Precision and Bias of the ASTM Test E1952 for Thermal Conductivity by Modulated Temperature DSC[1]

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ABSTRACT

An interlaboratory test program was conducted to determine the precision and bias of ASTM Method E1952 for specific heat capacity and thermal conductivity by modulated temperature differential scanning calorimetry. Results were received from 15 laboratories using two materials. For thermal conductivity, the within laboratory repeatability standard deviation was found to be $\pm$ 0.021 W m^{-1} K^{-1} while the between laboratory reproducibility standard deviation was $\pm$ 0.040 W m^{-1} K^{-1}. For specific heat capacity, the within laboratory repeatability standard deviation was 0.039 J g^{-1} K^{-1} and the between laboratory reproducibility standard deviation was $\pm$ 0.12 J g^{-1} K^{-1}. A bias of +6.8 % was observed for specific heat capacity and -6.1% for thermal conductivity by comparing the determined mean values with the literature.

INTRODUCTION

One of the requirements of a sound American Society for Testing and Materials (ASTM) standard test method is the inclusion of a precision and bias statement derived from an interlaboratory study (ILT). ILT results provide "real world" analytical precision that is typically not as good as estimates from single laboratory experiments. This study describes the ILT to obtain the precision and bias information for ASTM Method for Thermal Conductivity by Modulated Temperature Differential Scanning Calorimetry (E1952) *(1)*.

E1952 is based upon the work of Marcus and Blaine *(2)* in which the apparent heat capacity of two test specimens is measured. In the first experiment, a thin (ca. 0.5 mm) specimen is examined under experimental conditions that achieve temperature equilibrium throughout the sample. That is, the specimen thickness is less that the temperature penetration length *(3)*.

In the second experiment, a thick specimen (ca. 3.5 mm) is examined under conditions where the temperature sine wave is applied to one end and temperature equilibrium is NOT achieved throughout the sample. That is, the specimen thickness is greater than the temperature penetration length. The latter experiment produces thermal conductivity results that may be transformed into thermal diffusivity values through the

use of specific heat capacity results (derived from the first experiment) and specimen density.

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[1] Presented at the 29th Conference of the North American Thermal Analysis Society, 24-26 September 2001.

These results are mathematical treated by the approach described by Blaine and Marcus *(4)* and described in E1952 to obtain thermal conductivity. An alternative mathematical treatment has been proposed by Simon, Sobieski and McKenna *(5)*.

EXPERIMENTAL

      Two polymeric performance standards were obtained from the Laboratory of the Government Chemist, British National Physical Laboratory, a national reference laboratory. These include poly(methylmethacrylate) (PMMA) and poly(amide) (PA). The PMMA and PA samples were supplied as 5 x 30 x 30 cm slabs that were turned down on a lathe (using slow speed and no lubricant) to the 6.3 mm diameter rods called for in E1952. The rods were then lathe cut and the ends polished to achieve both the thin and thick test specimens. Each laboratory was supplied with 5 individual test specimens for testing. A third polymer sample, poly(styrene) (PS), was used as a method calibration material. It was obtained from the thermal conductivity kit supplied by TA Instruments (P/N 915064.901).

      The experimental protocol calls for temperature calibration using ASTM Method for Temperature Calibration (E967) *(1)* and a 99.99+% pure indium sample supplied. The heat flow signal is approximately calibrated using the heat of fusion of the same indium using ASTM Method for Heat Flow Calibration (E968) *(1)* and then is corrected at the temperature of measurement with a heat capacity determination using a supplied sapphire specimen. The purge gas is not specified. Apparent heat capacity values for five sets of thin and thick PS, PMMA and PA were determined at 47 °C after 15 minutes of temperature oscillation with amplitude of ± 0.5 °C and an 80-second period.

RESULTS AND DISCUSSION

      A total of 15 laboratories participated in the ILT. Of these, 8 laboratories each measured either PMMA or PA (one laboratory measured both). All participants used either the model DSC 2910 or DSC 2920, with MDSC® accessory, supplied by TA Instruments (New Castle, DE). The specific heat capacity and thermal conductivity results were treated by ASTM Method E691 to obtain within laboratory and between laboratory standard deviations. These results for specific heat capacity and thermal conductivity are summarised in Tables 1 and 2.

      The imprecision data for the PA sample appears to be larger than that for the PS and PMMA materials. To test this, the standard deviations were tested for similarly using the statistical "F test". This showed that the precision for PS and PMMA were similar

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Table 1 - Specific Heat Capacity Precision at 47 °C

| Polymer | No. | Mean (J g^{-1} K^{-1}) | Within Lab. | | Between Lab. | |
			Std. Dev. (J g^{-1} K^{-1})	RSD (%)	Std. Dev. (J g^{-1} K^{-1})	RSD (%)
PS	14	1.403	0.0423	3.0	0.128	9.1
PMMA	7	1.538	0.0297	1.9	0.0885	5.8
PA	8	1.870	0.105	5.6	0.249	13
pooled (PS & PMMA)			0.039	3.7	0.12	8.8

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while that for PA was statistically different. A review of the protocol provided two potential reasons for this dissimilarity; the first dealing with inexperience of operators for the PA sample and the second dealing with moisture content. These are discussed below. Based upon the dissimilarity observed above, only the data for PS and PMMA were evaluated for the remaining portion of the ILT.

The repeatability and reproducibility results for PS and PMMA were pooled according to Practice for Statistical Treatment of Thermoanalytical Data (E 1970) *(1)* and are also presented in Tables 1 and 2. The pooled specific heat capacity relative repeatability and reproducibility standard deviations are 0.037 J g^{-1} K^{-1} and 0.12 J g^{-1} K^{-1}, respectively. The pooled thermal conductivity relative repeatability and reproducibility standard deviations are 0.021 and 0.40 W m^{-1} K^{-1}, respectively.

