Measurement 155 (2020) 107556

Contents lists available at ScienceDirect

Measurement

journal homepage: www.elsevier.com/locate/measurement

A brief history of the thermal properties metrology

Bruno Hay

Laboratoire national de métrologie et d'essais (LNE), 29 avenue Roger Hennequin, 78197 Trappes Cedex, France

ARTICLE INFO

Article history:
Received 14 September 2019
Received in revised form 27 December 2019
Accepted 24 January 2020
Available online 29 January 2020

Keywords:
Thermal properties
Metrology
History
National Metrology Institutes

ABSTRACT

The metrology of thermal properties, which is more recent than that of length and mass, coincides with the creation of thermometers and the implementation of the temperature scales. The first major contributions to the study of thermal properties can be attributed to Franklin who devised in 1780 an experiment to evaluate the relative capacities of thermal conduction of different materials, and to Lavoisier who developed in 1782 an ice calorimeter for the relative measurements of specific and latent heat. It was not until 1807 that the first determination of an absolute value of thermal conductivity was done by Fourier. The experimental discovery of Joule around 1860, concerning the relationship between the heat generated and current flowing through a conductor, was the next important contribution to the development of metrology of thermal properties, as it provided for the first time the possibility of producing a known amount of heat by electrical way. The instruments involving generation or measurement of heat fluxes could be thus calibrated by Joule effect, enabling to improve the traceability to the International System of Units (SI) of thermal properties measurements. This principle was applied by the National Metrology Institutes, which have worked on the measurement of thermal properties from the beginning of the 20th century by developing reference facilities based on the implementation of "absolute" methods. This paper retraces the major developments in the metrology of thermal properties from its beginnings until now.

Contents

https://doi.org/10.1016/j.measurement.2020.107556
0263-2241/

1. Introduction

In many applications involving temperature change, the knowledge of the thermal behaviour of materials is needed in order to design and safely operate the concerned component. The metrology of the thermal properties is thus particularly useful to check the adequacy of materials with regard to a specific application and to understand heat transfer phenomena. Numerous measurement methods and experimental facilities have been progressively developed since the eighteenth century to produce reliable and accurate data of the thermal quantities over temperature domains close to those encountered in real situations.

The main objectives of this article are to present a brief history of the metrology of thermal properties (for thermal transport properties and caloric quantities), and to show the importance of the creation of the International System of Units (SI) and of the establishment of the temperature scales on its development.

The origins of the thermal properties metrology are first presented with the development of the temperature scales, the beginnings of the thermal conductivity measurements, the birth of the calorimetry and the first absolute measurements of thermal properties. The improvement of the traceability of the thermal properties measurements to the SI and the contributions of different National Metrology Institutes (NMIs) to the implementation of absolute measurement methods in that field during the 20th century are described in a second step.

2. The origins of the thermal properties metrology

2.1. The emergence of metrology

Metrology probably appeared in a concomitant way with the establishment of commercial exchanges, as soon as these ones could no longer be based on the simple enumeration of objects and needed a quantitative evaluation of suitable quantities (such as the length of a piece of cloth, the volume or the mass of a commodity, etc.), expressed in beforehand defined units. Many units of measurement, used for example for the collection of seigneurial rights or for the trade in fabrics, spices or metals, have coexisted in France for centuries despite numerous successive attempts of emperors and kings of France (from Charlemagne to Louis XV) to institute a unified measurement system in the country [1].

These units, generally of anthropometric origin (foot, cubit, span, fathom, toise…) could be different according to the places, the guilds or the nature of the measured objects. The multiplicity of units as well as the "random" distribution of their multiples and sub-multiples regularly led to errors and frauds in commercial transactions and also hampered the development of scientific activities. It was only at the French Revolution that the decimal metric system [2] replaced throughout the country the old systems of measurement inherited from feudalism.

This new system of weights and measures, unique and coherent, was based on a unit, the meter, having a natural and invariable character, and "which in its determination was neither arbitrary nor related to any particular nation on the globe" [3]. The other units were then deduced from the meter, the kilogram being, for example, equal to the mass of one cubic decimeter of pure water at the temperature of melting ice. The decree of 18 Germinal Year III related to the weights and measures also established that the decimal system applies to all units, including in the case of time scales. Decimal hour was thus briefly adopted as the official time of the French Republic, and clocks (whose some are still visible at the *Musée National des Techniques* of *Conservatoire National des Arts et Métiers*) were built.

2.2. The development of temperature scales

The first temperature-sensitive graduated instruments were air thermometers, also improperly called "thermoscopes" (although they had graduations), whose invention at the end of the sixteenth century have been attributed depending on the sources to Galileo (1564–1642) or to Santorio of Padua (1561–1636) [4]. These thermoscopes, whose the major drawback was the sensitivity to atmospheric pressure, were the precursors of liquid expansion thermometers, which appeared in 1654 at the instigation of Ferdinand II Grand Duke of Tuscany (1610–1670). These sealed-tube thermometers have been progressively improved, in particular with the use of mercury as a thermometric liquid in the device designed in 1714 by Daniel Gabriel Fahrenheit (1686–1736).

These developments have been naturally accompanied by the establishment of temperature scales enabling to quantify and to compare measurements. During the century following the invention of the thermometer, more than thirty different temperature scales emerged, all materialized by two fixed points, corresponding commonly to some physical phenomena encountered in everyday life, between which were arbitrarily distributed a number of identical intervals.

Honoré Fabri (1607–1688) used, for example, as fixed points in 1669 the temperature of the snow and that of the warmest day of the summer, while Carlo Rinaldini (1615–1698) proposed in 1693 the use of the melting point of ice and the boiling point of water, and defined twelve steps between these two temperatures. Among these more or less "exotic" scales, three of them were predominantly used from the middle of the 18th century for scientific works, and thus contributed to the growth of the metrology of thermal properties. These are thermometric scales of Fahrenheit, Réaumur and Celsius.

Based on previous works of the Danish astronomer Ole R∅mer (1644–1710), Fahrenheit developed in 1724 a two fixed points thermometric scale associating 0 °F to the freezing point of a mixture of water and ammonium chloride and 96 °F to the human body temperature (he initially used the horse blood temperature), and subdivided this range into 96 equal parts.

René-Antoine Ferchault de Réaumur communicated to the *Académie royale des sciences* in 1730 his "rules for constructing thermometers whose degrees are comparable, and which give ideas of hot or cold which may be related to known measurements" [5], and proposed a scale ranging from 0 for the melting ice to 80 for the boiling of water.

The Swedish physicist and astronomer Anders Celsius (1701–1744) developed in 1742 a mercury thermometer, where 0 and 100 corresponded respectively to the boiling point and the freezing point of the water, and divided the domain defined by these two points in 100 equal intervals. After his death, Carl von Linné (1707–1778), one of his collaborators, reversed in 1745 this scale while keeping its centesimal character, defining thus the Celsius scale as we currently know.

This latest scale would have had only a limited use if the Weights and Measures Commission, created by the Convention, had not imposed in 1794 that "the thermometric degree will be one-hundredth of the distance between the melting point of ice and the boiling point of water" [6].

2.3. The beginnings of thermal conductivity measurements

One of the first major contributions to the study of thermal transport properties can be attributed to Benjamin Franklin (1706–1790) who designed an experiment to evaluate the relative capabilities of different materials to conduct heat. During a visit to France in 1780 [7], he explained his experimental concept to Jean Ingen-Housz (1730–1799), a Dutch biologist and chemist, who applied it to seven metals: gold, silver, copper, tin, steel, iron and lead. The principle of this method consisted ① in coating wires of different materials having same length and same diameter with wax, ② in simultaneously immersing one of their ends over a same length in hot oil, ③ and then in observing the speed of propagation of the fusion of the wax along the wires. Fig. 1 presents a schematic representation of the facility developed by Ingen-Housz.

Ingen-Housz recorded the results of his works in a comparative basis, representing graphically for each test the lengths (expressed without unit) of wire on which the wax had melted. These lengths were measured after having removed the wires from the oil at the same time. The results from four of the twelve experiments that he carried out using the same seven metals are shown in Fig. 2. The horizontal marks represent for each metal the distance on which the wax had melted. The differences observed for the same material between several tests are attributable to immersion durations or oil temperatures varying from one experience to another. On the basis of this study, Ingen-Housz proposed to rank these seven materials from the "best conductor of heat" to the worst one, as follows: silver, copper, gold, tin, iron, steel and lead [9].

At the same period, Benjamin Thompson (1753–1814), known also as Count Rumford, studied in 1785 the propagation of heat in various materials: water, air, moist air, Torricellian vacuum and mercury [10]. The device used was mainly composed of a thermometer, graduated according to the Réaumur temperature scale, and hermetically sealed in a glass bulb (see Fig. 3) which had been filled beforehand with the material to be characterized. The procedure consisted in immersing the device first into a mixture of water and ice (at a temperature of 0 °Re), then into boiling water (corresponding to 80 °Re), and in observing the temperature increase as a function of time. Thompson measured for each material the time needed for the temperature at the center of the bulb to rise from 0 °Re to 70 °Re.

He established a relative scale of the "conducting powers" of the materials on the basis of the times measured, by assigning arbitrarily the value 1000 to mercury. By applying this scale, Thompson proposed the following hierarchy in terms of "conducting power" for the materials he had tested: mercury (1000), moist air (330), water (313), "common" air (80), and Torricellian vacuum (55).

By reading the interpretations of Ingen-Housz and Thompson concerning the results of their experiments, it appears that at the end of the eighteenth century the notion of thermal conductivity had been understood in an intuitive but imprecise sense. As pointed out by Jean-Baptiste Joseph Fourier (1768–1830), "the experiments of Ingen-Housz were in no way suitable for measuring the conductibility" [11]. The analyses of Ingen-Housz and Thompson were indeed erroneous since they attributed the differences in the rate of heat diffusion observed from one material to another to the sole effect of the thermal conductivity, forgetting the influences of the density and of the specific heat. In their defence, the concepts of latent heat and specific heat were introduced by Joseph Black (1728–1799) only in 1761, and Antoine Lavoisier (1743–1794) and Pierre Simon Laplace (1749–1827) had just invented in 1785 an ice calorimeter enabling to measure these two quantities. By applying transient experiments, Ingen-Housz and Thompson had in fact implemented the first methods of relative measurement of thermal diffusivity.

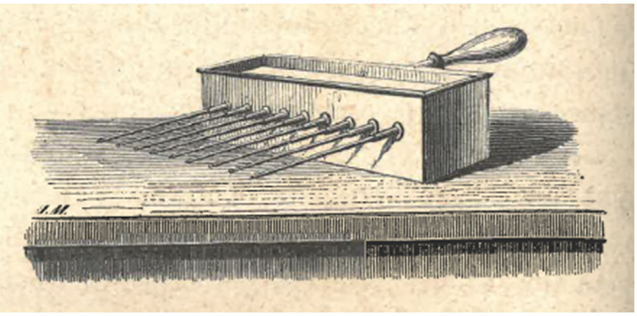


Fig. 1. Scheme of the facility designed by Ingen-Housz [8].

