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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
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ABSTRACT

As a preliminary step to discussion of thermal conductivity reference standards, some results of a mathematical analysis of longitudinal heat flow in a cut-bar apparatus (meter-specimen-meter) are presented graphically. The results lead to the conclusion that a guarded cut-bar apparatus is possible in which the heat flowing longitudinally in the centrally-located specimen is a fixed proportion of that flowing in the meters, which proportion depends only on a factor involving the conductivities of the specimen, the meters, and the surrounding powder insulation, and does not depend upon precise management of the guard temperatures. Such an apparatus is shown schematically, and a method of calibrating the meters of the apparatus by using a reference specimen of known thermal conductivity in place of the test specimen is described, with procedure and equations for its calibration and use. Information is given graphically on the variation of the conductivity factor with the conductivities of the specimen and the meters. Finally, the necessary or desirable properties and attributes of materials for use as thermal conductivity references are discussed.

1. INTRODUCTION

This report is a slightly modified version of a paper given by the author at the informal Second Conference on Thermal Conductivity, held at the National Research Council, Ottawa, Canada, on October 10-12, 1962. Since its contents relate to and complement, from an application point of view, an undertaking sponsored by the Bureau of Ships, Department of the Navy (Bu Ships 1700 S-716-62) for development of a specific thermal conductivity reference material, the paper is being made available as a complementary report to the sponsor.

In an earlier NBS Report\(^1\), reference was made to the use of thermal conductivity reference standards as a means of facilitating and improving the accuracy of thermal conductivity measurements. It was pointed out that such standards are best used in the role of substitute specimens, that close duplication of the accessory conditions of the apparatus is

FIGURE 1. SCHEMATIC ARRANGEMENT OF A GUARDED CUT-BAR APPARATUS FOR COMPARATIVE DETERMINATION OF THERMAL CONDUCTIVITY, SHOWING THE BAR ASSEMBLY (METER-SPECIMEN-METER) WITHIN A CONCENTRIC GUARD CYLINDER. STEADY TEMPERATURES AT THE INDICATED LONGITUDINAL POSITIONS OF THE BAR ASSEMBLY AND GUARD ARE V AND 0, AND T AND R, RESPECTIVELY.
essential to conserve the accuracy of the calibration of the test apparatus, and that therefore the design of the test apparatus is important as regards the precision with which the accessory conditions can be controlled and duplicated.

As a preliminary step to consideration of materials for reference standards, and to focus some attention on their uses and therefore on the attributes they should have, this report first presents a development of the ideas mentioned above, leading to a schematic design for a cut-bar comparative – i.e., calibrated – apparatus for measuring the thermal conductivity of small specimens, and to the procedure for its calibration and use. The apparatus that emerges from the development appears in prospect to be simple to build and use, and yet to be capable of satisfying the requirements indicated in the first paragraph.

2. A CUT-BAR APPARATUS FOR CALIBRATION USING REFERENCE STANDARDS

In the earlier report mentioned, a general mathematical solution was given by D. R. Flynn for calculating the heat flux at various longitudinal positions along a cut-bar apparatus assembly (meter-specimen-meter arrangement as shown in Figure 1), and the solution was developed and shown graphically for the case of matched guarding. It is sufficient for present purposes to take from the general solution the following information:

a) If the conductivity of the specimen differs from that of the meter bars, there is an interchange of heat between the bar assembly and the surrounding powder insulation in the vicinity of the specimen, even with perfectly matched guarding. This leads to a change in longitudinal heat flux in the bar assembly in the vicinity of the specimen. For the case of matched guarding, the net change of heat flux in the bar assembly, from a selected position or origin to a particular position is proportional to the product of a conductivity factor ($F_k$), which depends only on the conductivities of the specimen, the meters and the powder insulation, and a geometrical factor ($F_g$) which depends only on the dimensions of the bar assembly and the guard.

