NPL INITIATIVES IN THE DEVELOPMENT OF THERMAL PROPERTIES REFERENCE MATERIALS

by

R. P. Tye & D. R. Salmon

National Physical Laboratory

Teddington, England

1. ABSTRACT

Reference materials and transfer standards have been identified as being essential tools required both to validate techniques and apparatus based on primary methods of measurement and for use in the calibration of techniques based on secondary or indirect methods. In order to cover the wide ranges of material types and their overall conductivity and temperature ranges of use it is seen that a broad variety of materials and specimens be required to satisfy the total needs. The development of new measurement techniques, often transient in nature and involving small specimens, especially thin films, for specific applications has further exacerbated the need for additional materials and artefacts to be made available in different forms.

Little attention had been paid to this recurring need until the mid 1990s when various workers from national organisations were stimulated into taking some collective action to address the problem. The present paper describes the status of a number of studies involving NPL which are directed towards development of internationally accepted reference materials to serve different requirements. These include:

1. Thermal diffusivity and thermal conductivity measurements on candidate molten metal reference materials.
2. Co-operative flash diffusivity measurements on glassy carbon, a dense fine grain alumina, and other ceramics.
3. Inter-European studies, one using different steady-state and transient methods to evaluate the properties of a high temperature ceramic and the other using the guarded hot plate method to produce a high temperature thermal insulation reference.
4. A six laboratory European programme to certify a replacement European thermal insulation reference material for use at room temperature.
5. An intercomparison between standards organisations in five countries on the current reference materials supplied in each country or geographical area.

An example involving the use of some of the above materials to validate the performance of a new measurement technique is also included together with recommendations concerning materials to address additional needs. Brief mention is made concerning other on-going and planned work together with recommendations for materials to address additional needs.

2. INTRODUCTION

During the past two decades there has been a huge increase in the development and use of new and modified materials for a very broad range of engineering, physical, chemical, biological and medical applications. In a majority of cases involving temperature and temperature change, the thermal properties - thermal conductivity or diffusivity and specific heat are necessary in order to model, design and safely operate the system involved. The levels of precision required can vary depending upon the application but once established by the user the onus is the responsibility of the experimental worker to satisfy the requirements. Reliability and confidence in the measured value is the primary intention and use of reference materials is an essential ingredient towards attaining this goal.

One of the present author has drawn attention to this major issue on a number of occasions during his half century involvement in this field. In particular he has been at the forefront of recommending that more international co-operation is necessary for providing solutions to the problem[(1,2)]. In particular he has outlined the gaps that exist and the potential materials and means to fill them especially for thermal insulations, molten materials and high temperature ceramics.

The overall problem has been exacerbated by the recent activities in the development of various forms of so-called transient multi-property measurement techniques[(3)]. In many cases high precision (<±3%) claims are made for thermal properties directly measured and/or derived from them. However, it has been found that values, particularly of thermal conductivity for a material, vary significantly by amounts well outside the individual claimed precision levels. In addition, some concern has been expressed by the occurrence of cases where significant discrepancies appear to exist between directly measured thermal conductivities and values derived from measurements of thermal diffusivity and specific heat for certain well known isotropic materials[(4)].

Clearly such differences and uncertainties create serious problems for the scientists and engineers requiring "reliable data" for whatever material and/or application of concern to them. In some cases there can be valid reasons why such differences occur; for example material anisotropy and different heat flow direction, but not for an isotropic material. Thus there is now an additional requirement that ideally, and where appropriate, a proposed reference material should have accepted values of thermal conductivity, thermal diffusivity and specific heat.

During the ensuing three years since the workshop at the European Thermophysical Properties Conference there has been some significant progress in certain of the areas that were seen to be deficient. Much of this work has involved the national standards laboratories and in particular the National Physical Laboratory (NPL) in the UK under one of its standard mission programmes funded by the Department of Trade and Industry. Projects, some either initiated and stimulated by NPL or that have its direct involvement are now underway in various areas. The present paper contains details of the progress of these activities to date and their significance with respect to current and future needs.

3. TOPICS

3.1 THERMAL PROPERTIES OF MOLTEN MATERIALS

The molten state, especially of metals and alloys, has been considered a prime area where an urgent need has been established for thermal conductivity/diffusivity reference materials[(2)]. Thermal properties are required by the process industries to provide data for computer models which have been established to ensure that products are manufactured to correct specification and with minimum material waste. The use of computer simulation is employed increasingly for prediction and quality control for various reasons, especially costs, improved product consistency, time savings and increased utilisation of capital equipment.