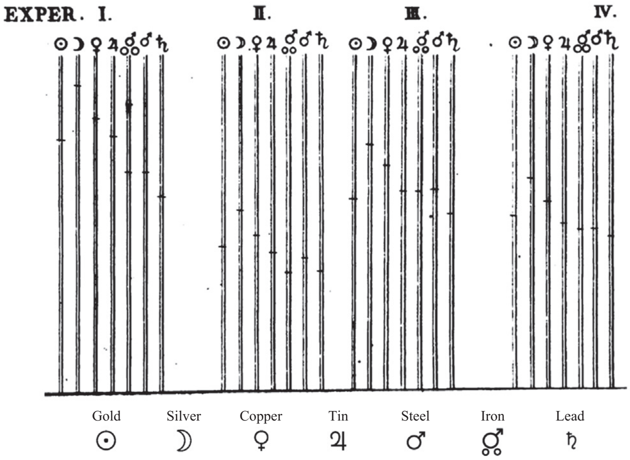


Fig. 2. Relative measurements of "thermal conductivity" performed by Ingen-Housz [9]. *Source gallica.bnf.fr / BnF.*

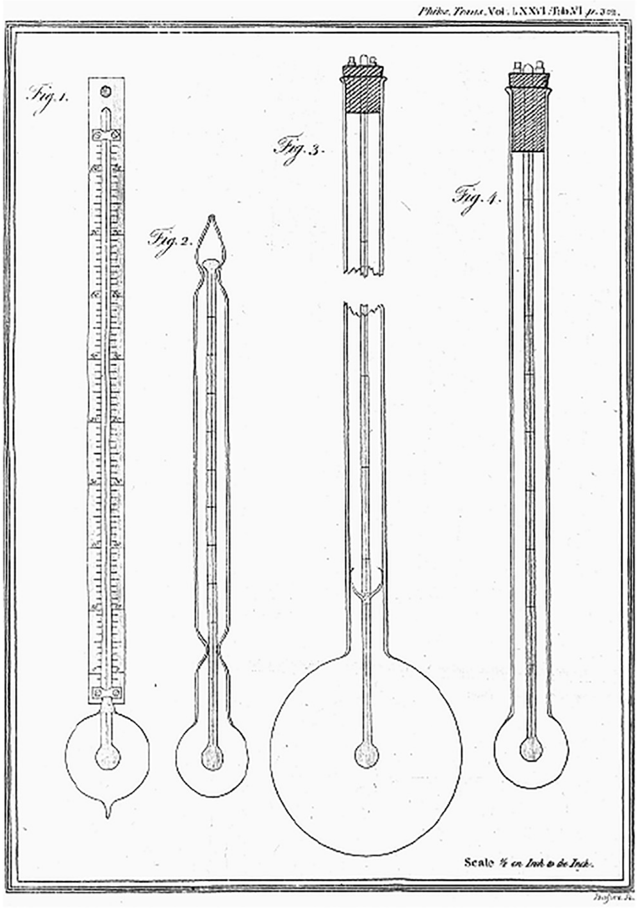


Fig. 3. Benjamin Thompson's device for measuring the "conducting powers" of materials [10].

It should be noticed here that the term "thermal diffusivity" seems having been associated for the first time to the ratio (thermal conductivity)/(specific heat × density) around 1890 by William Thomson (1824–1907), more known as lord Kelvin [12]. James Clerk Maxwell (1831–1879) had proposed some years before in 1871 to use the expression "thermometric conductivity" for this ratio, in order to distinguish it from the thermal conductivity which he named "calorimetric conductivity" [13].

Adapting an experiment initiated by Jean-Baptiste Biot (1774–1862) [14], César-Mansuète Despretz (1791–1863) performed relative measurements of thermal conductivity around 1820, by heating a horizontal bar at one end with a lamp and by measuring the longitudinal profile of temperature with thermometers placed in holes at various points of the bar (see Fig. 4). The temperature measurements were carried out in steady state conditions (reached for some materials after several hours), the intensity of the flame being regulated "so that the thermometer closest to the lamp indicates a fixed temperature". This experimental approach was applied to eight different materials coated with the same black varnish in order to have identical radiative properties from one metal bar to another one [15]. The choice of this black coating was not optimum as it increased the heat transfer coefficient between the bar and its surrounding causing a strong decrease of the temperature along the bar, making thus difficult to accurately measure the temperature difference with the ambient.

As he only measured thermal conductivity ratios, Despretz determined that the "conductibility" of iron was lower than that of copper by a ratio of 5 to 12 (which is inaccurate, this ratio being approximately 1 to 5), and that those of iron, zinc, and tin did not differ very much. He established the following ranking from the most thermal conductive material to the least conductive one: copper, iron, zinc, tin, lead, marble, porcelain and brick. However, without knowledge of the fluxes or of the quantities of heat used in his experiments, results of Despretz remained relative values in essence.

Gustav Heinrich Wiedemann (1822–1899) and Rudolph Franz (1827–1902) improved the Despretz's method [16] by enhancing the control of the experimental conditions to have better reproducibility of the heat transfer coefficient h (often named "external conductibility coefficient" by the nineteenth century scientists). The studied bar was put horizontally in a glass vessel, enabling to work in vacuum or in air, which was immersed in a tank containing water at constant temperature. One end of the bar being heated at 100 °C by steam, the temperature was measured in several positions along the bar using small thermocouples connected to a galvanometer. This was proposed few years before by Lorentz Christian Langberg (1810–1857) to replace the thermometers used by Despretz which disturbed the temperature distribution in the bar [17]. All tested bars were coated by electroplating with very thin uniform silver layer in order to have the same low emissivity.

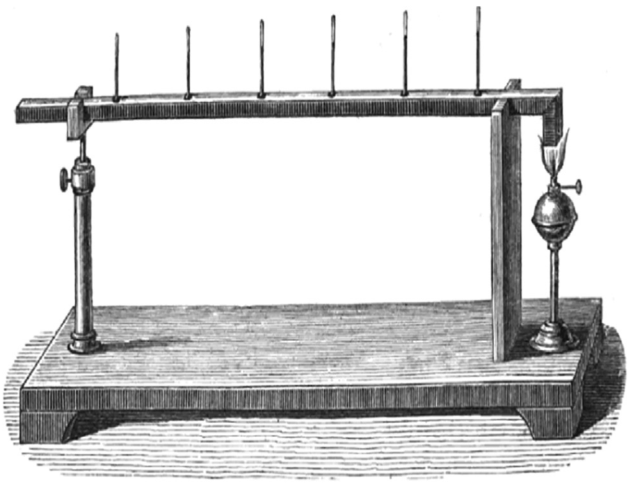


Fig. 4. Apparatus developed by Despretz.

The experiments of Wiedemann and Franz, performed in steady state as those of Despretz and Landberg, led to relative thermal conductivities, where the value 100 was assigned to silver. By comparing the thermal conductivities determined with this method on several metals with electrical conductivities measured by various scientists, Wiedemann and Franz concluded that the ratio of the thermal conductivity k to the electric conductivity σ was approximately the same for all metals at the same temperature [18]. The Danish physicist Ludvig Valentin Lorenz (1829–1891) demonstrated in 1872 that this ratio k/σ was in fact proportional to the absolute temperature [19].

2.4. The birth of calorimetry

In parallel with these developments, the mid-eighteenth century saw the emergence of the calorimetric techniques in particular thanks to advances in the field of thermometry. The Scottish physicist Joseph Black designed in 1761 one of the first devices for the measurement of quantities of heat. His calorimeter, based on the mixing method, consisted of a simple block of ice with a hole in the center of which a sample at a given temperature was positioned [20–21]. When thermal equilibrium was reached, the amount of molten ice was measured after being collected with a sponge, the specific heat of the substance introduced into the calorimeter being proportional to this quantity. The relative specific heat values determined by applying this simple methodology were affected by errors due to parasitic heat exchanges with the environment which inevitably caused a partial melting of the ice block.

Having noticed that the phenomena of ice melting or water boiling absorbed heat without change of temperature, Black proposed the concept of "latent heat". He also demonstrated that the supply of the same quantity of heat to different bodies did not generate the same temperature rise, and introduced the notion of "specific heat" or "sensible heat". He chose the terminology "latent heat", considering according to his own words that this heat could not be perceived because it was concealed or latent within the material, as opposed to "sensible heat" which had a sensitive effect on temperature [22].

Twenty years later, Lavoisier and Laplace developed in 1782 a much more elaborated ice calorimeter to measure the specific heat and latent heat of various materials, as well as the quantities of heat released by different types of reaction. The substances to be characterized were put in a container placed in two concentric enclosures each containing ice (see Fig. 5). The outer enclosure ensured the isothermal character of the calorimeter by maintaining a constant surrounding temperature equal to 0 °Re. The quantity of ice melted in the inner enclosure, collected in a vessel situated under the calorimeter, was used to quantify the heat released by the exothermic phenomenon studied (cooling, combustion, freezing, etc.). The amounts of heat measured, given in pounds (489.5 g) of molten ice, were compared to the heat needed to raise the temperature of one pound of water from 0 °Re to 60 °Re. Lavoisier observed that "the heat needed to melt the ice is equal to three quarters of that which can raise the same weight of water from the temperature of melting ice to that of boiling water" [23].

He also demonstrated experimentally with this isothermal calorimeter that the respiration process released heat, by putting a guinea pig in the calorimeter for several hours and measuring the amount of melted ice. During the winters from 1782 to 1784,

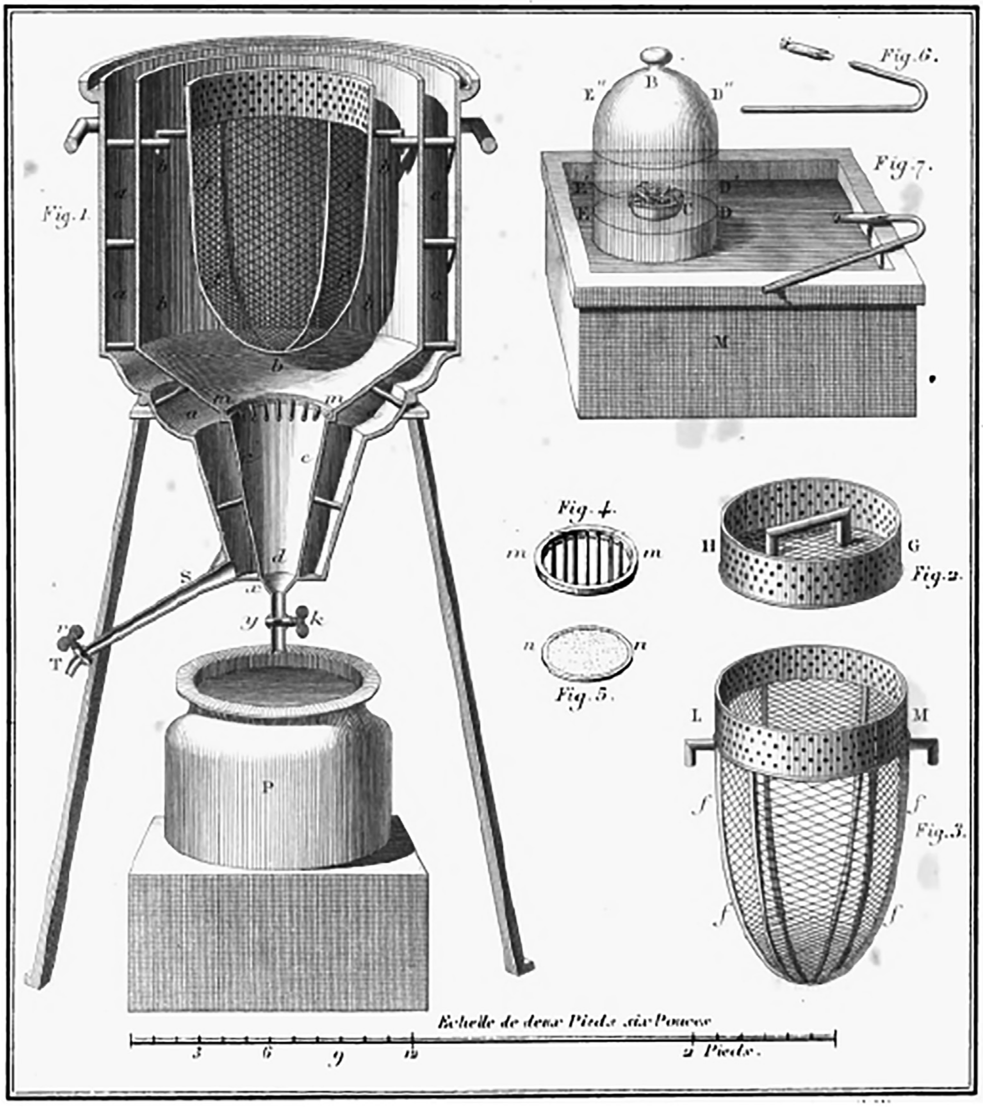


Fig. 5. Ice calorimeter of Laplace and Lavoisier [23].

he carried out numerous experiments with this calorimeter, and measured notably the specific heats of several solid and liquid substances by cooling them from 60 °Re to 0 °Re.