b) If the temperature of the guard varies linearly with longitudinal position from end to end, the change in bar assembly heat flux with position is equal to the product of the same factor $F_k$ as in a) and a modified geometrical factor ($F'_g$) which takes into account also the integrated radial heat interchange between the bar assembly and guard, if the guard matches the bar assembly in temperature at the origin and at an equal distance on the other side of the specimen. If the guard temperatures at these positions do not match those of the bar assembly, an additional term involving the temperature differences must be added.
FIGURE 2. LEFT DIAGRAM ILLUSTRATES TEMPERATURE DISTRIBUTION IN A CUT-BAR COMPARATIVE APPARATUS ALONG THE METER-SPECIMEN-METER ASSEMBLY (DASHED LINE) AND ALONG A LINEAR GUARD MATCHED AT ENDS (SOLID LINE). RIGHT DIAGRAM SHOWS CHANGE IN LONGITUDINAL HEAT FLUX IN BAR ASSEMBLY WITH POSITION, FOR (M) A MATCHED GUARD, (L) A LINEAR GUARD MATCHED AT ENDS, (L0) A LINEAR GUARD 0.01V COOL AT ENDS
These observations are illustrated in Figure 2. The schematic bar assembly considered has the specimen and meter bars of equal length (w/3), equal to their diameter (2a), which is one-third of the guard diameter. Such dimensions seem practical for many applications, and were selected to avoid excessive effects due to integrated radial heat exchange with the guard. The bar assembly has the temperatures V and zero at its two ends; the corresponding guard temperatures are T and R. In the diagram at the left, the dashed line represents the idealized temperature along the bar assembly, assuming unchanging longitudinal heat flux, and the solid line a linear guard matched at the ends (that is, with T = V, and R = 0). If a matched guard were used, its temperature would be given by the dashed line. If a guard isothermal at the mean temperature of the specimen were used, T = R = V/2.

The diagram at the right of Figure 2 shows the change in longitudinal heat flux in the bar assembly, versus distance from the hotter end of the hotter meter, for matched guarding (M), for a linear guard matched at the ends (L), and for a linear guard with its temperatures at the ends 0.01V cooler than those of the bar assembly (Lp). (The case for an isothermal guard, with T = R = V/2, cannot be shown well on this diagram. The power change (γ) at z/w = 0.5 is -15.9 percent.)

The power change curves show that if the specimen and guard temperatures have polar symmetry, about a point at the center of the specimen, the indications of heat flow by the two meters will be equal. If they are polarly asymmetrical, as in the case of the linear guard displaced one percent, the two meters will disagree. However, in both cases, the indications of the meters do not correspond to the actual heat flow through the specimen if the conductivity factor Kp is not zero, i.e., if the conductivity (Kg) of the specimen does not equal that of the meters (Km).

In Figure 2, the fractional power change γ for the case of a matched guard was calculated using equation (28) of D. R. Flynn’s paper. For the case of a linear guard, his general equation (16) yields, in the nomenclature of this paper,

\[ \gamma(z) = K_L \left( \frac{1}{K_m} - \frac{1}{K_g} \right) \cdot \frac{8w}{\pi^2 a} \sum_{n=1}^{\infty} \frac{2w}{\pi^2 a} \left( \frac{\cos \frac{nw}{w}}{w} \right) \left[ 1 - \cos \frac{nw}{w} \right] \sin \frac{nw}{2w} \cos \frac{nz}{2w} \]

\[ + \frac{1}{K_m} \cdot \frac{K_L}{K_g} \cdot \frac{2w(T-V)z + (R+V-T)z^2}{a^2 w/n b/a} \]

(1)
Figure 3. Geometrical factor as a function of the ratio of guard and specimen diameters, for four types of guarding: (M) matched guard, (L) linear guard matched at ends, (I) isothermal guard at specimen mean temperature, (I') isothermal guard almost wholly at mean temperature of specimen, but matched at ends.
This equation (and equation (28)) involved in its development the assumption that \( K_S S_S = K_m S_m \), rather than the truer relation that

\[
K_S S_S = \left[ 1 + \gamma(z=w/2) \right] K_m S_m
\]

where \( S_S \) and \( S_m \) are the longitudinal temperature gradients in the specimen and meter bars, respectively. For tolerable values of \( \gamma \), the error in \( \gamma \) due to this assumption is of secondary importance.

