | 422 | | 190 | 194 |
| | 614 | | 187 | 192 |
| | 700 | | 186 | 187.3 ± 2.4 |
| | | 00 | 186 | 187.7 ± 3.6 |
| | | 03 | 188 | 192 |
| | | 21 | 187 | 192 |
| | | 30 | 192 | 196 |

The overall means retain an inherent bias due to the greater numbers of particular types of sample holders, there being six participants using instruments classed as 422 in the sample holder code and five of these had temperature sensors in the 03 position. The next largest sample holder group was 700; of the three 700's, two had temperature sensors in the 00 position. Because of the demonstrated differences between instruments and because the certified materials are only the batches taken for distribution, no attempt is made to relate the overall means to equilibrium temperature values (1—6).

TABLE 3

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

| | Sample holder code | Thermocouple location code | Extrapolated onset | Peak |
|---|---|---|---|---|
| All data | | | 237.3 ± 2.0 | 241.6 ± 4.3 |
| | 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 |
| | | 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 4

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

| | Sample holder code | Thermo-couple location code | Extrapolated onset | Peak |
|---|---|---|---|---|
| All data | | | 278.0 ± 1.1 | 280.2 ± 1.9 |
| | 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 |
| | | 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 |

## DATA INTERPRETATION AND DISCUSSION

To aid in the interpretation of the reported data, Table 7 was prepared. In this table, whole number differences between the overall means (from Tables 2—6) and the values for each sample holder and sensor location types are listed. Sample holders 422, 614, and 700 were used by more than one investigator, as were sensor locations 00, 03, 21 and 30 (Fig. 1). Discussion of the

TABLE 5

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

| | Sample holder code | Thermo couple location code | Extrapolated onset | Peak |
|---|---|---|---|---|
| All data | | | 298.6 ± 2.2 | 301.9 ± 2.3 |
| | 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 |
| | | 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 6

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

| | Sample holder code | Thermo-couple location code | Extrapolated onset | Peak |
|---|---|---|---|---|
| All data | | | 328.2 ± 2.2 | 331.1 ± 3.1 |
| | 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 |
| | | 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 |

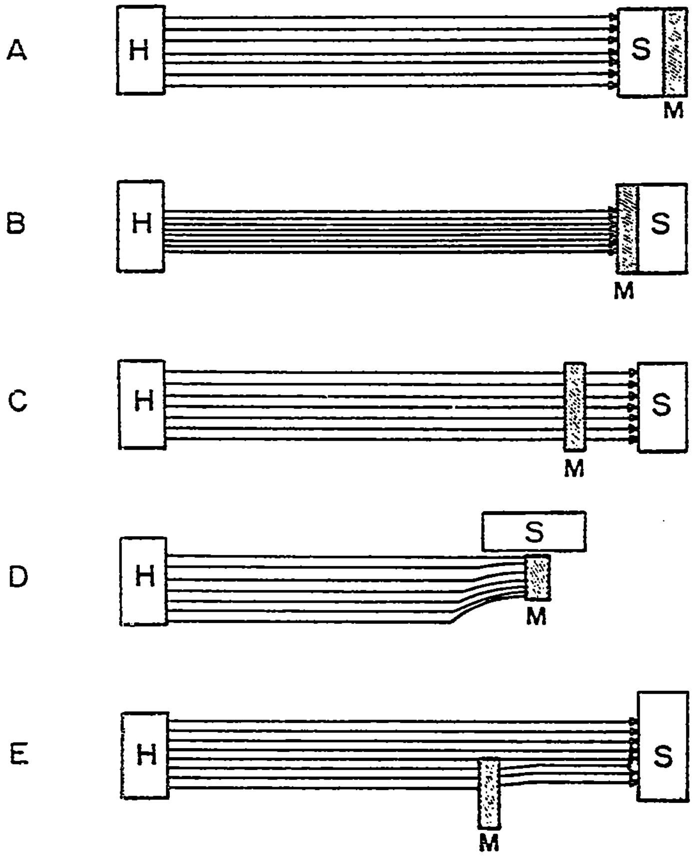

Fig. 2. Representations of typical relationships of the measuring point to the heat source and the sample. The measuring point, M, may be within the sample, S, or at any of a number of points more or less directly in the path between the sample and the heated wall or other heat source, H.