As he had no dedicated system of units, he expressed the results obtained in comparison with the specific heat of the water taken as unit: Water (1.000000), iron (0.109985), lead-free glass (0.192900), mercury (0.029000), lead (0.028189), tin (0.047535), sulphur (0.208500) and alcohol (0.678786) [24]. Lavoisier estimated the accuracy of the relative values of specific heat measured to one-sixtieth (1.7%), provided that the outside temperature was only one or two degrees. Even if the order of magnitude seems plausible, this value appears underestimated given the device used and the control of the experimental conditions. The values he obtained for the materials listed above deviate in fact from 10% to 15% of the values commonly determined nowadays.

2.5. Towards the adoption of a coherent system of units

The vast majority of thermal properties measurements carried out up to the end of the eighteenth century had a relative character. In the absence of scales and dedicated units, scientists often established their own units and relative scales according to their needs. This approach enabled a quantification of the measured thermal properties, but made very difficult the comparison of the published results from one book to another. The industrial revolution and the unification of experimental and classical sciences made the harmonization of the units and scales more and more necessary. Carl Friedrich Gauss (1777–1855) was one of the first scientists who employed a coherent system of units for his own works, the objective being that his results could be accessible to as many people as possible [25]. He used therefore for this purpose from 1832 the decimal metric system created at the time of the French Revolution, associated with the second defined in astronomy.

The *British Association for the Advancement of Science* (BAAS) introduced in 1874 the CGS system: a coherent three-dimensional system of units based on the three mechanical units centimeter, gram and second. After the signature of the Meter Convention on 1875, new international prototypes of the meter and kilogram were manufactured, then approved by the 1st *General Conference on Weights and Measures* in 1889. With the second as unit of time, these units constituted a three-dimensional mechanical units system similar to the CGS system, but whose basic units were meter, kilogram and second (MKS system). In order to complete the CGS system for the electricity field, the BAAS and the *International Electricity Congress* approved around 1880 a coherent system of practical units, which included ohm, volt and ampere. The experimental development of the physical sciences has relied subsequently on the use of these systems of units [26].

2.6. First absolute measurements of thermal properties

A major advance in thermal metrology was the first determination of an absolute value of the thermal conductivity of a material by Jean Baptiste Joseph Fourier in 1807 [27]. As he did not have a direct heat flux measurement method, he proposed to estimate the thermal conductivity of iron from the following two series of experiments: 1) Steady-state measurement of the temperature distribution in a ring (called also *armille*) heated locally at one point by means of an Argand oil lamp. The ring was drilled with six holes, as shown by the handwritten note of Fourier in Fig. 6, in which were put thermometers, 2) Measurement of the rate of cooling of a sphere with a thermometer (calibrated according to the Reaumur temperature scale) positioned in its center.

He deduced from these two experiments the values of the two ratios h/K and $h/(C{\cdot}D)$, where K, h, D and C were respectively, according to the vocabulary used by Fourier, the "proper conductibility", the "external conductibility", the "density" and the "specific capacity of heat". These quantities are identified now by the terms thermal conductivity, exchange coefficient, density and specific heat. The density and the specific heat having been determined beforehand, Fourier estimated the thermal conductivity and the coefficient of exchange equal to 3/2 and 1/5, respectively. He pointed out that the units of length, time, mass and temperature were meter, minute, kilogram and °Re, and that the unit for the quantity of heat was "the quantity needed to convert one kilogram of ice at temperature 0 to one kilogram of water at the same temperature 0".

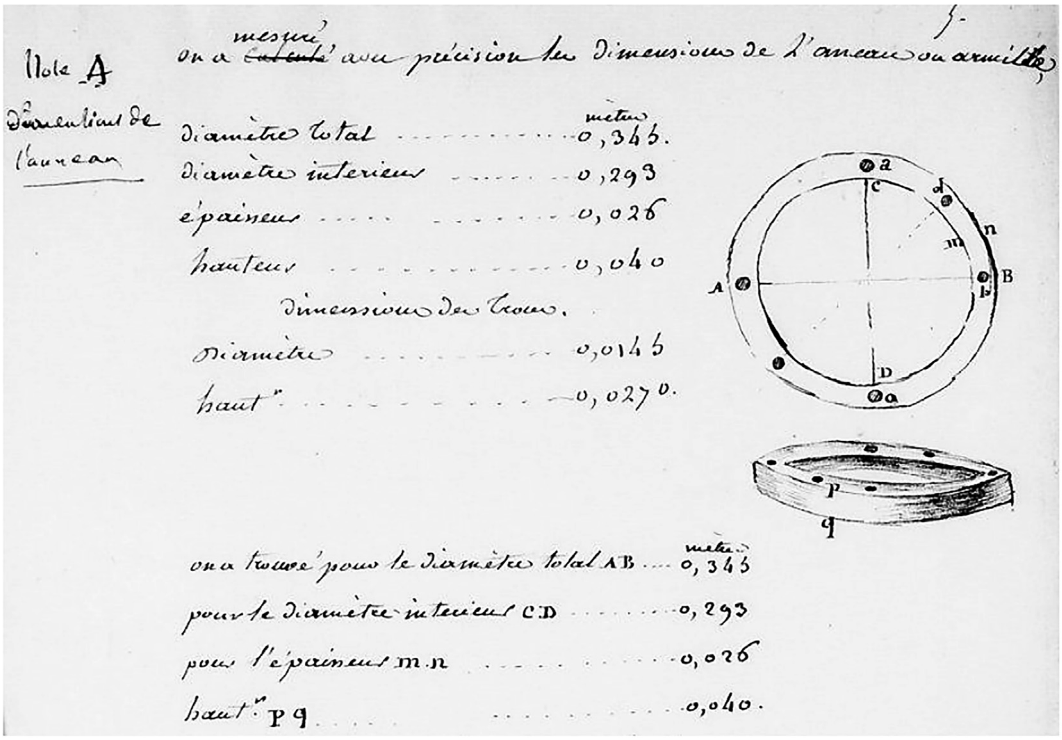
Transposing the Fourier approach to the case of a bar, James David Forbes (1809–1868) determined in 1862 absolute values of the thermal conductivity of iron as a function of temperature by applying two series of experiments carried out in steady state conditions and then in cooling [28]. In a first experiment (called "statical experiment" by Forbes) close to that performed by Despretz, a long bar was heated at one end in a hot bath of molten lead, the other end being supposed to be at room temperature (left part of Fig. 7).

The temperature distribution in the bar was measured by means of ten thermometers when the thermal equilibrium was reached. By considering that the quantity of heat passing through any section of the bar was equal at steady state to the quantity of heat lost by radiation and convection in the remaining part of the bar, it was possible to determine absolute values of thermal conductivity if the amount of heat lost by convection and radiation (or the corresponding heat transfer coefficient h) was known.

The determination of this quantity was done in a second test (named "dynamical experiment") where another bar of the same material, shorter in length, was heated uniformly up to the maximum temperature reached by the hot end of the bar during the "statical experiment" and was cooled in the same surrounding as previously (right part of Fig. 7). The temperature of the bar was measured in its center as a function of time until it reached ambient temperature.

By applying this method, Forbes measured the thermal conductivity of wrought iron from 0 °C to 275 °C. Unlike Despretz who implicitly assumed in all his experiments that the thermal conductivity had a constant value whatever the temperature, Forbes proved that it depended on temperature [30], even if the values he obtained were vitiated by errors due to improper evaluation of the heat transfer coefficient h. Like Fourier before him, he did not associate an explicit unit to the values of thermal conductivity he had obtained, indicating in his result tables "Units: Centimeter, minute, centigrade degree" and explaining in a comment that K expressed the "absolute conductive power" in terms of heat capacity of water.

The French physicist Jean-Claude Eugène Péclet (1793–1857) experienced different direct methods for determining absolute


5.

Note A

Dimensions de l'anneau

On a ~~calculé~~ mesuré avec précision les dimensions de l'anneau ou armille

diamètre total .... mètre 0,345.
diamètre interieur 0,293
épaisseur 0,026
hauteur 0,040

dimensions des trous.

diamètre 0,0145
haut.r .... 0,0270.

on a trouvé pour le diamètre total AB .... mètre 0,345
pour le diamètre interieur CD 0,293
pour l'épaisseur m.n 0,026
haut.r pq .... 0,040.

Fig. 6. Description and dimensions of the ring used by Joseph Fourier [29]. *Source gallica.bnf.fr / BnF.*

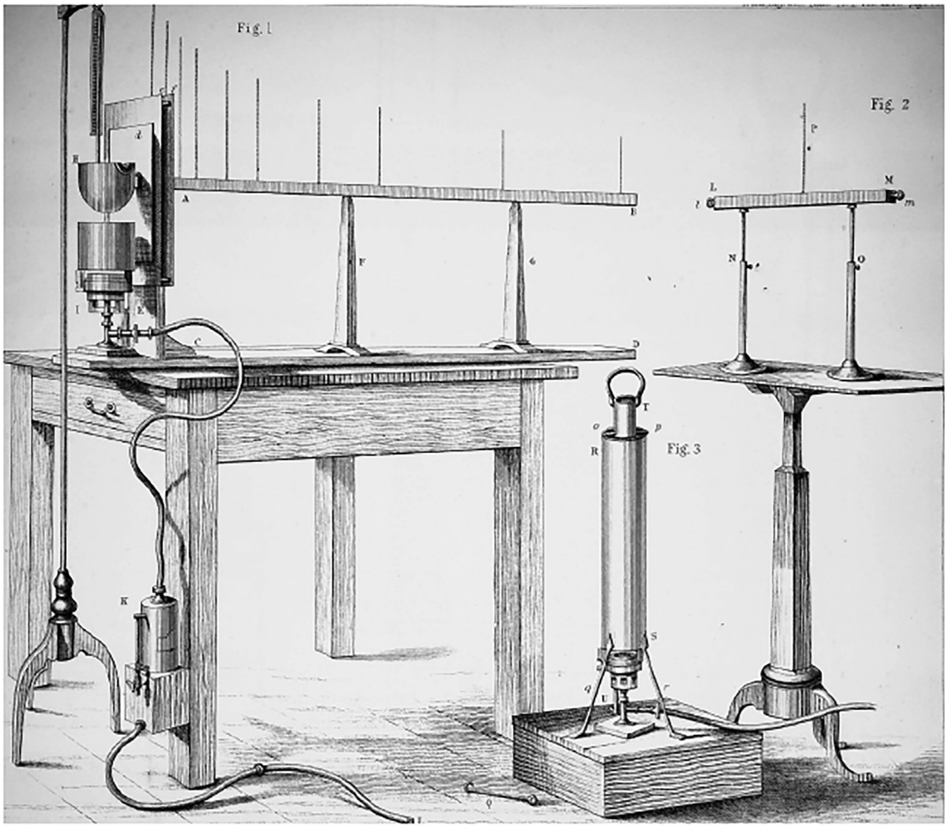


Fig. 7. Experiments of Forbes [28].

thermal conductibility of solid materials. These methods were all based on the heat conduction equation introduced by Fourier in 1807 which stated the proportionality between the quantity of heat crossing a unit surface area in unit time and the spatial gradient of temperature perpendicular to the surface.

He reported at first in 1830 [31] a method consisting to take a spherical metallic vase of uniform thickness whose inner and outer surfaces were respectively maintained at 100 °C by continuous supply of steam and at 0 °C by melting of ice. The conductibility of the metal constituting the vase was calculated from the measurement of the quantity of melted ice (assumed proportional to the amount of heat transferred from inside to outside during the experiment), the dimensions of the vase being known. Jacques Babinet (1794–1872) used also the fusion of a substance to determine the quantity of heat going through a plate during a given time whose both faces were maintained at constant temperature, one by water at 100 °C and the other by cylinders of spermaceti of whale (fusible at 33 °C) [32]. Considering that the use of melting of materials induced errors in the measurement of the quantities of heat, Péclet proposed in 1839 another approach where the upper face of a horizontal plate of metal was in contact with water and its lower face was heated by steam, the conductibility of the metal being deduced from the warming rate of the water [33]. Experiments performed on plates of copper, lead, zinc or iron have led to the same values whatever the material. These anomalous results were mainly due to the temperature gradient in the water volume and to the presence of condensed water vapour on the inner face which strongly influenced the heat transfer in the plate introducing a parasitic thermal resistance.