For a linear guard matched in temperature at \( z = 0 \) and \( z = w \), the second term of \( \gamma(z) \) equals zero, and

\[
\gamma(z) = K \left( \frac{1}{K_m} - \frac{1}{K_S} \right) \cdot \frac{8w}{n^2 \pi^2} \sum_n \frac{F_1 \left( \frac{n\pi a}{w}, \frac{n\pi b}{w} \right)}{F_0 \left( \frac{n\pi a}{w}, \frac{n\pi b}{w} \right)} \left[ 1 - \cos \frac{n\pi a}{2w} \right] \sin \frac{n\pi b}{2w} \cos \frac{n\pi}{2} \tag{2}
\]

or,

\[
\gamma(z) = F_k \cdot F_g' \tag{2a}
\]

Figure 3 shows values of the geometrical factor at \( z = w/2 \), for various ratios of guard diameter to specimen diameter for the case of a specimen (and meters) of length equal to their diameter, for four types of guarding. Curve \( M \) is for a matched guard, curve \( L \) for a linear guard matched at the ends, curve \( I \) for an isothermal guard with its ends at the mean temperature of the specimen, and curve \( I_k \) for a guard isothermal at the specimen mean temperature over the length 0.01w to 0.99w, but changing linearly in the length 0.01w to match the temperatures at the ends of the bar assembly.

Of major interest is the fact that for three types of guarding (\( M, L, I_k \)), the geometrical factors practically coincide at a value of 2.93 for guard diameters greater than about seven specimen diameters. Thus, for these cases, the power change fraction \( \gamma \) is equal to 2.93 \( F_k \), if the diameter ratio is seven or greater, and the precise management of the temperatures of the guard is immaterial, provided that its mean temperature is substantially equal to the mean temperature of the bar assembly. All three of these cases are characterized by the condition that the virtual plane surfaces \( z = 0 \) and \( z = w \) in the insulation between the bar and guard are isothermal at the corresponding temperature of the bar assembly. (In the case of curve \( I \), the temperature of these virtual plane surfaces is a function of the logarithm of the radius.) In short, the geometrical factor
Figure 4. Schematic for a Guarded Cut-Bar Apparatus designed for calibration of meters by means of thermal conductivity reference specimens, with the calibration substantially independent of precise guard temperature management.
attains a unique and constant value when the ends of the insulation between
the bar assembly and the guard are isothermal at the corresponding tempera-
tures of the bar assembly, and the guard diameter is large enough.

The apparatus shown schematically in Figure 4 is designed to satisfy
the conditions developed above. Thick disks of conductive material of
radius \( b \approx 7a \), approximately, are used to provide substantially isothermal
surfaces at \( z = 0 \) and \( z = w \); the guard is a suitable thin-walled cylinder
of internal radius slightly larger than the disk radius, positioned on
poorly-conducting supports carried by the lower disk. A guard so arranged
might possibly attain the mean temperature of the two disks; if necessary,
electrical heating of the guard could be used to establish the desired mean
temperature. The heaters on the disks, indicated schematically, establish
their temperatures and provide the heat flowing longitudinally between them.
For very high temperature operation the total assembly probably should be
placed within an enclosing furnace.

3. CALIBRATION AND USE OF THE APPARATUS

Assume that an apparatus of the kind, and geometry, shown in Figure 4 has been constructed, with thermocouples installed as indicated by the
solid circles. The position normally occupied by a specimen is occupied
by a reference specimen of known thermal conductivity \( (K_r) \), with which the
apparatus \( (i.e., \) the installed meter-bars, or meters) are to be calibrated.

Assume that the upper disk has been brought to a steady temperature
suitably higher than that of the lower disk and that the average of the
temperatures of the two guard thermocouples approximates the average of
the temperatures of the two specimen thermocouples. Under these condi-
tions, measurements are made to ascertain \( S_r \) and \( E_{mr} \), the temperature
gradient in the reference specimen, and the average of the temperature
gradients in the two meters, respectively. With these data, one can write

\[
\pi a^2 K_r S_{mr} (1 + \gamma_r) = \pi a^2 K_r S_r
\]

in which the subscript \( r \) refers to values pertinent with the reference
specimen in place, and \( (1 + \gamma_r) \) is the fractional power flowing in the bar
assembly at the position of the mid-plane of the reference specimen.