TABLE 7

Deviations of sample holder and sensor location temperatures from mean values

| Material | Sample holder | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 422 | | 502 | | 614 | | 632 | | 700 | |
| | Onset | Peak | Onset | Peak | Onset | Peak | Onset | Peak | Onset | 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 |

| Material | Sensor location | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 00 | | 03 | | 13 | | 21 | | 30 | |
| | Onset | Peak | Onset | Peak | Onset | Peak | Onset | Peak | Onset | 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 |
| Phenylether | −1 | −4 | 0 | 0 | 4 | | 0 | 0 | −3 | −1 |
| *o*-Terphenyl | 0 | −2 | +1 | 0 | +3 | +8 | −1 | 0 | −3 | −2 |

trends with temperature will be limited to these.

The data from 614 and 700 showed no trend with temperature but 700 has a predominantly negative deviation. This arises principally from the sensor location. The hint of a + to a — trend in 422 arises from the paucity of data from 422's for the cyclohexane transition. For the more easily accessible temperatures, 422 had a low deviation because it dominated the statistics.

The 00 location used by two of the three 700 instruments had a very clear negative deviation from the mean, the deviations for the peak being greater than for the onset. The reason is straightforward; the heat necessary to raise the thermocouple temperature must first pass through the sample, so the sensor temperature cannot exceed that of the sample. On the other hand, each of the other types has the sensor location either in the heat path or even more isolated from the sample. It follows that the temperature is rising continuously, the rate of rise being influenced to varying degrees by the heat demands of the sample. From this, with the aid of Fig. 2, it can be deduced (in agreement with experiment) that the spread between the onset and peak temperatures will be greater than for 00 and, because of the near-constancy of temperature in 00, the already negative tendency in the onset becomes accentuated in the peak.

Figure 2 shows a few of the types of relationship between the heat source, the flow of heat, the measuring point, and the sample in some typical commercial instruments. The placement of the temperature sensor determines whether or not the uptake of heat by the sample influences the measured temperature. For example, an isolated thermocouple (coded as 30 in Fig. 1) would rise in temperature quite independently of the sample. So does location code 21, in which the temperature of a dummy specimen is measured but there are differences in the temperature response. Location code 21 experiences nearly the same influences as the sample holder because of the thermal "mass" of the dummy specimen. Location code 30 has no such thermal mass.

The most substantial and significant trend with temperature is found for location code 30. The data have a very distinct trend from higher-than-mean values at low temperatures to lower-than-mean values at the higher temperatures (Fig. 2). At the very low temperatures, at which heat transfer is almost entirely by convection, the low heat capacity of the thermocouple and its support enables an upward progress of temperature without the need for further transfer of part of the heat inward to a sample or reference. The high ratio of surface to mass enables transfer of heat rapidly enough to raise the temperature faster. At the higher temperatures, the increasing kinetic energy of the atmosphere enables more rapid transfer of heat, especially to surfaces nearer the heated wall, so the sign of the deviation reverses.

The data from this program are in agreement with those from the earlier test program for inorganics (7). There, too, when the temperature sensor was in intimate contact with the specimen, the temperature interval over which the transition took place was smaller than for other locations. Heating and cooling data were in better agreement and the spreads of data were smaller than for the other locations.

The 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 sample 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 here.

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, for those instruments in which there is an option, the choice can be made to obtain the best data in the material or to closely approximate another type of instrument for comparison of data.

## AVAILABILITY OF MATERIALS

This set of materials can be purchased from the U.S. National Bureau of Standards, Washington, D.C. 20234. They are listed under the category of Special Materials and designated as GM-757. The certificate supplied with GM-757 can be purchased separately by sending a check for four dollars ($ 4) payable to ICTA to the first-named author (PDG).

## CONCLUSIONS

The individual participant's data show good reproducibility; the materials are known to be stable; they are from single homogeneous batches; and the peaks are readily discernible and measureable. These qualities make them useful reference materials.

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

## ACKNOWLEDGEMENTS

The material contained in this report represents the labors of persons, named in Table 1, in fourteen laboratories. The Committee on Standardization is grateful to them and to their supporting organizations.

The initial testing, the discussions and decisions, and the administration of the test program were carried out by the Committee on Standardization; present members of the Committee during the selection of materials and preparation for the data gathering were, in addition to the present authors, H.G. McAdie (Chairman), R.P. Graham, A.P. Gray, M. Harmelin, K. Heide, H. Kambe, C.V. Keattch, G. Lombardi, R.C. Mackenzie, H.R. Oswald,

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