To avoid this problem, Péclet developed an improved version of his apparatus where the upper and lower faces of the metallic plate to be characterised were put in contact with water (contained in the two vases ABCD and GG represented in the Fig. 8) initially at two different temperatures. Sophisticated system of mechanical stirrers enabled to renew 1600 times per minute the water in contact with the two faces of the metallic plate and therefore to have good temperature homogeneity of the two volumes of water and a slow warming of the water contained in the lower vase. Using this apparatus, Péclet measured the conductibility of lead at room temperature by calculating the quantity of heat transferred between the two faces of the plate from the increase of temperature of the lower volume of water and from its heat capacity. It could be noticed that he published the obtained result (which is two times lower than the true value) in different ways in 1839 and 1860: 3.84 [33] and 13.83 [34]. These values correspond respectively to the quantity of unit of heat (heat needed to raise 1 kg of water by 1 °C) transmitted through a one square meter plate for a temperature difference of 1 °C, in the first case in one second for a thickness of one millimeter and in the second case in one hour for a thickness of one meter.

Péclet developed later a steady state method for the determination of the “conductibility of bad conductor materials” that can be considered as the ancestor of the hot plate method [34]. Using rectangular plates of known thickness with parallel walls, insulated around the edges, one face heated by steam and the other exposed to free air of a chamber at constant temperature, he has determined the conductivity coefficient of various solid (marble, wood, cork, rubber, glass) or pulverulent (sand, chalk, iron filings) materials. The plate method proposed by Péclet seems to have been abandoned during three decades in favour of the bar method, because of the difficulties to manage the parasitic lateral heat flows and the thermal contact resistances.

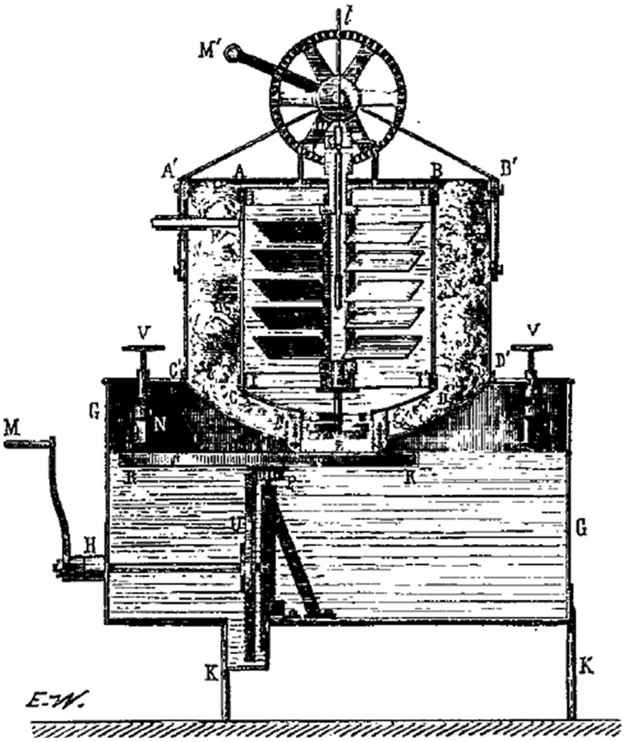
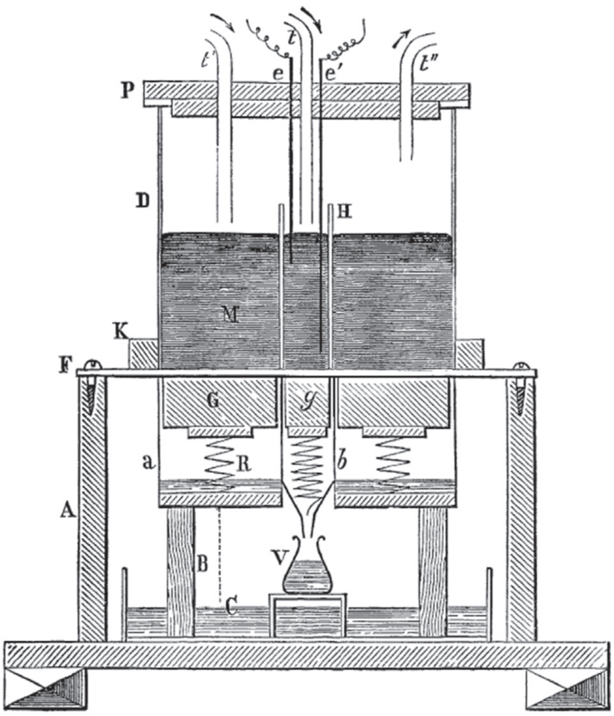


Fig. 8. Peclet's apparatus for measuring conductibility of metals [34]. *Source gallica. bnf.fr / BnF.*



D	External glass enclosure	e / e'	Thermocouples
F	Iron plate	g / G	Ice blocks
H	Internal glass enclosure	M	Mercury
P	Wood lid with holes	R	Springs
V	Vessel	t' / t''	Tubes

Fig. 9. Guarded-axial heat flow method proposed by Berget [36].

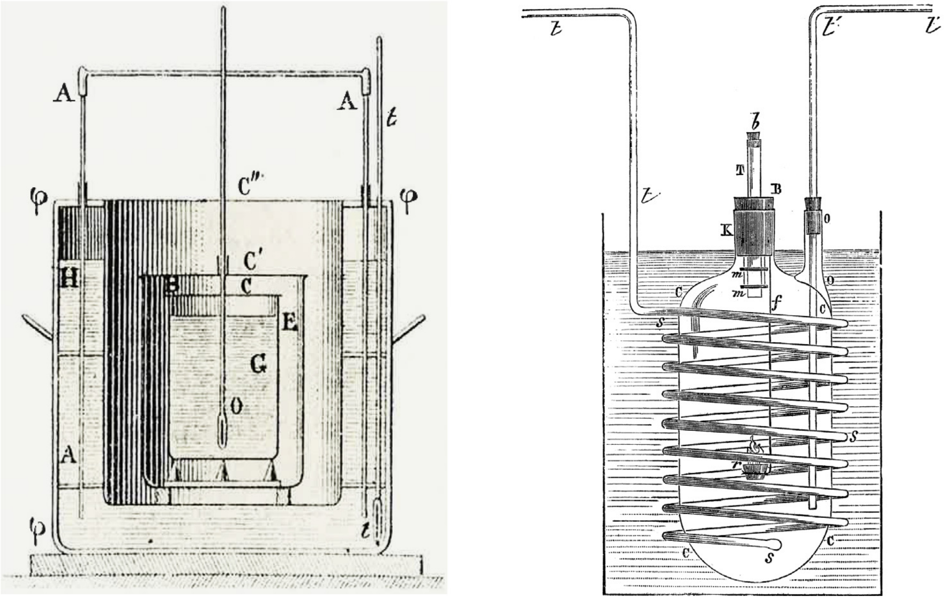
To avoid these biases, Alphonse Berget (1860–1934) designed in 1887 a guarded axial heat flow method with two major improvements [35]: (1) use of a guard cylinder (or guard ring) to insure a unidirectional heat flux in steady state, (2) determination of the temperature gradient between the upper and lower faces of the sample by measuring the temperatures of two points inside the sample instead of using the temperature of the fluids or solids in contact with the two faces for maintaining them at constant temperatures.

He applied this method to measure the thermal conductivity of mercury using the apparatus presented in Fig. 9. It was composed by two concentric cylindrical enclosures *D* and *H* filled with mercury and fixed on an iron plate *F* in contact with ice (thanks to springs *R*), which ensured a temperature of 0 °C at the lower part of the enclosures. The top of the enclosure was maintained at 100 °C with steam coming by the tube *t'*. The external enclosure *D* acted as a longitudinal thermal guard avoiding radial heat losses from the enclosure *H* to the surrounding. Temperatures were measured at two different positions in the mercury using the thermocouples *e* and *e'*. The longitudinal temperature distribution in the internal enclosure *H* being assumed linear, the difference of temperature between the upper and lower face of the mercury volume was deduced from these two measurements. The mean thermal conductivity of the mercury between 0 °C and 100 °C was calculated from the thickness of the sample, the temperature difference between its two faces and the heat flowing through the mercury contained in the enclosure *H*. This last quantity was determined by measuring the mass of the ice bock *g* which melted during a given time and was collected in the vessel *V*.

Berget used a second method to determine this quantity of heat by measuring the volume of ice melted with a Bunsen calorimeter. The thermal conductivity values of mercury obtained by applying these two procedures differed by less than 0.7% [36].

At the same time, significant progresses have been made in the determination of caloric quantities. Pierre-Antoine Favre (1813–1880) and Jean-Thiébault Silbermann (1806–1865) developed in 1843 a water calorimeter equipped with an "isothermal" jacket enabling them to carry out heat of combustion measurements, by limiting the influence of the temperature variations of the environment [37]. They determined the "heat of combustion" of coal and hydrogen expressed as a "unit of heat" (corresponding to a calorie) per gram of fuel, by measuring the temperature rise of the volume of water in which the combustion chamber was immersed.

About forty years later, Marcelin Berthelot (1827–1907) adopted this principle and developed an isoperibolic calorimeter (ie whose periphery is maintained at constant temperature) for which he adapted a large number of devices to measure the specific heat of solids and liquids (by the mixing method), as well as the thermal effects associated with most physicochemical processes (dissolution, mixing, phase change, combustion ...) [38]. A general view of this calorimeter and a scheme of the combustion chamber are presented in Fig. 10. The calibration of this calorimetric system was obtained by calculating its "water value". The objective was to determine its heat capacity by evaluating the energetic equivalence of the various elements which in the calorimetric device underwent the temperature increase measured. In order to be able to determine this "water value", which corresponds to the fictive water mass having the same heat capacity as the elements involved, it is needed to know beforehand their respective mass and the specific heat of the materials which constitute them. Some experimental results obtained by Berthelot proved to be inaccurate due to a lack of precise knowledge of the specific heats used for the calculation of the water value of his calorimeter.



a) Vertical section of the calorimeter

b) Combustion chamber

Fig. 10. Calorimeter of Berthelot [38]. *Source gallica.bnf.fr / BnF.*

In his book "Thermochimie - données et lois numériques" [39], Berthelot presented a large number of experimental data adopting the "calorie" as unit of heat, but specifying that two kinds of calories were used: the small calorie for the physical phenomena ("sensible heat" for example), and the large Calorie for the chemical phenomena (such as combustions) for which the heat absorbed or released is much more important. He defined the small calorie (in lowercase) and the large Calorie (in uppercase) as the quantities of heat needed to increase from 15 °C to 16 °C the temperature of 1 g of water and 1 kg of water, respectively. In continuation of the works initiated by Lavoisier, Robert Wilhelm Bunsen (1811–1899) designed in 1870 an isothermal calorimeter containing a diphasic system of water and ice in thermal equilibrium. The amount of heat released into the calorimeter by the substance or reaction studied, which results in the melting of part of the ice, is deduced from the volume variation of the water/ice mixture. Like Favre and Silbermann before him, he expressed the specific heat that he determined for different metals in unit of heat per gram [40].

Although the use of decimal metric system (made compulsory in France from 1840) and of the CGS system gradually became widespread in the field of sciences during the second half of the 19th century, it appears in all the works described above that the harmonization of units relating to heat and to thermal quantities still remained to be done.

Whereas the calorie was first defined by Nicolas Clément (1779–1841) as early as 1825 [41] as "the amount of heat necessary to raise a kilogram of water by one degree centigrade", its use as a heat unit remained confidential at the dawn of the 20th century. William Thomson (Lord Kelvin) indicated moreover in 1890 that this quantity of heat, generally called "thermal unit centigrade", was sometimes called "calorie" by French scientists [12]. The first specific heat measurements of gas by John Apjohn (1796–1886) [42] and Henri Victor Regnault (1810–1878) [43] are a symptomatic example of the lack of coherence of the units used in thermal metrology, where the first expressed his results relative to the specific heat of the air taken as unity, while the second made it in comparison to that of water.