Similarly, in a similar test conducted with a test specimen \( (subscript
s) \) in place in the bar assembly, one can write

\[
\frac{\pi a^2 K_s S_{mb} (1 + \gamma_s)}{\pi a^2 K_s S_s} = K_s S_s
\]
If in both tests the average values of the temperatures of the two meters were the same (or if the meters do not change significantly in conductivity with temperature), \( K_m \) and \( K_m^r \) will be equal and these two equations then yield the relation

\[
\frac{K_s}{K_r} = \frac{E_{ms}}{E_{mr}} \cdot \frac{S_r}{S_s} \cdot \frac{1 + \gamma_s}{1 + \gamma_r}
\]

(3)

It has been shown that for the assumed apparatus

\[
\gamma(z = \frac{W}{2}) = 2.93K_k = 2.93K_k^r \left( \frac{1}{K_m} - \frac{1}{K_{spec}} \right)
\]

Accordingly,

\[
\frac{1 + \gamma_s}{1 + \gamma_r} = \frac{1 + 2.93K_k^r \left( \frac{1}{K_{ms}} - \frac{1}{K_s} \right)}{1 + 2.93K_k^r \left( \frac{1}{K_{mr}} - \frac{1}{K_r} \right)}
\]

This is awkward to evaluate, since \( K_m \) (\( K_{ms} \) will here be assumed equal to \( K_{mr} \)) may not be accurately known. However, \((1+\gamma_s)/(1+\gamma_r)\) may be approximated by \(1+\gamma_s-\gamma_r\), with a fractional error equal to \(\gamma_r(\gamma_s-\gamma_r)/(1+\gamma_s)\). Within the uncertainty with which \(K_s\) and \(K_m\) may be duplicated in the use of the apparatus, and the fractional error involved in the above approximation, one can use the approximation and avoid needing to know \(K_m\). Thus equation (3) becomes

\[
\frac{K_s}{K_r} = \frac{E_{ms}}{E_{mr}} \cdot \frac{S_r}{S_s} \cdot (1+\gamma_s-\gamma_r) = \frac{E_{ms}}{E_{mr}} \cdot \frac{S_r}{S_s} \cdot \left[ 1 + 2.93K_k^r \left( 1 - \frac{K_r}{K_s} \right) \right]
\]

(4)

wherein \(K_s/K_r\) is ascertained by a few repetitive calculations using improved values of \(K_s/K_r\) in the bracketed term.

Some obvious precautions or arrangements desirable in the use of the envisaged apparatus include the following:

a) The powder insulation of conductivity \(K_2\) should be installed, and if necessary, renewed from a uniform stock, so that \(K_2\) is substantially the same in all tests at the same temperatures.
b) Contacting surfaces of the meter bars and specimens should be clean and quite flat to avoid perturbations of the calibration and tests due to altered thermal resistance at contacts.

c) The reference specimen and the test specimens should always have the same dimensions, quite closely. Thermocouples should be attached in both by the same method, and should be equidistant from the mid-plane of the specimen, with the separation the same for all specimens.

4. SELECTION OF METER BARS

A cut-bar apparatus of the kind envisaged, if calibrated and used according to the procedure described, should be capable of good accuracy over a wide range of specimen conductivities. However, for precision of observations, it is desirable that the temperature differences measured in the specimen and the meters be of approximately the same magnitude.

As a guide in selecting suitable meter bars for particular measurements, and as a means of estimating the range of specimen conductivities most appropriate for measurement with particular meter bars, Figure 5 presents negative values of the conductivity factor \( F_k \) (in percent) versus the reciprocal of the specimen conductivity (specimen thermal resistivity), for three different meter bar materials: Armco iron, Pyroceram 9606, and fused silica. Two straight lines are shown on Figure 5 for each meter material, one corresponding to its use at 0°C, and the other to its use at 1000°C (the 1000°C line for fused silica is hypothetical, assuming that it is, or can be made, opaque to thermal radiation). The conductivity factors are predicated on pure fine alumina powder insulation having the conductivities given on Figure 5, and intermediate values which vary substantially linearly with temperature. The values of thermal resistivity used for the meter bar materials are indicated by the value of \( 1/K_b \) at the intersection of the meter bar line with the zero value line for the conductivity factor.