However, models are only as good as the input data and for many materials including metals, alloys and polymers available data is found to be widely scattered[(5)]. For a number of reasons the measurement of thermal properties of materials in the molten state have been found somewhat difficult to undertake. Discrepancies of 50% are not uncommon and there are numerous cases where the temperature coefficients are found to be opposite directions. There is no accepted standard method(s) or totally reliable data available to enable any measured data to be assessed.

To address these issues NPL is developing national standard apparatus for measurement of the thermal diffusivity of molten materials. The overall aims encompassed under the programme are three-fold:

- develop a thermal diffusivity/conductivity measurement standard in support of the process industries.
- identify candidate reference materials
- prepare the measurement standard (which may consist of more than one apparatus) to be an accredited measurement service under the UK NAMAS system.

and to measure thermal diffusivity in the following ranges:

metals: 0.01 cm^3/s to 0.5 cm^3/s, at temperatures 500°C to 1600°C.

polymers: 0.005cm^3/s to 0.01 cm^3/s, at temperatures 100°C to 400°C

Currently the project has been underway for approximately a year or so and the major activities were outlined recently[(6)].

1. A decision that, due to the diversity in properties between the range of materials involved, the approach will involve two methods each involving an adaptation of an existing method or apparatus used at NPL. For molten metals and alloys a laser-flash system will be used while for molten polymers, a modified probe version of the line-source method is the preferred technique. In this latter case the system will be modified such that measurements can be made up to 400°C and under pressures up to 250 MPa. This latter parameter is considered important due to the fact that large pressures are involved during extrusion or compression processing and this may affect the material properties.
2. Candidate reference materials have been selected for each material type. For the metallic range these include pure copper, tin, and lead each of which appear to present the fewest problems and are readily available and some data does exist. It should also be mentioned that mercury and gallium are other good materials but for temperatures below the minimum of the current study. These recommendations are similar to those made by a group of interested parties during a workshop held at the Thermal Conductivity Conference in Nashville several years ago and reported earlier(2).

   For the polymer range a number of high viscosity fluids and solid polymers were considered. As a result three materials - glycerol, polydimethysiloxane and polyethylene - have been suggested as the initial materials for study.
3. Measurements of thermal diffusivity have been completed on the copper specimens and those on the other two metals are in progress. Electrical resistivity measurements are also to be included on all electrically conducting materials. The results for the

copper together with comparisons with the recommended value and values derived from thermal conductivity measurements by other workers are shown in Figure 1.

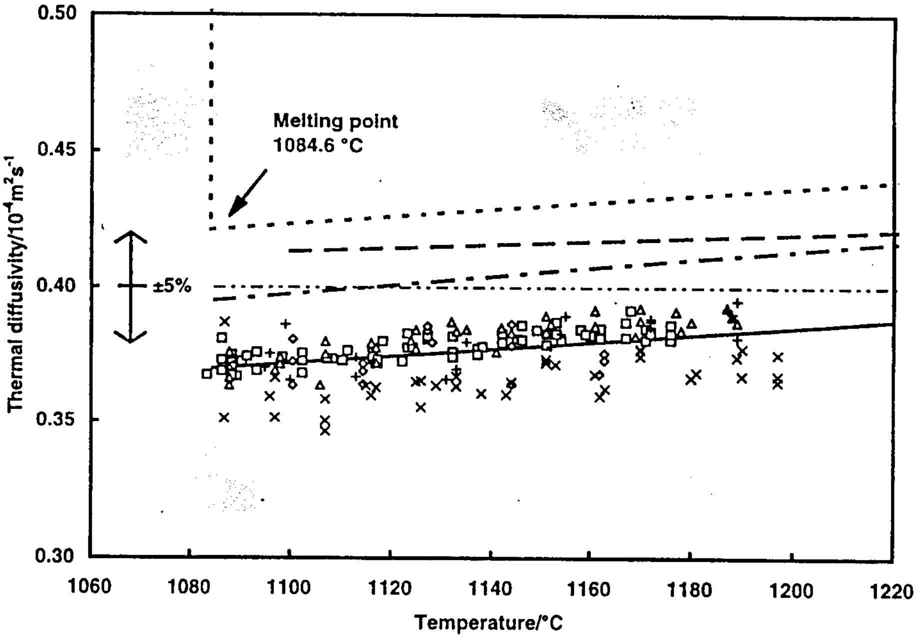

Figure 1. Thermal diffusivity of molten copper

The current values are some 3 to 5% lower than the latter values. However, if these results are used to derive thermal conductivity in conjunction with electrical resistivity it is found that the resultant values help to confirm that the use of the theoretical Lorenz number in assessing the validity of values for molten metals is a recommended first course of action. This is especially helpful since measurements of electrical resistivity are usually somewhat easier to carry out than thermal conductivity. Measurements are also underway on the polyethylene in both the solid and molten phases.