It should be noted in this regard that in the 2nd edition of his reference book "Units and physical constants", to which Pierre Chappuis (1855–1916) from BIPM (*International Bureau of Weights and Measures*) has notably collaborated, Joseph David Everett (1831–1904) defined in 1886 the units of thermal conductivity and specific heat as follows [44]:

- The thermal conductivity has the dimension $M\cdot L^{-1}\cdot T^{-1}$, with a unit of heat defined as the amount of heat required to raise by one degree Celsius the temperature of one gram of pure water at a temperature between 0 °C and 4 °C.
- The specific heat of a substance at a given temperature is a dimensionless quantity corresponding to the ratio of the increments of heat to be provided to a same mass of substance and of water in order to raise their temperature by the same temperature increment.

As already mentioned, the lack of units specific to the thermal quantities shared by the entire scientific community was sometimes source of confusion when analyzing results. This point was underlined for instance by Kelvin [12] when he compared thermal conductivity measurements performed on copper by Péclet [33] and Anders Jonas Ångström (1814–1874) [45].

3. The implementation of absolute measurement methods

3.1. Creation of the BIPM and advent of the derived units

The *International Bureau of Weights and Measures* (BIPM) was set up by the Metre Convention signed in Paris on 20 May 1875 by seventeen States during the final session of the diplomatic Conference of the Metre. Since its inception, its missions have been to ensure worldwide unification of measurements and the development of the *International System of Units*, to establish fundamental standards and scales for the measurement of the principal physical quantities and to maintain the international prototypes. The BIPM operates under the exclusive supervision of the *International Committee for Weights and Measures* (CIPM) which itself comes under the authority of the *General Conference on Weights and Measures* (CGPM) [26]. The CIPM has set up over the years about ten specific consultative committees to coordinate the international work carried out in their respective fields and to propose recommendations concerning the units. The Consultative Committee for Electricity and Magnetism (CCEM) was the first to be set up in 1927, followed by the Consultative Committees for Photometry and Radiometry (CCPR) in 1933, for Thermometry (CCT) in 1937, for lengths (CCL) in 1952, for Time and Frequency (CCTF) in 1956, for Ionizing Radiation (CCRI) in 1958, for Units (CCU) in 1964, for Mass and Related Quantities (CCM) in 1980 and for Amount of Substance (CCQM) in 1993. The interest of the *International Committee for Weights and Measures* for the metrology of thermal properties is very recent compared to other quantities, as an ad hoc working group was set up only in 2001 within the CCT.

The MKS system of units set up at the end of the 19th century underwent a first evolution in 1946 when the CIPM adopted a quadridimensional system based on the meter, the kilogram, the second and the ampere (MKSA system). The 10th CGPM subsequently approved in 1954 the introduction of the ampere, the kelvin and the candela as base units, respectively for electric current, thermodynamic temperature and luminous intensity. This set of units, which took the name *International System of Units* (SI) in 1960, was finally completed by adding the mole in 1971 as the base unit for amount of substance, bringing thus to seven the number of base units of the SI as we know it today.

Derived units were defined as the product of powers of base units in 1960 at the 11th CGPM. When the product of powers includes no numerical factor other than one, the derived units are called coherent derived units, and form with the base units the set of "coherent SI units". When coherent units are used, equations between the numerical values of quantities take exactly the same form as the equations between the quantities themselves. Thus, the use of a coherent set of units enables to avoid conversion factors between units [26].

It was not until 1960 that the joule and the watt were integrated into the SI as energy and power units, and not until 1968 that the CGPM formally adopted the units $\mathrm{J{\cdot}kg^{-1}{\cdot}K^{-1}}$ and $\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$ for the specific heat and the thermal conductivity. The use of the joule and the watt units however became widespread since the *British Association for the Advancement of Science* had advocated their use as early as 1882. The calorie, whose definition is based on the specific heat of water and varies therefore as a function of temperature and atmospheric pressure, was nevertheless widely used in scientific and industrial communities during the 20th century. It was never included in the derived units of the SI, although the CIPM recommended in 1950 a value of 4.1855 joule and defined it as the amount of heat needed to raise the temperature of one gram of pure water from 14.5 °C to 15.5 °C under a pressure of one atmosphere [46].

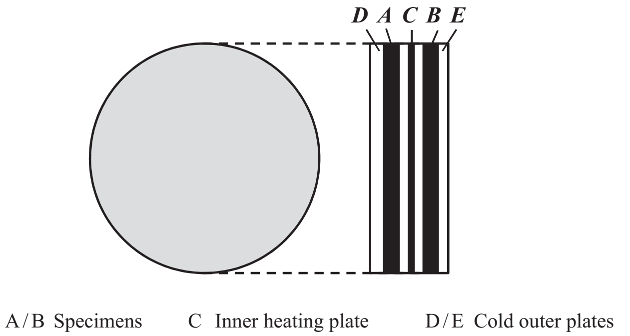


Fig. 11. Scheme of the assembly proposed by Lees.

3.2. Improvement of the traceability of thermal properties measurements to the SI

An important contribution to the development of metrology of thermal properties at the end of the 19th century was the experimental discovery (circa 1860) by James Prescott Joule (1818–1889) of the law setting out that the heat generated per unit of time during the passage of an electric current through a material is equal to the product of its resistance by the square of the current. For the first time, this law gave the possibility of producing electrically a known quantity of heat whose value could be expressed with a coherent system of units. The facilities involving the generation or measurement of heat fluxes (guarded hot plate, calorimeter, etc.) could thus be calibrated by Joule effect, making hence possible to improve the traceability of the thermal properties measurements and the control of the associated uncertainties.

A typical example of this metrological "revolution" concerns the measurement of thermal conductivity. Until the end of the 19th century, the precise measurement of thermal conductivity was impeded by the need to indirectly estimate heat fluxes from knowledge of the emissivity or the specific heat of the studied materials [47]. The introduction by Charles Herbert Lees (1864–1952) in 1898 of electric heating systems as controlled heat sources for the measurement of thermal conductivity enabled to remedy this situation [48]. Fig. 11 shows the assembly that he proposed to measure the thermal conductivity of solids by steady state method. Based on the approach described by Péclet [34], his method consisted in clamping two disk specimens between three copper circular plates, a constant heat flux (assumed unidirectional) being electrically generated by the inner plate C and conducted through the specimens A and B to the outer copper plates D and E maintained at a constant temperature. The thermal conductivity λ was determined from the heat flow φ, the temperature difference ΔT between the two faces of the specimens and their dimensions (thickness e and surface S).

$$\lambda = \frac{\varphi}{S} \cdot \frac{e}{\Delta T} \tag{1}$$

Adapting the works performed by Berget [35] to his experimental configuration, Richard Poensgen [49] improved in 1911 in Germany the Lees's method by adding a copper guard ring around the heating plate and by maintaining it at the same temperature as this one, in order to avoid radial heat losses.

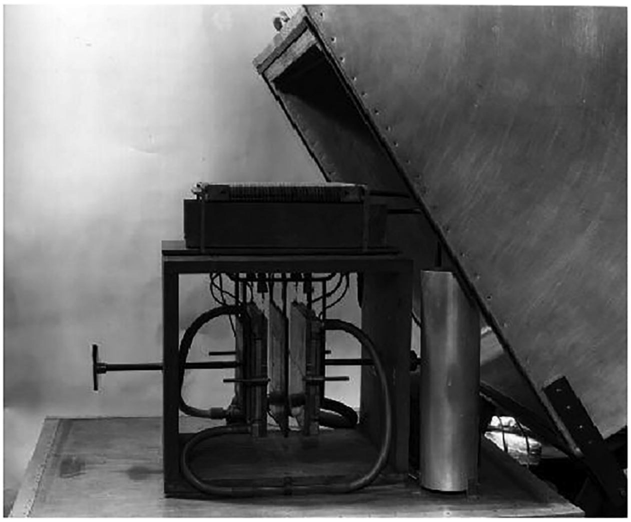


Fig. 12. Guarded hot plate of NBS built in 1929 by Van Dusen. Reprinted courtesy of the National Institute of Standards and Technology, U.S. Department of Commerce. Not copyrightable in the United States.

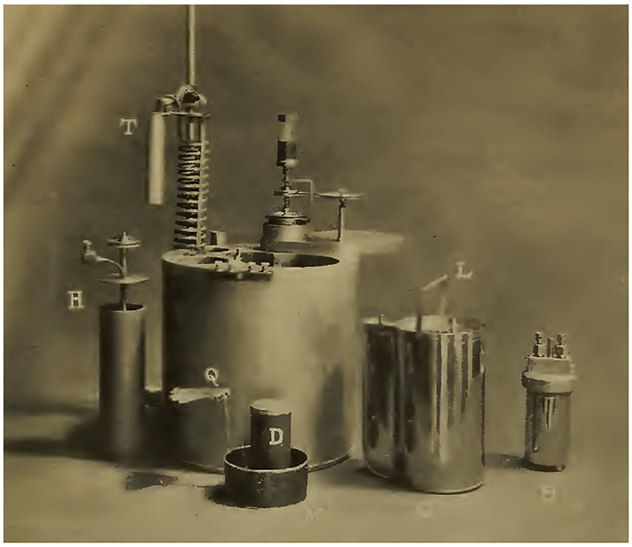


Fig. 13. Calorimetric bomb of NBS (1915) [59]. Reprinted courtesy of the National Institute of Standards and Technology, U.S. Department of Commerce. Not copyrightable in the United States.

3.3. Metrology of thermal properties in the National metrology Institutes during the 20th century

Despite the late recognition of the metrology of thermal properties by international bodies (CIPM), whose efforts were mainly focused on the seven base units of the SI, the National Metrology Institutes (NMIs) have been interested in this specific field since their origin. The main contributions of NIST (USA), PTB (Germany), NPL (UK), LNE (France), NMIJ (Japan) and VNIIM (Russia) to the development of absolute methods for the measurement of thermal properties during the 20th century are detailed hereafter.

3.3.1. National Bureau of Standards (NBS)

The *National Bureau of Standards* soon after its founding in the United States in 1901 began an intense research activity in thermal metrology, as proved by the hundred of articles published in this field during the first three decades of its existence.

NBS undertook notably the development of guarded hot plate apparatus for the quantitative study of the thermal conductivity of insulating materials. Hobart Dickinson (1875–1949) designed in 1912 the first "guarded hot plate" of NBS on the basis of the concept proposed by Poensgen, and performed with Milton S. Van Dusen (1892–1953) thermal conductivity measurements (expressed in $\text{cal}\cdot\text{s}^{-1}\cdot\text{cm}^{-1}\cdot{}^{\circ}\text{C}^{-1}$) on more than sixty insulating materials [50,51].

Van Dusen built in 1929 an improved version of this setup (shown in Fig. 12) that has been used for more than fifty years at NBS until 1983 [52]. From the mid-1980s onward, NBS certified reference materials (SRM1450 - Fiberglass Insulators) characterized in thermal resistance [53,54] using a guarded hot plate enabling to test large specimens (diameter of 1016 mm) [55]. Robert Zarr assessed the relative expanded uncertainty (k = 2) associated to these thermal resistance measurements from 1% for 25 mm thick specimens to 3% for specimens with thickness of 230 mm [56].

Hobart Dickinson initiated also between 1909 and 1915 the development of different types of calorimeter at NBS for the measurements of specific heat, enthalpy of fusion and heat of combustion. He designed in particular isoperibolic [57] or adiabatic calorimeters [58] as well as a calorimetric bomb (shown in Fig. 13), which he all calibrated by electrical substitution. He associated $\text{cal}_{15°}$/g or $\text{cal}_{20°}$/g units to his values of enthalpy of fusion and combustion heat, and indifferently expressed his results of measurement of specific heat in $\text{J}\cdot\text{g}^{-1}\cdot{}^{\circ}\text{C}^{-1}$ or $\text{cal}_{20°}\cdot\text{g}^{-1}\cdot{}^{\circ}\text{C}^{-1}$.