It may be of interest to note that the product of the negative percentage conductivity factor and the geometrical factor for a cut-bar apparatus (the latter could easily have values as large as 3 or more) indicates the percent error in the obtained conductivity of the specimen, if the latter were to be calculated simply on the basis of the heat flow indicated by the meters. For example, with an Armco iron meter at 0°C, the negative conductivity factor for a specimen of 0.025 conductivity \( (1/K_b = 40) \) is about 4 percent, and with a geometrical factor of 3 the error of the uncorrected conductivity would be about 12 percent.
Figure 5 shows that, as might be anticipated, the negative conductivity factor, and therefore the error in conductivity, is relatively small for Armaco iron meters, for specimens of resistivity 10 cm deg C/watt and less. For Pyroceram 9606 meters, the values are relatively small at 0°C for specimens of resistivity between 10 and 50, and at 1000°C, for specimens of resistivity between 50 and 50. Similar observations can be made for fused silica meter bars, which at 0°C seem well suited for measurements of specimens of resistivity between 60 and 100 cm deg C/watt. (The line for a hypothetically-opaque fused silica at 1000°C should not be construed as realistic; rather, it sets a goal for such a material.)

The light dashed lines labeled "Inconel 702 specimen" and "fused silica specimen" (again hypothetical) indicate how the conductivity factor for these specimens, tested with Pyroceram 9606 meters, would vary as the mean temperature of the test increased from 0°C to 1000°C.

5. TYPES OF MATERIALS FOR THERMAL CONDUCTIVITY REFERENCE STANDARDS

One can imagine one of P. W. Bridgman's aboriginal Bushmen setting up a system of thermal conductivity reference specimens on the basis of a series of solids of different colors or weights, or other qualities. The interesting thought is that if he had only one standard, and it (and each other solid) was stable in conductivity, an effective aboriginal thermal conductivity regime would exist. However, trouble could be anticipated if he attempted to have two basic standards in this regime. Perhaps, after much confusion, Bridgman's Bushman would conclude that stability was the important desideratum for a regime, and that (in our terms) absolute thermal conductivity was really secondary, if not actually a nuisance.

This vignette contains much truth, but for us not all of it. Modern man requires absolute values of conductivity, to fit into his broad system of physics, and for applications ranging from submarines to space vehicles. The uncertainties in his absolute values of conductivity depend, of course, on the state of the art. Obviously, it is important to reduce them as much as feasible to promote concordances of conductivity values, one with another, and with related other properties of the materials. Nevertheless, it remains true that stability of conductivity, and uniformity, are prime requirements for thermal conductivity reference standards - so much so that it is logical to classify possible materials for standards in categories based on these qualities, as follows:
FIGURE 5. CONDUCTIVITY FACTOR FOR CUT-BAR APPARATUS AS A FUNCTION OF SPECIMEN THERMAL RESISTIVITY (1/Kₜₐₐₜ), FOR THREE DIFFERENT METER BARS AT TEMPERATURES OF 0°C AND 1000°C.
1. **Materials not sufficiently uniform to forgo need for measuring each reference specimen**

Such materials often must be used because there is no better alternative material. An example is the semi-rigid fiber-glass insulating board furnished by NBS for checking ASTM G177 hot plate equipment, or calibrating comparative apparatus for measuring the thermal conductivity of good thermal insulators. Again, an experimenter may use a particular material as a heat flow meter, and later may require the best possible value for its thermal conductivity. The fault in such materials is their need for individual measurement, which is uneconomic; they may be excellent in all other important respects, including stability under well-defined conditions.

2. **Stocked materials of proven uniformity: batch samples**

These are materials known, or found, to be quite uniform in thermal conductivity within a batch or lot, so that measurements made on a relatively few samples of it are sufficient to define the conductivity of the entire batch. Considerable exploratory work may be needed to assure that a material is satisfactory for this purpose, but if the batch (and the demand) is large enough, the cost per specimen may be quite moderate. Batch operations have the advantages that often the material can be given properties peculiarly suitable for the proposed use by compounding, doctoring, or special specification, that it may be possible to furnish specimens in a variety of shapes or sizes, and that generally the custodian of the stock becomes known as a source from which specimens can readily be obtained.

It is evident that batch materials are likely to be compounds or mixtures of elements, selected in part because they have conductivities appropriate for reference use for particular purposes, and perhaps other desirable properties obtained by doctoring.