In the overall context of reference materials for molten metals, measurements of thermal conductivity of molten mercury, gallium and tin using a new absolute method were reported by Wakeham[7,8]. This work forms part of a co-operative European Union

Programme of work on molten materials together with the NPL work. The intention is to utilise the technique for measurements on higher temperature materials including tin and lead.

The overall intent of both programmes is that ultimately there will be independent accepted thermal conductivity and/or thermal diffusivity values for a number of well characterised materials over respective ranges of temperature. Furthermore, within the NPL programme plans are well underway for an interlaboratory study on the chosen reference materials using a number of international laboratories that are currently using the flash method of measurement.

3.2 HIGH TEMPERATURE CERAMIC MATERIALS

In Japan Dr. T. Baba and his colleagues at National Research Laboratory of Metrology (NRLM) have undertaken studies by flash thermal diffusivity on several recommended high temperature reference materials in the solid state. Initially they obtained confirmatory values on the POCO AXM-5QI isotropic graphite reference material. As a result of the validation of the apparatus they undertook a comprehensive series of measurements to 1200°C on a commercial glassy carbon (GC-20) and a fine grain, high density pure alumina (Referceram) developed specially by the Japanese Fine Ceramics Centre. In addition measurements have been made on Pyroceram 9606, another material used widely by the thermophysical measurements community[9].

The glassy carbon is a promising candidate because it has no radiation contributions, the alumina is a highly pure reproducible fine-grained solid having minimum porosity while the commonly used Pyroceram 9606 values still have an uncertainty of the order of ±6% in thermal conductivity. It also happens to be one of the materials mentioned earlier where thermal conductivity values derived from thermal diffusivity appear to show significant difference from the measured values at higher temperatures.

At the present time the work on the first two materials has been completed by a series of measurements on different thicknesses of each material and also at low temperatures[10]. The results indicate that the values are unaffected by thickness. As a consequence a final certification as a Japanese Standard Reference Materials for thermal diffusivity is expected soon for both materials. Measurements of specific heat are also being undertaken in order to assist in the process of derivation of thermal conductivity values. Specimens of both materials have now been given to NPL for additional studies of thermal diffusivity and specific heat that also includes Pyroceram 9606. As a result of the various measurement series it is hoped that they will all become internationally accepted reference materials for thermal diffusivity and ultimately for thermal conductivity.

In this context of thermal diffusivity an intercomparison between seven European laboratories, including NPL, using the flash method is also underway. The materials involved are polycrystalline silicon, copper and a high density alumina. Specimens of each material have been distributed to each laboratory. It is also expected that the glassy carbon and Referceram specimens will be circulated to each participant as further standard candidates.

3.3 EUROPEAN HIGH TEMPERATURE REFERENCE MATERIAL

Following an earlier unsuccessful study by European laboratories involving several different methods on a high temperature calcium silicate material mentioned in reference (2), a new European project was finalised recently and is now underway.

Several potential materials including a cordierite, a high density zirconia and Pyroceram 9606 were considered candidates. The final choice was Pyroceram 9606 (see Figure 2), based particularly because it appeared to be reproducible and stable and a great deal of work had been carried out already but that there were still uncertainties in measured and derived values. In addition there had already been an intercomparison in the USA involving mainly thermal diffusivity. However, the overall results of this were unsatisfactory due mainly to the lack of a well defined measurement protocol regarding the overall temperature range of the programme. As a result it was not possible for the organisers, National Institute of Standards and Technology (NIST), to issue certification as a thermal diffusivity reference.

The current programme, co-ordinated by NPL, involving 12 partners from within Europe consists of two major phases. The first is a careful characterisation of the homogeneity and stability of a batch of the material using a number of chemical, physical and thermal property tests in order to establish the suitability of the material as a candidate reference material. The second phase will involve a series of direct measurements of thermal conductivity and thermal diffusivity on different specimens from the batch of characterised material using steady state and transient techniques in order to establish reference values for both properties with acceptable uncertainty levels. The calculation of thermal conductivity from the thermal diffusivity measurements will also be carried out.

A batch of material was purchased from Corning Glass Co. consisting of thirty blocks of approximate size 300 x 95 x 76 mm. Six blocks were selected at random from the batch (20% of the batch was considered to be sufficiently representative) from which specimens were prepared for the characterisation measurements. The characterisation study involved an investigation of

- homogeneity using chemical analysis, microstructure, density, porosity and ultrasonic velocity
- anisotropy by measurements of thermal expansion, thermal diffusivity and ultrasonic velocity
- stability on thermal cycling between 20°C and 1000°C by measuring thermal expansion, thermal diffusivity and ultrasonic velocity and attenuation
- long term stability and reproducibility of thermal conductivity and thermal diffusivity over the length of the programme