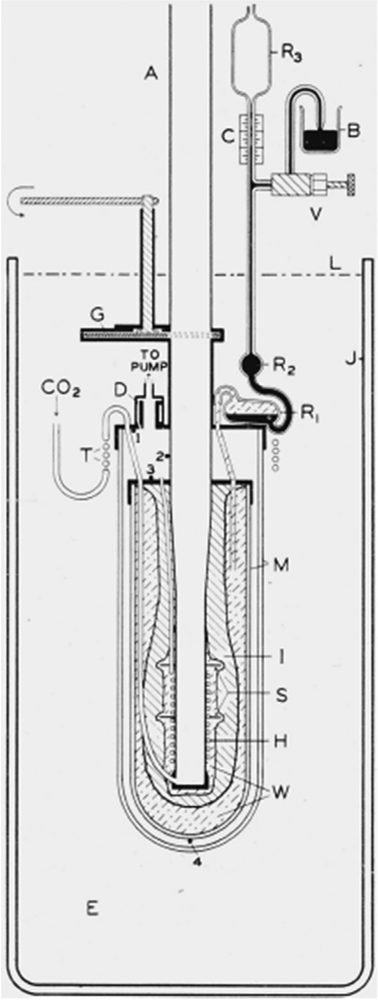


Fig. 14. Ice calorimeter designed at NBS in 1947 [64]. Reprinted courtesy of the National Institute of Standards and Technology, U.S. Department of Commerce. Not copyrightable in the United States.

Frederick Dominic Rossini (1899–1990) subsequently built an isoperibolic calorimeter [60] inspired from that of Berthelot, and used it to measure the calorific value of different gases. The average of the values he obtained in 1931 for methane at 25 °C [61,62] was still taken in 2005 as reference in the ISO 6976 Standard [63].

NBS, which became the *National Institute of Standards and Technology* (NIST) in 1988, has had a very prolific activity in calorimetry in the post-war period, with the development of very accurate devices.

They were used for the certification of reference materials, some of which are still used today. Defoe C. Ginnings (1906–1971) designed a drop calorimeter in 1947 to measure the specific heats of materials between 0 °C and 900 °C [64,65], and whose principle was based on the measurement of the enthalpy variation of a specimen between two temperatures T_i and $T_0 < T_i$. In this device, the specimen is maintained at a temperature T_i in an oven and then drops in a Bunsen type calorimeter stabilized at T_0 = 0 °C (cf. Fig. 14). The change in volume of the water / ice mixture is theoretically proportional to the energy released by the specimen to cool from T_i to T_0. The relationship giving the specific heat as a function of the temperature is determined by repeating this

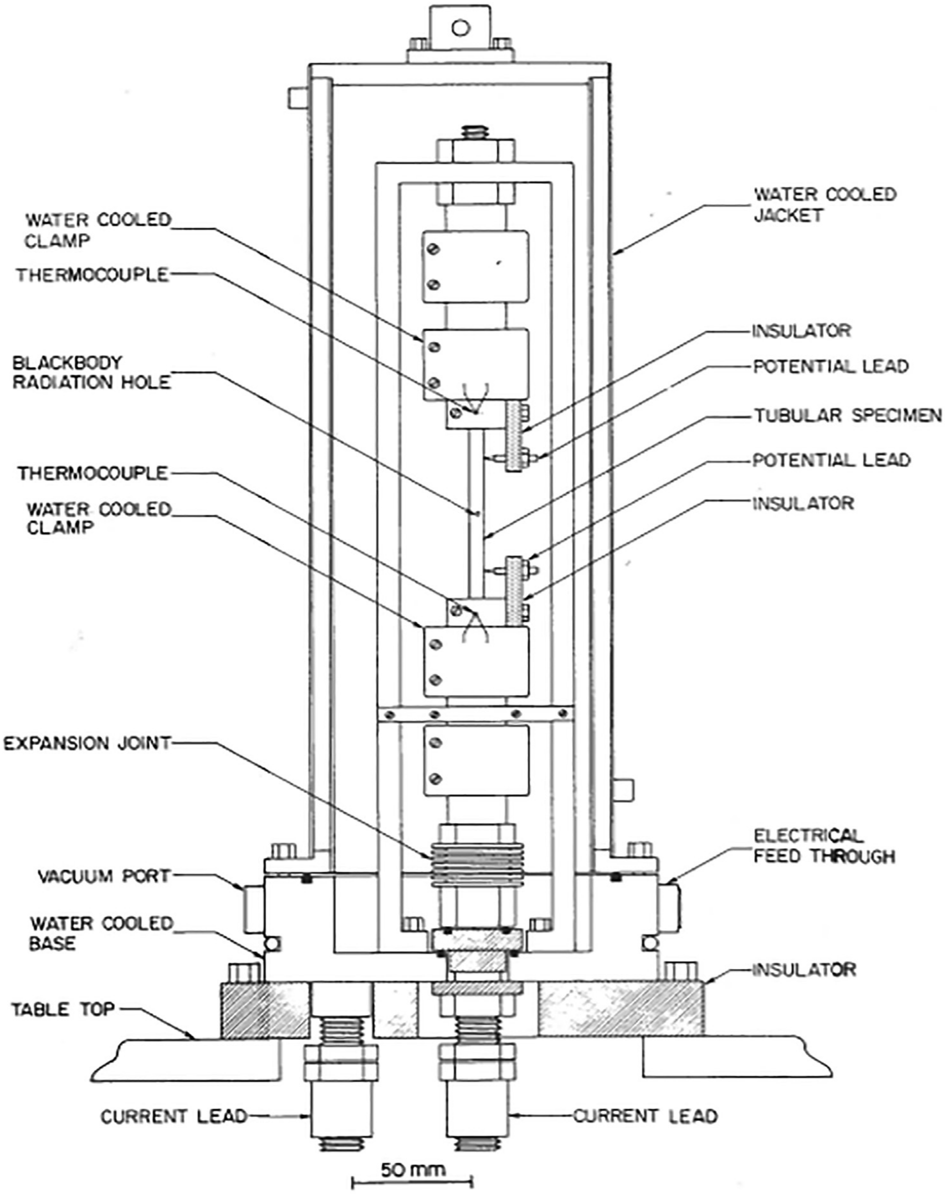


Fig. 15. Pulse calorimeter of NBS in 1970 [74]. Reprinted courtesy of the National Institute of Standards and Technology, U.S. Department of Commerce. Not copyrightable in the United States.

operation for different temperature levels T_i and by deriving the experimental curve obtained with respect to the temperature. The uncertainties associated to the measurements of enthalpy variation and specific heat between 0 °C and 900 °C performed using this drop calorimeter were estimated, respectively, from 0.1% to 0.3% and from 0.3% to 0.5% [66–68].

For measurements at lower temperatures, Sterrett constructed in 1965 an adiabatic calorimeter operating from 10 K to 360 K [69]. In this type of calorimeter, the specific heat c_p of a material is obtained by dissipating a power P by joule effect in a specimen of mass m for a time Δt, and by measuring the resulting temperature increase ΔT. If the test conditions can be assumed as adiabatic, the specific heat is equal to:

$$c_p = \frac{P}{m} \cdot \frac{\Delta t}{\Delta T} \tag{2}$$

This technique, which is based on the minimization of heat exchanges between the calorimetric cell and its surrounding, has the advantage, unlike drop calorimetry, to provide a direct determination of the specific heat of a material. It is mainly used for measurements carried out at low and medium temperatures (up to about 400 °C), because beyond that it becomes very difficult to guarantee the adiabaticity of the calorimeter.

The expanded uncertainties associated to the measurements performed with the Sterrett's calorimeter have been estimated to 0.1% for temperatures between 100 K and 350 K. For temperatures below 100 K, the uncertainty becomes progressively higher until reaching 1% at 50 K and 10% at 10 K [70]. An adiabatic calorimeter operating between 30 °C and 500 °C was also built at NBS to perform c_p measurements [71].

An improved version was used by Donald Archer for the certification of reference materials for enthalpy of fusion measurements with an expanded uncertainty lower than 0.05% [72,73].

Ared Cezairliyan (1934–1997) implemented in 1970 a setup (cf. Fig. 15) based on the pulse calorimetry [74]. The principle consists in dissipating a given energy (up to several thousand joules) by self-heating for a very short duration (few ms) in a tubular specimen made of an electrically conductive material, and in determining its c_p from the measurement of its temperature increase by non-contact thermometry.

This facility was used for the certification of molybdenum as reference material for specific heat measurements, with an uncertainty estimated to 2% at 2000 K and 3% at 3000 K [75].

A similar setup was developed by Francesco Righini in Italy [76] at the *Istituto di Metrologia Gustavo Colonnetti* (IMGC), which became in 2006 the *Istituto Nazionale di Ricerca Metrologica* (INRiM), and by Kosta Maglic (1934–2018) at the Institute of Nuclear Sciences VINČA (Serbia) [77]. Maglić [78], Cezairliyan [79] and Righini subsequently extended the use of these pulse techniques to the study of many thermophysical properties (hemispherical total emissivity, electrical resistivity, melting temperature, etc.) of electrical conductive materials up to their melting point. The main difficulty inherent in applying this method is the estimation of the correction term related to the heat losses during the measurement.

3.3.2. Physikalisch-Technische Reichanstalt (PTR)

The *Physikalisch-Technische Reichanstalt* (PTR), founded in Charlottenburg in 1887 at the initiative of Ernst Werner von Siemens (1816–1892) and led by Hermann Ludwig Ferdinand von Helmholtz (1821–1894) at its inception, was the first National Metrology Institute to study the thermal properties.

Friedrich Wilhelm Georg Kohlrausch (1840–1910), who succeeded in 1895 von Helmholtz as president of the PTR, described in 1899 a simple experiment for the measurement of the ratio of thermal conductivity k to electrical conductivity σ (Wiedemann-Franz ratio) in the case of electrical conductive materials [80,81]. This method consisted in heating by joule effect a metallic rod with a constant electric current while keeping its ends at the same constant temperature. At steady state, a parabolic-shaped temperature distribution was then established along the cylindrical specimen with the maximum temperature at the center. The ratio k/σ was calculated from the measurements of the temperature difference (T_2-T_1) between the middle of the rod and two points equidistant on each side, and also of the potential difference V between the two outer points. By considering negligible lateral heat losses, the ratio of thermal conductivity to electrical conductivity is given by the following simple equation:

$$\frac{k}{\sigma} = \frac{1}{8} \cdot \frac{V^2}{\Delta T} \tag{3}$$

The French physicist Marcel Émile Verdet (1824–1866) seems to have been in fact the first to suggest to apply this electrical method, and to propose an expression for the distribution of temperature along an electrically heated metallic rod subjected to lateral loss of heat [82].

Wilhelm Ludwig Jaeger (1862–1937) and Hermann Diesselhorst (1870–1961) implemented this method in 1899 by thermally insulated the rod on its periphery with a lagging of cotton wool in order to limit the lateral heat loss between the rod and the surrounding by convection and by radiation. They applied it to a large number of materials at 18 °C and 100 °C [83], and determined their thermal conductivity from the ratios k/σ obtained and the electrical conductivities measured with a specific facility. They observed an increase in thermal conductivity with temperature for aluminum, constantan, gold, palladium and platinum and a decrease for bismuth, iron, copper, nickel, silver and zinc. This method was also used by Walther Meissner (1882–1974) in 1915 [84] to measure the ratio k/σ for copper at very low temperatures (down to 20 K).

Eduard Grüneisen (1877–1949) and Erich Goens [85] improved in 1927 the "bar method" proposed by Forbes for measuring the thermal conductivity which was based on the measurement of the longitudinal temperature gradient along a solid cylinder, when one of its ends is heated and the other is maintained at a constant temperature. They positioned the specimen in a vacuum enclosure to limit heat losses by convection or gas conduction, and heated one end of the specimen using a resistive coil, controlling thus the dissipated power.

After the second world war, the PTR, which merged in 1953 with the *Physikalisch Technische Bundesanstalt* (PTB) founded three years earlier in Braunschweig, has continued researches on thermal conductivity measurements. Fritz [86] in 1962 and Karl-Heinz Bode [87] in 1980 developed for example guarded hot plate apparatus for measuring the thermal conductivity of liquids. An improved version of these guarded hot plates was used in 1995 by Ulf Hammerschmidt to measure the thermal conductivity of several refrigerants with an expanded uncertainty assessed to 2% between ambient temperature and 180 °C [88].