A commonly used rule-of-thumb for interlaboratory studies is that the between laboratory reproducibility should be about twice the within laboratory repeatability. This is the case for the individual PS, PMMA, and PA results as well as the overall pooled value. This satisfaction of the rule-of-thumb test indicates that the experiments are "in control".

Thermal diffusivity information is also obtained by E1952 using the thermal conductivity and specific heat capacity data already obtained. The precision of thermal diffusivity data is estimated by propagation of uncertainties method. Thermal diffusivity repeatability is estimated at 12 %.

In ASTM standards, the repeatability value (r) and the reproducibility value (R) are used to anticipate the within and between laboratory variance. The repeatability and reproducibility valued estimate the 95% confidence interval between two results. The repeatability and reproducibility values are obtained by multiplying the within and between laboratory standard deviations by 2.8.

Bias

Bias is determined by comparing the mean results obtained by the ILT with standard, known or literature values. That is, bias = (observed value) - (reference value).

PS and PMMA specific heat capacity reference values are taken from E1952 *(1, 6, 7, 8)* while that for the thermal conductivity of PMMA was obtained from the Certificate provided by the Laboratory of the Government Chemist. The pooled PS and PMMA specific heat capacity bias is 6.8%. The PMMA thermal conductivity bias is -6.1 %.

Table 2 -Thermal Conductivity Precision at 47 °C

Polymer	No.	Mean $(W\ m^{-1}\ K^{-1})$	Within Lab. Std. Dev. $(W\ m^{-1}\ K^{-1})$	RSD (%)	Between Lab. Std. Dev. $(W\ m^{-1}\ K^{-1})$	RSD (%)
PS	14	0.176	0.0230	13.	0.0478	27
PMMA	8	0.185	0.0161	8.7	0.0186	10
PA	8	0.290	0.0675	23.	0.0888	31
pooled (PS & PMMA)			0.021	12.	0.040	23

Comparison to Other Methods

To assess whether these precisions are reasonable, the precision of other thermal conductivity measurement was examined. ASTM lists over 30 methods for the measurement of thermal conductivity, only a few of these methods, however, have precision and bias information derived from an interlaboratory test. A few methods (D2214, D4351, D5334, E1225) *(1)*, requiring specific dedicated apparatus, indicate within laboratory repeatability of 6 to 10%. The values determined here are in the same range as those results but are slightly higher.

For specific heat capacity values, comparison may be made to the results for ASTM E1261 Heat Capacity by DSC (E 1261) *(1)* showing within laboratory repeatability relative standard deviation of 2.2 % and a between laboratory reproducibility relative standard deviation of 3.0 %. The polymer sample bias for that method is identified as -1.1 %.

Discussion

Earlier, it was observed that the imprecision in the PA was statistically different (poorer) than that for the PS and PMMA. The reason for this dissimilarity was examined. One source of this imprecision was thought to be the experience of the operator since the participants in the ILT were selected in a non-random basis. That is, in response to an appeal for volunteers, packages containing the PMMA performance materials were first distributed until a total of 10 volunteer laboratories were reached. This was done to ensure that a sufficient number of laboratories would be obtained for at least one of the

materials. Once this participation goal was reached, packages containing the PA performance material were distributed. A total of 18 volunteer laboratories were eventually obtained, 9 for each material. As the results were returned by participants, they were immediately treated by E 691 to screen for outliers. As the first few results arrive the within and between laboratory results were very close with a relative standard deviation of 3%. As more and more results arrived, the precision became poorer. Indeed, as the deadline approached, the technical contact for the method received an increasing number of queries concerning interpretation of basic calibration steps in the method, indicating that the participants were neophytes. Once all of the data was in and the full statistical treatment applied, all of the outliers were among the actual late arrivals.

This is interpreted to indicate that those laboratories familiar and practiced with the method are able to achieve higher precision and accuracy. While those who were running the method for the first time, suffered with poorer results. This, of course, is not an unexpected result.

This was confirmed by examination of the results from one laboratory that performed measurements on both PMMA and PA. The precisions of these two measurements was uniform showing a range of 3.4% (absolute) among the thermal conductivity results and 0.49% (absolute) among the specific heat capacity precision values. This further supports the position that increased imprecision in the PA results derives from the inexperience of the operators.

A second potential explanation for the imprecision in the PA result lies with its hygroscope nature. Due to its polar nature, PA material may readily absorb up to 4% moisture from the atmosphere. As the ILT protocol called for analysis of the materials on an "as received" basis, it is thought that differences in moisture contact might be a source of the PA imprecision.

The specific heat capacity of water is 1.5642 J g^{-1} K^{-1} while that of poly(hexamethylenediamineadipate) is 4.180 J g^{-1} K^{-1} *(7, 8)*. Thus a 2.25 % difference in specific heat capacity may result from 3% change in moisture content of the PA. From the principle of propagation of uncertainties, this results in a 6.8% change in thermal conductivity and could easily account for the observe PA imprecision.

CONCLUSIONS

The precision and bias of ASTM Method E 1952 for thermal conductivity by MTDSC was evaluated by interlaboratory testing. The within laboratory repeatability standard deviations was found to be 12 %. The between laboratory reproducibility relative standard deviation was found to be 23 %. The bias of the method was similarly found to be - 6.1 %.

In addition, the precision and bias of MTDSC measurement of specific heat capacity was also evaluated and found to be 3.7%. The between laboratory reproducibility relative standard deviation was found to be 8.8 %. The bias of the method was found to be 6.8 %.

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