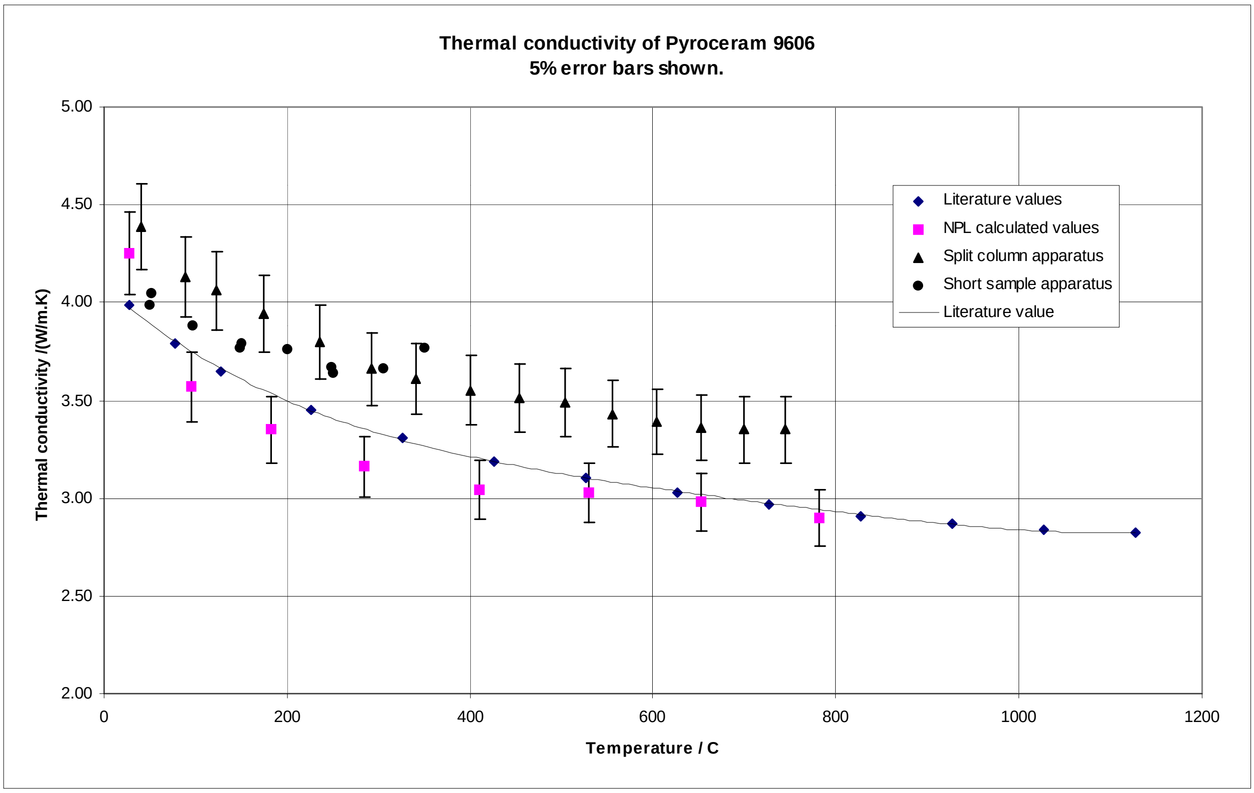

Figure 2. Pyroceram 9606 thermal conductivity

It was also seen as essential not only for full characterisation but also to determine thermal conductivity from the measured values of thermal diffusivity that reliable measured values of the following thermal properties were required for this particular batch of material

- specific heat
- thermal expansion and coefficient of thermal expansion
- thermal radiation transmissivity and emissivity

The initial characterisation has now been completed, an initial analysis of the results carried out and a report written and distributed to the participants and the EC. The details of the various individual measurement results cannot be reported in this paper. However a summary of the major findings of the characterisation study indicate the following

<u>Chemical analysis and microstructure</u>

Pyroceram is an opaque glassy ceramic with high strength and elastic modulus and an operational temperature covering the range -200 °C to 1000 °C, the material starts to soften at 1350 °C. The chemical composition consists of refractory oxides of aluminium, magnesium, titanium and predominantly silica. These are present in amorphous phases of cordierite, armarcolite and cristobalite.

<u>Homogeneity</u>

Of the 30 blocks of material acquired 6 randomly chosen blocks have been tested which is considered to be a more than sufficient sample to represent the properties of the entire batch. All the results obtained by the partners on sound velocity, density, thermal expansion, thermal diffusivity and specific heat show that the batch of Pyroceram 9606 is homogeneous both within blocks and between. The results for each property agree to well within the uncertainty limits for the relevant apparatus of each partner.