In the field of calorimetry, Wilhelm Jaeger and Hellmuth von Steinwehr (1874–1951) proposed in 1903 to electrically calibrate a Berthelot-type calorimetric bomb, in order to determine its water value (i.e. its heat capacity) that they expressed in electric units ($\mathrm{W \cdot s \cdot {}^\circ C^{-1}}$) [89]. This device enabled them to carry out measurements of the calorific value of solid materials in an absolute way, without using a comparative approach with a standard material. PTB began from the mid-1980s to study the calibration of Differential Scanning Calorimeters (DSC) between ambient temperature and about 400 °C [90], and continued to work on this theme for about thirty years. At the same period, Wolfgang Hemminger and Karlheinz Raetz determined the enthalpy of fusion of several pure metallic materials (indium, bismuth, tin) [91–93] using a heat flux Calvet calorimeter calibrated by electrical substitution, the uncertainty associated with the obtained values being estimated to about 0.3% to 0.4%.

3.3.3. National physical Laboratory (NPL)

The *National Physical Laboratory*, founded in Teddington in 1900 under the impetus of John William Strutt, Lord Rayleigh (1842–1919), seems to have started to study thermal properties at the late 1910s, with the development of a first prototype of adiabatic calorimeter used for the measurement of the specific heat of solid materials [94]. Its designer, Ezer Griffiths (1888–1962), constructed a more advanced adiabatic calorimeter in 1940, with which he measured this property in the case of iron up to 950 °C [95].

In this device, the specimen must be machined in such a way to receive a heating system and a thermocouple. It is surrounded by an isothermal enclosure maintained at a temperature as close as possible to its own temperature, in order to minimize the heat transfer with the outside. It is then possible to directly quantify the specific heat of the studied material by measuring the temperature rise induced by the dissipation of a known amount of energy inside the specimen and by knowing its mass.

Griffiths has been also interested in the thermal conductivity measurement of solid materials. After having started by studying the thermal conductivity of refractory materials up to 900 °C [96], he developed in 1923 a non-guarded hot plate setup for characterizing the thermal conductivity of insulating materials around room temperature, assessing the uncertainty associated with his measurements to 1% [97].

Two years later, his colleague Schofield improved the method proposed at PTR by Jaeger and Diesselhorst [83] for estimating the ratio λ/σ, by positioning around the bar a cylindrical guard subjected to the same temperature gradient as the latter [98]. This procedure, which enables to limit the parasitic heat fluxes between the periphery of the bar and its environment, was applied to the measurement of the thermal conductivity of several metals up to 700 °C, the electrical conductivity being known. In the two articles [97] and [98], the thermal conductivity values obtained are given in CGS units, the power being expressed in watt or cal·s^{-1}.

From 1950 to the present day, NPL has continuously worked on developing and upgrading guarded hot plate facilities [99], which makes NPL one of the most experienced NMIs for this method of measurement.

A guarded hot plate operating with a single specimen was developed in the mid-1980s to measure the thermal conductivity between −10 °C and +60 °C of low density insulating materials having a thickness between 25 mm and 300 mm [100]. The expanded uncertainties were estimated by David Salmon from 1.3% to 2.4% over the thickness range from 50 mm to 250 mm. This apparatus was used in particular for the certification of two reference materials on behalf of the European *Institute for Reference Materials and Measurement* (IRMM): a pyrex glass [101] and a mineral wool (whose certification process was piloted by LNE) [102]. A high temperature guarded hot plate covering the range from 100 °C to 850 °C was also designed at NPL in 1996 for the study of insulating or refractory materials with thickness from 25 mm to 50 mm and having a thermal conductivity lower than 1 W·m^{-1}·K^{-1} [103]. The expanded uncertainty associated to these measurements was estimated to be about 5% over the entire temperature range, with reproducibility better than 1%.

3.3.4. Laboratoire national de métrologie et d'essais (LNE)

The *Laboratoire d'Essais* was created in France in 1901 within the *Conservatoire National des Arts et Métiers* in order to "enable industries, merchants and consumers to subject raw or manufactured products of any kind, machinery and apparatus to tests, studies and researches necessary to qualify them", as written by the physicist Alfred Perot (director from 1901 to 1907, and co-inventor with Charles Fabry of the Fabry-Pérot interferometer) in an article describing the organization of this new laboratory [104].

Soon after its creation, studies related to the thermal characterisation of materials were launched, in particular to measure the calorific value of combustible materials with calorimetric bombs [105] or to perform the evaluation of the thermal performance of pipe insulation materials [106]. In this last case, the method proposed by Alfred Boyer-Guillon in 1905 [107] consisted in measuring the powers W_1 and W_2 that must be released inside a copper pipe with an electrical resistance in order to keep constant its internal temperature T, respectively when the pipe is bare and when it is covered with the insulating material to be characterized.

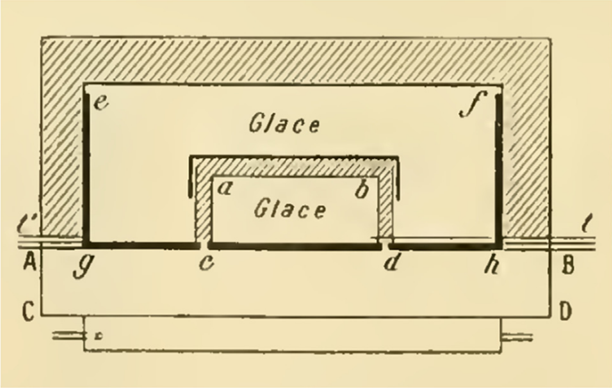


Fig. 16. Setup of Biquard for measuring thermal conductivity.

Boyer-Guillon applied this method for several types of material (cotton, asbestos, cork, felt…) and for several temperature differences ΔT = T-T_0 (where T_0 is the room temperature). From the obtained values W_1 and W_2, he calculated for each material the "energy savings coefficient" $e_{\Delta T}$ of the material as a function of ΔT as follows:

$$e_{\Delta T} = \frac{W_1 - W_2}{W_1} \tag{4}$$

Since then the *Laboratoire d'Essais* has continuously worked on the measurement of thermal conductivity of insulating materials by steady state methods. A first arrangement, similar in some respects to that of Lees, was adopted by Robert Biquard in 1910 for the measurement of the thermal conductivity of insulating materials. It is detailed in the Fig. 16, which comes from a paper presented by Biquard to the *Académie des Sciences* [108].

The material ABCD in the form of circular plate is placed between two copper plates. The lower face CD is maintained at constant temperature by a warm water circulation, and the upper face AB is in contact with a copper plate *cd* surrounded by a guard ring *gh* (separated by a 3 mm wide groove), on which are placed two concentric tanks *abcd* and *efgh* full of crushed ice. Cork plates are used to fill the gap between the two tanks and to thermally insulate the whole arrangement from the ambient atmosphere. Tubes *t* and *t'* enable to collect the melting water coming from the two tanks. The temperatures of the faces AB and CD are measured with copper-constantan thermocouples.

When the steady state is reached, the heat flux going through the specimen is determined from the water flow rate induced by the melting of the ice in the central part *abcd*. The thermal conductivity of the material is calculated from the surface of the plate *cd*, the thickness of the specimen, the water flow rate and the temperature difference between the two faces AB and CD. Biquard indicated that *S* is taken as the surface delimited by the center of the groove between the plate *cd* and the guard ring *gh*. He specified in addition that the width of the guard ring shall be twice that the thickness of the specimen in order to insure the validity of the assumption of negligible radial heat losses [109]. He studied with this apparatus the influence of moisture content on the thermal conductivity of some insulating materials (typically cork board) [110].

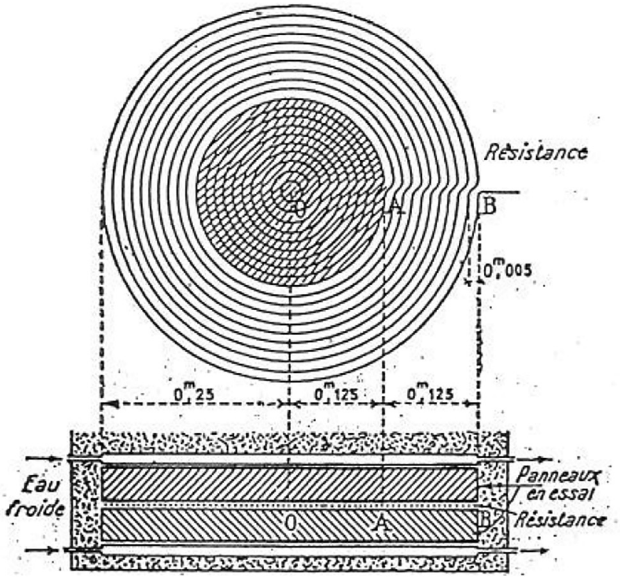
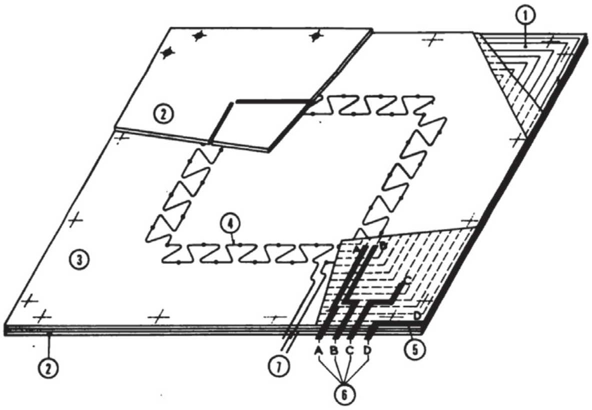


Fig. 17. Guarded hot plate developed by Heyberger [113].

Fig. 18. Guarded hot plate of LNE in 1962.



1. Resistance (heater)
2. Aluminium plates
3. Thermopile support
4. Thermopiles
5. / 6. Heating wires connections
7. Thermopiles wire connections

Fig. 19. Exploded view of the guarded hot plate.

L. Heyberger developed in 1927 a guarded hot plate apparatus for the measurement of the coefficient of thermal conductivity of insulating materials [111]. In this setup, the tested specimens were positioned between a hot plate equipped with a guard ring, both being heated by electrical resistances, and two cold plates cooled by water circulation (see Fig. 17). This apparatus, which operated up to 600 °C, enabled to avoid the inconveniences of that of Biquard concerning the use of crushed ice. Heyberger described in 1946 several apparatuses based on steady state methods that were designed at the *Laboratoire d'essais* for the measurement of the thermal conductivity of metals (by the bar method) or of insulating materials in tubular form, as well as for the measurement of the overall heat transfer coefficient of wall (by guarded hot box) [112]. These devices were progressively improved during the following decades. Fig. 18 presents the guarded hot plate of the *Laboratoire d'Essais* in 1962 (whose name became *Laboratoire National d'Essais* at the beginning of the 60′s).

LNE built in 1967 a guarded hot plate apparatus for measuring the thermal conductivity of insulating materials from −80 °C to +100 °C [114]. An exploded view of the square guarded hot plate is shown in Fig. 19. This plate (500 mm × 500 mm) is constituted by a resistance ① inserted between two black painted aluminum plates ② (5 mm thick). The resistance is composed by Nichrome wires wound in two square shaped spirals, one for the central area (250 mm × 250 mm) and one for the guard ring. Two sheets of silicone coated glass cloth ③ bearing the thermopiles ④ (made of 0.2 mm chromel-alumel wire) are tightened between the resistance ① and the two metallic plates ②. The connections of the resistances wires and of the thermopiles wires are respectively represented by ⑤-⑥ and ⑦. The influence of the mode of construction of such guard-ring heating plates on the thermal conductivity measurements of insulating materials was studied at LNE by Robert Doussain [115]. A similar apparatus was used by LNE in 1982 in the first certification process of a reference material in thermal conductivity at the European level (BCR 64). The maximum relative error reported by LNE for its thermal conductivity measurements was 2.5% [116].

An axial heat flow apparatus based on an absolute steady-state technique was developed by Doussain in the early 70s for the measurement of thermal conductivity of metals [117]. The principle consisted in generating a constant heat flow in a cylindrical bar-shaped specimen (heated at one end with an electrical resistance and cooled at the other end by circulating water or liquid nitrogen) and in measuring the induced longitudinal temperature gradient. The setup of LNE, which could operate under vacuum, was equipped with a guard cylinder concentric with the specimen used to minimize lateral heat exchanges between the specimen and the surrounding. The results obtained with this device on Armco iron between −190 °C and +200 °C showed a maximum deviation from the values given by NBS [118] lower than 2%.