3. **Materials of high purity**

Chemical elements of high purity are expected to have unique thermal conductivities, as well as other properties, which may be defined as their limiting values as impurities are reduced. Single-crystal materials can be regarded in a similar way. Thermal conductivity reference materials of this kind are attractive in that once the conductivity of the pure material had been adequately determined, reference specimens could be obtained from any source capable of supplying material of adequate purity. Relatively simple measurements may suffice in some instances to determine the degree of purity. For example, the purity of platinum is readily ascertained by the ratio of its electrical resistance at 100°C to that at 0°C.
In considering pure elemental materials, however, it must be recognized that at present the thermal conductivities of almost none have been measured and confirmed or cross-checked, over a wide range of temperatures, to the accuracy probably possible to the current state of the art. Further, their stability may be questionable because highly pure elements are quite reactive chemically, and protecting them from adverse contamination during use, especially at high temperatures, may be difficult, even in inert atmospheres or in a vacuum.

An assessment, in general, of the comparative merits of batch materials versus high-purity materials as reference standards cannot, of course, be conclusive. An important point, however, is that the electrical conductivity, and therefore presumably the thermal conductivity, of ultra-pure elements is usually markedly affected by the first traces of impurity, at least at low and moderate temperatures. On the other hand, the conductivities of multicomponent materials (sometimes delicately referred to as "garbage up") are often relatively insensitive to moderate variation in composition, although there may arise a greater sensitivity to thermal history or heat treatment, or to phase transformations in the range of working temperatures. It is also pertinent that few usable pure elements have thermal conductivities in the range in which reference specimens appear currently most needed, that is, below about 0.1 watt/cm °C. An argument in favor of pure materials is that they are used and are available now as references in other respects, such as chemical, spectroscopic, and freezing-point standard samples.

6. PROPERTIES OR ATTRIBUTES DESIRABLE FOR REFERENCE STANDARDS

In addition to the qualities already discussed, of appropriate, stable, and uniform thermal conductivity, a number of other attributes are desirable for reference standards. It is not essential that a reference standard be usable over a wide range of temperature, but it is desirable. Consequently, the remarks as to desirable properties below are meant to denote that adherence to the quality over a wide range of temperature is also, and in itself, desirable.

In most cases rigid and hard materials, capable of being finished to and retaining polished surfaces, are preferable. Materials easily subject to strain or surface work-hardening which cannot be largely relieved, or having large or anisotropic thermal expansion coefficients, or Poisson's ratio values, or which have significant rheological characteristics, are less desirable. Hygroscopic or highly sorptive materials may, of course, not be suitable for some purposes.
Since thermocouples must almost always be used with reference specimens, the physical properties of the material which might affect, for example, setting a thermocouple in a groove must be considered, as well as chemical reactions which might contaminate the thermocouple. Electrical insulation of the thermocouples is much simpler, and their use is therefore more precise, if the material is substantially non-conducting electrically.

Very substantial opacity to thermal radiant energy appears essential, a requirement that may seriously restrict the usefulness of single-crystal materials. Other not adequately opaque materials may be capable of being made more opaque by doctoring.

Resistance to chemical inter-reactions with other materials which might affect the conductivity of either is, of course, required, and an associated question is that of vapor pressure at elevated temperatures. Materials that do not require a protective atmosphere or use of a vacuum may be preferable, not merely because of convenience, but because the conductivity of the reference, or other critical parts of the testing apparatus, especially if there are porosities, may be altered by these conditions. In some instances, references for use in special atmospheres may be needed.

Materials not having transformations affecting their thermal conductivity in the working temperature range are, of course, much to be preferred over those which have them. However, in the latter cases, it may be possible, by suitable heat treatment, or doctoring, to put a material in the condition of one extreme or the other of the transformation, and thus render it stable over a wide temperature range.

A further desirable quality of a thermal conductivity reference material is that it have a specific heat not subject to discontinuities of slope. Such materials would be satisfactory also for use as thermal diffusivity references, for which there may be a need paralleling that for conductivity references.

If this survey and listing of desirable or undesirable attributes of thermal conductivity reference standard materials were to be made more complete or detailed, it would undoubtedly be even more formidable. Fortunately, it is more of a check list than a bill of particulars, and in many instances its force or impact can be softened or avoided by limiting the working temperature range for a material.