Density and Porosity

A mean density of 2602 kg/m3 with a standard deviation of 0.25 % and a maximum porosity of 0.48% were obtained. The material is claimed by the manufacturer to have zero porosity and the virtually negligible porosity measured is an advantage for a reference material for use at high temperature. It reduces the possibility of radiative heat transfer within the bulk of the material so that the predominant mode of heat transfer is conductive.

Anisotropy

The results from ultra sound velocity, thermal expansion and thermal diffusivity measurements show that within the limits of measurement uncertainty for the respective apparatus the Pyroceram 9606 batch is isotropic and that the thermal properties do not vary with orientation by more than 1%

Stability on thermal cycling.

There is some evidence from the thermal expansion and density measurements of a small, 0.28%, permanent expansion that takes place on heating the material to 1000 °C and cooling to room temperature. This effect is very small and is extremely unlikely to have any effect on the thermal properties of the material. It may be that the material will have to be heat treated by taking it up to 1000 °C and holding it there for a few hours before cooling to room temperature.

The specific heat results from all the partners also showed some evidence of a small phase change in the temperature range 150 to 180 °C. This may be linked to the small permanent thermal expansion that was observed. Again this effect is minor and unlikely to effect the thermal properties of interest. As far as the partners in the project are concerned this anomaly has not been observed before with this material.

NPL cycled 35 mm and 50 mm thick hot wire specimens up to 1000 °C and back several times in carrying out measurements using the parallel wire and resistive wire mode in order to obtain the best operating conditions for the measurement of thermal conductivity with no visible detrimental effect to the specimens. However, Corus, another partner, found that after one thermal cycle of their 35 mm thick hot wire specimens that one of them cracked along the groove machined in the specimen surface for the thermocouple. This was unfortunate but it is believed that the crack was initiated by micro-cracks introduced during the machining of the test specimen. Current values for both thermal conductivity and thermal diffusivity are within the current uncertainty limits provided for this material, for example the values of thermal conductivity shown in Figure 2.

Long term stability

These tests are to be carried out during the lifetime of the project by Laboratoire National D'Essai (LNE) measuring the thermal diffusivity of tungsten coated samples in argon and in vacuum and by NPL on thermal diffusivity and thermal conductivity specimens in air. These tests should show up any reactions that take place with the environment over a long series of measurements to high temperatures.

Thermal radiation transmission properties

Physikalisch-Technische Bundesanstalt (PTB) and Institut National des Sciences Appliquées (INSA) measured the thermal transmissivity of the material and found it to be essentially opaque to wavelengths in the range 4 μm to 20μm corresponding to that of radiation transmitted from bodies at temperatures of the order of 1000 °C. This again is an important result indicating that the main heat transport mechanism in the material is by conduction. This rules out any possibility of coupled radiative and conductive heat transmission and confirms that the thermal conductivity can be derived using the accepted simple relationship between the thermal properties.

<u>Conclusions and recommendations</u>

The results clearly indicate that this batch of material is uniform, isotropic, highly stable and has reproducible thermal properties in the temperature range up to 1000°C. Furthermore where values have been reported for certain of the properties such as density, ultrasonic velocity and chemical analysis for other batches the agreement indicates that the material is reproducible on a batch to batch basis. Finally the results of measurements undertaken to evaluate possible anisotropy of properties indicate that the material is isotropic since any differences are well within the uncertainty limits of the various measurement methods.

All the above evidence collected by the partners show that Pyroceram 9606 has excellent characteristics that make it an ideal candidate for a Certified Reference Material. It is stable in the short term, the long term stability is being investigated throughout the project but this is thought to be a low risk factor in the light of previous experience of other workers. The partners therefore had no hesitation in recommending to the European Commission that the project should progress to the second stage i.e. full Certification of the thermal diffusivity and thermal conductivity over the temperature range 200 °C to 1000 °C. Inter-laboratory testing using various measurement methods is in progress.

3.4 EUROPEAN THERMAL INSULATION REFERENCE MATERIAL FOR MODERATE TEMPERATURES

An intercomparison measurements programme has been completed on the characterisation and properties evaluation of a new thermal insulation reference material developed for use within the European Union[(11)]. This material is a moderate density (~70kg/m^3) fine fibre glass blanket produced by Saint Gobain Industries to replace the previous European reference material stocks (CRM 064) which had become depleted. Careful characterisation by the manufacturer and LNE indicated that this stock of material was highly reproducible and stable. Measurements were undertaken over the range -10 to 50°C by guarded hot plate in accordance with the ISO 8302 standard and a strict protocol. In total individual national standard or equivalent laboratories from six European Union countries (France, Germany, Italy, Sweden, Switzerland and United Kingdom) undertook the measurements.

The results, analysed both statistically and technically, by LNE are summarised in Figure 3. They indicate that the overall uncertainty is the order of ±0.8%. This extremely good agreement validates the precision claims of the individual participating apparatus (±2% or better) and the efficacy of the current international standard for the temperature range close to ambient. The material is now available as IRMM-440 in four different sizes from 300 x 300 mm to 1000 x 1000 mm all 35 mm thick. The certified thermal conductivity over the temperature range -10 to +50°C is given by the equation

$$\lambda = 0.0293949 + 0.000106\,T + 2.047.\,10^{-7}\,T^2 \quad \text{W/m.K}$$

where T is the mean specimen temperature in °C. The equation is valid for a specimen density in the range 64 to 78 kg/m3 with an uncertainty of ±0.00028 W/m.K.

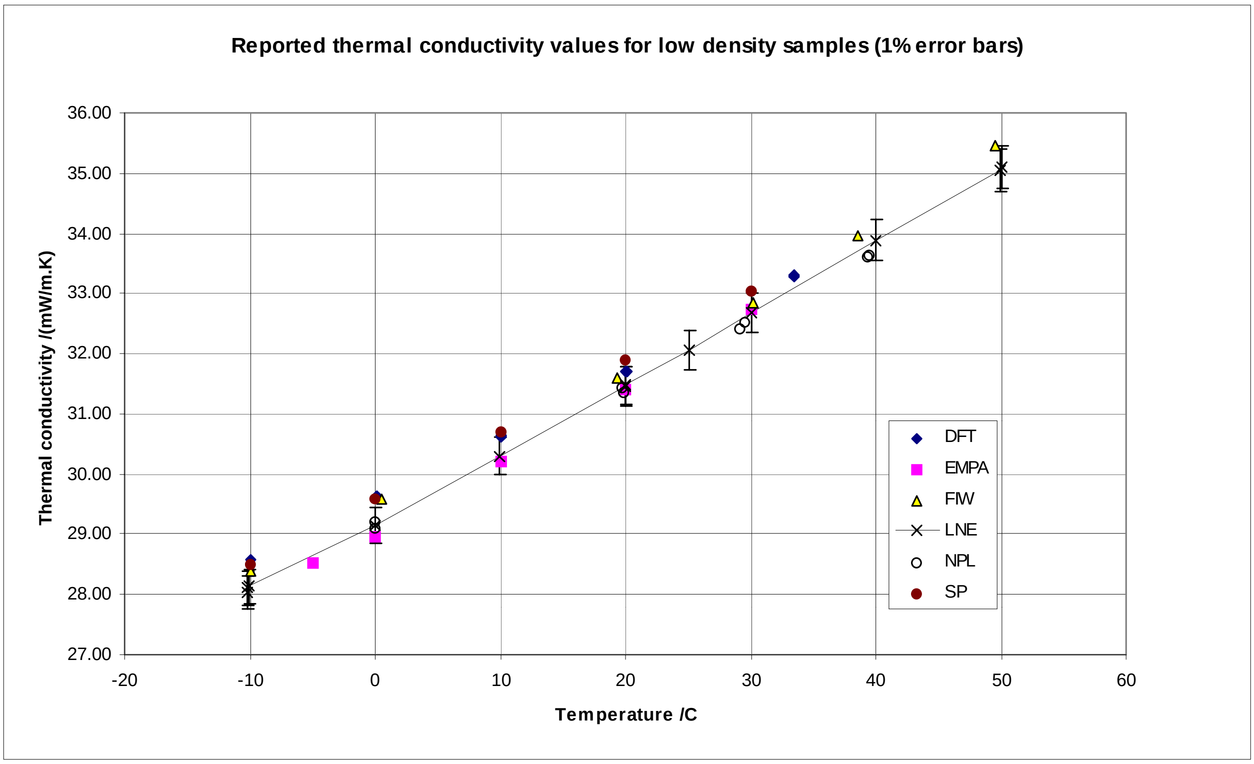

Figure 3. Thermal conductivity of IRMM-440 versus temperature over the range -10°C to +50°C

3.5 INTERCOMPARISON OF CURRENT NATIONAL REFERENCE MATERIALS

The aim of this NPL initiated intercomparison between different countries is to establish the degree of agreement of the results of basic hot plate measurements of the national measurement organisations. Measurements have been carried out on some of the national reference materials currently available in different countries in order to ensure that the respective reference materials can be used internationally with an accepted level of precision in their values.

Measurements were carried out by NPL in the UK, NIST in the USA, National Research Council (NRC) in Canada, LNE in France and Japanese Construction Materials Laboratory UCML) in Japan. The reference materials measured are the European fibrous glass board (IRMM-440), a lower density fibrous glass blanket (SRM 1451) and a polystyrene bead board (SRM 1453) from the USA and a high density mixed oxide-glass fibre from Japan. Measurements have been completed and a statistical analysis of the results is being carried out by NIST in the USA, a report is expected later this year. It is hoped that the overall agreement will be very good and thus illustrate that any of these references will be suitable for use world wide. This is especially important for the case of heat flow meter apparatus (ISO 8201) calibration. Some NPL results using the apparatus during a recent study[(12)] on expanded polystyrene (EPS), extruded polystyrene (EXPS), and a rockwool, shown in Table 1, indicate that real differences in values of the

Material	Thickness /mm	Thermal Conductivity / (mW/m.K)				Difference %	
		Supplied calibration*		NPL calib. (IRMM)			
		10°C	24°C	10°C	24°C	10°C	24°C
EPS	48.88	35.8	37.4	34.5	36.3	2.9	3.0
EPS	24.56	35.0	36.5	33.9	35.7	3.2	2.2
XPS	50.38	29.7	31.2	28.8	30.3	3.1	3.0
XPS	32.54	28.0	29.2	27.2	28.5	2.9	2.5
Rockwool	51.02	36.6	38.1	35.6	37.1	2.8	2.7
Rockwool	32.10	36.4	37.9	35.3	36.8	3.1	3.0

Table 1. Heat flow meter values measured in one apparatus based on two different calibration specimens

*Data supplied by USA manufacturer attributed to independently measured specimen.

order of between 2 and 3% are possible depending on which type and source of calibration material is used. The use of certified reference materials for the above purpose is highly recommended. and the ready availability and acceptance of various national materials having values of a common known precision will further improve this secondary method of measurement and help to obtain more uniformity in results by this technique.

3.6 EUROPEAN THERMAL INSULATION REFERENCE MATERIAL FOR HIGH TEMPERATURES

There is an increasing need for one or more thermal insulation reference materials that can be used at high temperatures. Industry members manufacturing such insulations will need to substantiate performance claims under forthcoming European regulations. As discussed at the Reference Materials Workshop[(2)] a series of measurements by seven co-operating laboratories from Europe and USA on a potential reference material (a high density 150 kg/m^3 rock fibre board) indicated that uncertainties of greater than ± 12% existed between the different guarded hot plate apparatus used for the measurement This level of uncertainty would suggest that the current ISO 8302 standard requires some revision to address potential problems and issues that do not occur at lower temperatures where ±2% or better is the norm. The study also indicated that the proposed rock fibre material was not sufficiently reproducible in density for consideration as a reference material.

A proposal to the European Commission has been made by NPL together with several European laboratories for a research study to be carried out in order to provide basic information that can be used for revising ISO 8302 for high temperature operation and to attain precision levels of ±5% or better. This parametric study would involve the use of at least two possible candidate reference materials.

Current materials under consideration are a high density calcium silicate block, a high density glass/iron oxide fibre board (both being evaluated in Japan as reference materials) an aluminosilicate blanket and a highly refined blown fine fibre (3 μm) low density (8 kg/m^3) aluminosilicate modified with boric oxide blown fibre (Nextel) blanket. The latter material has been shown to be very uniform, highly stable and to have improved performance properties over other commercially available (7 to 10 μm) materials of comparable density(13). A major advantage of this material is that it can be compressed to a given uniform density and recover completely after release. This property addresses the problem of differences in performance due to density variations since a given piece of material can be compressed to any desired value. It is hoped that this proposal can be funded and that the work progresses rapidly since revision of ISO 8302 is overdue.

4. EXAMPLE OF THE VALUE OF REFERENCE MATERIALS

The NPL provided some of the reference materials that were used by Sinku Riko Inc. to validate a newly developed apparatus(14). This was the laser scanning version of the original ac calorimetric technique(15) and was developed as a more precise instrument for the measurement of specimens having broader ranges of thermal diffusivity/conductivity and thickness. Some of the validation measurements are shown in Table 2. Table 3 contains and compares values obtained on some CVD diamond

Material	Thermal Diffusivity cm^2/s		
	Present work		Reference Data
	In air	In vacuum	
99.99% O_2 free copper	1.174 ±3%		1.17
99.99% nickel	0.225 ±3%		0.229
304 Stainless steel	0.034 ±3%		0.035
Referceram AL-1	0.103 ±3%		0.104 ±3%
Glassy carbon GC-20	0.065 ±3%	0.0608 ±1.5%	0.0603 ±4%
Borosilicate glass	---	0.00573 ±1.5%	0.0053
Plexiglas (acrylic)	---	0.00127 ±1.5%	0.00128 ±2%

Table 2. Thermal Diffusivity of Various Reference Materials Using Modified AC Calorimetry

films. An earlier inter-comparison on these latter films using different measurement methods but including the original ac calorimeter had shown differences of ±45% overall[(16)].

Thermal Diffusivity cm^2/s			
	Laser Scanning	**Traditional**	
Material	**Sinku Riko**	**Sinku Riko**	**Range for 3 organisations**
LB-X (high)	**8.56**	**8.36**	**8.36 - 9.97**
LB-T (Intermediate)	**6.75**	**6.57**	**6.57 - 8.2**
LB-E (low)	**2.25**	**2.28**	**2.28 - 2.5**

Table 3. Thermal Diffusivity of First Round Robin CVD Specimens

The results shown in Table 2 and 3 illustrate a high level of agreement that is possible for specimens having a broad property range. Without the use of well characterised artefacts any definite claims of precision would have been difficult to substantiate.

5. SUMMARY

A review has been given of a number of recent activities devoted to the development and use of reference materials and artefacts having known thermal properties. During the past two or three years there has been far greater attention paid to this subject overall. There is now much more international co-operation on the subject. In particular the NPL in the UK has had the opportunity to initiate and partake in various studies and intercomparisons which should result in several new reference materials becoming available in the near future.

6. REFERENCES

1. R. P. Tye, 1996, Thermal Conductivity 23, Eds. K.E. Wilkes, R.B. Dinwiddie and R. S. Graves Technomic Publishing Co. Lancaster, PA, pp 419-430.
2. R. P. Tye, 1999, High Temp-High Press, 31, pp 17-22.
3. L. Kubicar and V. Bohac, 1999, Thermal Conductivity 24-Thermal Expansion 12 Eds. P. S. Gaal and Daniela E. Apostolescu, Technomic Publishing Co. Lancaster, PA, pp 135-149

   See also Meas. Sci. Technol., 2000, 11, 252.
4. Anne Kibble, 1999, Presentation at Workshop on Transient Methods held at 15th European Conference on Thermophysical Properties, Würzburg, Germany, 5-9 September.

5. E. P. Sakonidu, M. J. Assael, C. Nieto de Castro, H. R. Van Den Berg and W. A. Wakeham, 1999, Thermal Conductivity 24 - Thermal Expansion 12, Eds. P. S. Gaal and Daniela E. Apostolescu, Technomic Publishing Co., Lancaster, PA. pp 516-530.
6. L. Cusco and B Monaghan, 1999, "UK National Standard for the Thermal Properties of Molten Materials.-Thermal Diffusivity of Molten Copper, paper presented at the 15th European Conference on Thermophysical Properties, Würzburg, Germany, 5-9 September.
7. A. Peralta, M. Dix and W. A. Wakeham, 1999, Thermal Conductivity 25 Thermal expansion13, Eds. C Uher and D Morelli, Technomic Publishing Co., Lancaster, PA, pp 333-339.
8. V Peralta-Marrtinez, M Dix and W A Wakeham, 1999, Proceedings of 1st International Conference on Thermophysical Properties of Materials (TPPM99), Ed Peter Hing, AMRC, Nanyang Technological University, Singapore pp 149-154.
9. M. H. Suliyanti, T. Baba and A. Ono, 1994, Thermal Conductivity 22, ed T. Tong Technomic Publishing Co., Lancaster PA, pp 80-91
10. H. Kato, T. Baba and M. Okaji, 1999, Thermal Conductivity 24 - Thermal Expansion 12, Eds. P. S. Gaal and Daniela E. Apostolescu, Technomic Publishing Co. Lancaster, PA, pp 647-654.
11. Sylvie Quin and G Venuti, 1999, "Thermal Conductivity of Glass Fibre Boards Replacement of CRM064 Creation of a New Batch of Reference Material" final report IRMM/ST/96-191 EC 9600488, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium.

12. D. R. Salmon and R. P. Tye, 2000, High Temp.-High Press., 32, pp 19-28. See also 15 ECTP Proceedings pp 47-56.

13. R. P. Tye, A. O. Desjarlais and S. E. Smith, 1985, Thermal Conductivity 18, Eds. T. Ashworth and D. R. Smith, Plenum Press, New York, pp 317-326.

14. R. Kato, A. Maesono and R.P. Tye, 1999, Thermal Conductivity 24 - Thermal Expansion 12, Eds. P. S. Gaal and Daniela E. Apostolescu, Technomic Publishing Co. Lancaster, PA, pp 572-580.

15. I Hata, R. Kato, Y. Gu and A. Maesono, 1994, Thermal Conductivity 22. Ed. T. Tong, Technomic Publishing Co. Lancaster, PA, pp 461-472.

16. A. Feldman, 1995, Applications of Diamond Films and Related Materials Third International Conference, Eds. A. Feldman, Y Tzan and W. A. Yarbrough, M. Yoshikawa and M. Mirakama, National Institute of Standards and Technology, Washington DC, pp 627-630