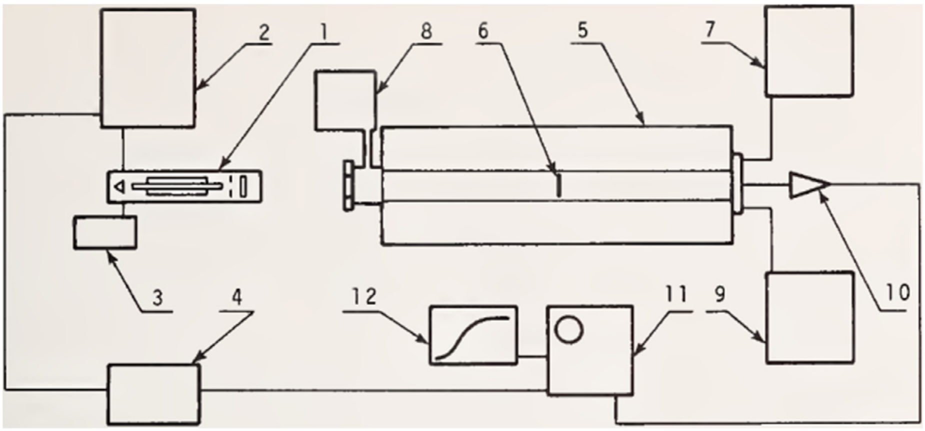
The first apparatus of LNE devoted to the thermal diffusivity measurement by the "flash" method, which was proposed in 1961 by William J. Parker [119], was designed about 1975 [120]. This method is based upon the measurement of the transient temperature rise on the rear face of a thin disk sample resulting from a short energy pulse on the front surface. The sample ⑥ is placed in the vacuum furnace ⑤ and heated at uniform temperature (cf. Fig. 20). Then, a short pulse (0.5 to 1.3 ms) generated by a neodymium glass laser ① (1.06 μm wavelength) irradiates one side of the sample. The induced temperature rise on the opposite sample face is measured versus time with type K thermocouples. A storage oscilloscope collects data representing the temperature rise. The thermal diffusivity is calculated from the shape of the temperature–time curve and the thickness of the sample.

Thermal diffusivity of Armco iron, copper, germanium, gallium arsenide and cadmium telluride was measured with this device by Le Bodo from 100 K to 1000 K [120], and the measurement errors were estimated to be better than 8%. In the original method proposed by Parker which assumes an adiabatic experiment and considers the laser pulse as a Dirac function, the thermal diffusivity a is simply calculated from the sample thickness d and the half rise time $t_{1/2}$ (time needed by the rear face to reach one half of its temperature increase after the laser pulse) as follows:

$$a = 0.1388 \cdot \frac{d^2}{t_{1/2}} \tag{5}$$

For his measurements, Le Bodo [120] applied methods based on an improvement of the Parker's method, introducing correction factors in the calculation of the thermal diffusivity to take into account the unavoidable heat losses and the pulse duration [121–123].

LNE seems to have been less active until the late 1980s in the metrology of caloric quantities (specific heat, enthalpy of fusion, calorific value…) than in that of thermal transport properties (thermal diffusivity and thermal conductivity), even if some pictures show the existence of "Calvet" calorimeters at LNE in 1964 (see Fig. 21).



1. Laser head
2. Laser power supply
3. Cooling unit
4. Laser trigger
5. Furnace
6. Specimen
7. Electrical power supply
8. Vacuum system
9. Temperature readout
10. High gain differential amplifier
11. Storage oscilloscope
12. Camera record
13. Liquid nitrogen container
14. Aperture for the exit of nitrogen

Fig. 20. Schematic of the diffusivimeter of LNE in 1975.

Fig. 21. Calvet microcalorimeters at LNE in 1964.

The research activity of LNE related to the thermal properties metrology was reorganised and revived at the end of 80s by Claude Meyer, then head of the department "Energy and Materials", and has been in constant growth since then. During the last thirty years, LNE has developed metrological facilities based on absolute methods for measuring the following thermophysical properties with reliable uncertainties in a large temperature range:

- Thermal diffusivity of bulk materials and coatings [124–126],
- Thermal conductivity of bulk materials and thin films [127–129],
- Specific heat and enthalpy of fusion [130–132],
- Gross calorific values of gas [133–134],
- Radiative properties of solid materials [135–137],
- Thermal properties at nanoscales [138–139].

The corresponding measurement means have been grouped together in a metrological platform (named MATIS), within the Scientific and Industrial Metrology Direction of LNE. It is currently one of the most complete platforms devoted to the study of thermal properties existing in the National Metrology Institutes.

3.3.5. The other national metrology institutes

Some other NMIs have also worked on these topics during the 20th century, especially the *National Research Laboratory of Metrology* (NRLM), established in Japan in 1903 and the *D.I. Mendeleyev Institute for Metrology* (VNIIM) which succeeded in 1945 to the *Depot of Measures and Weights* founded in St. Petersburg (Russia) in 1842. The short review presented hereafter about the research activity of these two institutes in this particular field is not exhaustive. It is based on articles published in English or translated from Russian or Japanese journals, the scientific key articles from NRLM and VNIIM being often published in Russian or Japanese until the end of the 70s.

NRLM, renamed *National Metrology Institute of Japan* (NMIJ) in 2001, is with LNE one of the few national metrology institutes which have developed reference facilities for measuring the thermal transport properties of materials by photothermal methods. In general terms, these methods consist in subjecting a specimen to a radiative excitation and in measuring its temperature variations versus time.

From the mid-1980s, NRLM sought in particular to increase the control of the experimental parameters inherent to the application of the "flash" method in order to reduce the uncertainty associated with thermal diffusivity measurements [140–142]. Tetsuya Baba and Akira Ono used then the diffusivimeter developed at NRLM to perform thermal diffusivity measurements at high temperature (up to 1200 K) on pyroceram 9606 specimens [143].

Taketoshi and Baba implemented in 1997 an absolute method for measuring the thermal diffusivity of metal thin films by thermoreflectance [144]. The technique applied is a transposition of the laser flash method, usually used for the measurement of thermal diffusivity at macroscopic scale, to the case of a thin film deposited on a substrate (that is transparent at the wavelength of the excitation laser). A picosecond laser beam is divided into two parts, so-called "pump" beam and "probe" beam: the "pump" beam is focused at the interface between the metal film and the substrate, and the temperature response of the opposite face is observed by thermoreflectance using the "probe" beam.

One of the first metrological investigations on the determination of thermal properties in USSR was performed by the All-Union Scientific-Research Institute of Metrology in 1928 [145]. It aimed to establish uniformity in the measurement of amounts of heat by using benzoic acid as a standard material for calibration of calorimetric installations [146]. A specific calorimeter was then produced at VNIIM between 1933 and 1936 under the direction of S. V. Lipin for the measurement of the specific heat of combustion (named now calorific value) of standard materials. At that time, Lipin and the USSR delegation proposed in 1933 to use a calorie defined at 20 °C as unit of amount of heat, which was refused by the 8th General Conference on Weights and Measures [147–148].

Since then, VNIIM has pursued its metrological activity related to caloric quantities in the Thermal Measurements Laboratory, created in 1958 under the initiative of G. M. Kondrat'ev, later in the Thermal Measurement Section and more recently in the Laboratory of Combustion Calorimetry. In the 60s and 70s, VNIIM performed several determinations of calorific value of benzoic acid by using calorimetric bombs [149,150]. Yuri Aleksandrov estimated in 1974 the error associated to these measurements to 0.01% [150]. Twenty five years later, he also developed an original isothermal calorimeter device to determine the gross calorific value of natural gas at 25 °C with an expanded relative uncertainty of 0.1% [151,152]. Adiabatic and isoperibolic calorimeters were also designed for the absolute measurements of specific heat of solid materials between 0 °C and 1100 °C [153,154].

In the same way, VNIIM has worked on the development of metrological devices for measuring the thermal conductivity and the thermal diffusivity of solid materials [155]. Apparatus were notably designed for thermal conductivity measurements in the range from 1 to 100 W/(m·K) at temperatures between 20 °C and 400 °C using the axial heat flow method with an error of 3% [146,156], and for measurements of thermal diffusivity (named temperature conductivity by Yuri Kirichenko) between room temperature and 300 °C with an accuracy of about 3% [157].

VNIIM certified with these apparatus several standard samples of heat properties such as benzoic acid for specific heat of combustion (with relative error 0.03%), polymethyl methacrylate for thermal conductivity, and corundum for enthalpy and specific heat from 0 °C to 1500 °C (with relative error about 0.3% and 1% respectively). A list of standard samples was established in 1965–1966 at VNIIM under the direction of Oleinik and published by NBS in 1971 [158].

4. Conclusions

Since the beginning of the Industrial Revolution in the late 1700s, scientific and technological progresses periodically observed have resulted among others from the development of new materials. In many industrial fields (energy, buildings, transportation…) where these materials are exposed to temperature changes, it is necessary to determine values of thermal quantities such as thermal conductivity, thermal diffusivity or specific heat as a function of temperature.

However, whatever the thermal property, there is no universal measurement method enabling to study with the same uncertainty all types of materials for all temperatures. For that reason, ingenious scientists have gradually imagined during the last three centuries various measurement methods to respond to the different scenarios. Some of these methods (guarded hot plate method or isothermal calorimetry for instance) that have proved their robustness and relevance are still used in academic and industrial laboratories.

At the end of the 19th century, National Metrology Institutes started to work on the improvement of the existing methods for the measurement of thermal properties and on the design of "reference" facilities based on the implementation of "absolute" methods. Their main objectives were always to increase the reliability and the accuracy of measurements as well as to ensure their metrological traceability to the International System of Units (SI), in particular through the characterization of reference materials.

Although extended, the current measurement capabilities of the NMIs in the field of thermal properties characterisation do not meet all needs coming from industry, in particular for nanostructured materials and devices (such as thermoelectric materials, micro- and nano-systems or carbon nanotubes), as well as for new advanced materials (3D non-homogeneous composites, thermal barrier coatings, molten salts, thin films…) used in high temperature applications.

As an example, new measurement techniques and analytical models have appeared to study the heat transfer at the micro and nanoscales: Time-domain thermoreflectance method (TDTR), Scanning Thermal Microscopy (SThM), Modulated Photothermal Radiometry (MPTR). It is however not possible nowadays to perform reliable and accurate quantitative measurements of thermal properties with nanometric spatial resolution by using these methods, in absence of a dedicated metrology (including relevant calibration protocols).

These metrological needs have been notably identified in the European roadmap for thermophysical properties metrology published in 2015 [159] by the ad hoc working group of the Technical Committee for Thermometry of EURAMET (European Association of National Metrology Institutes). This roadmap shows how the development of thermal properties metrology should be oriented over the next 15 years in order to address future societal and economical needs in the fields of energy, environment, advanced manufacturing, public safety and security, and health.

The main current and future challenges of NMIs in the field of thermal properties metrology will be to extend their measurement capabilities in terms of spatial resolution, type of materials and temperature range, by adapting existing devices and measurement methods, or by designing new suitable metrological means.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] G. Bigourdan, Le système métrique des poids et mesures. Son établissement et sa propagation graduelle, avec l'histoire des opérations qui ont servi à déterminer le mètre et le kilogramme, Gauthier-Villars, Paris, 1901.

[2] Décret du 18 germinal an III (7 avril 1795) relatif aux poids et aux mesures (Bull. 135, n° 749, B.53, 114).

[3] Décret du 30 mars 1791 relatif aux moyens d'établir l'uniformité des poids et mesures (L.3, 1163, B.12, 305).

[4] T. Quinn, A short history of temperature scales, PTB Mitteilungen 3 (2007) 243–250.

[5] R.A. Ferchault de Réaumur, Règles pour construire des thermomètres dont les degrés soient comparables, et qui donnent des idées d'un chaud ou d'un froid qui puissent être rapportés à des mesures connues, Histoire de l'académie royale des sciences, Année 1730, Imprimerie royale, Paris, 1732, pp. 452–507.

[6] Instruction sur les poids et mesures, déduites de la grandeur de la terre, uniformes pour toute la république, et sur les calculs relatifs à leur division décimale, par la commission temporaire des poids et mesures républicaines en exécution des décrets de la convention nationale, Imprimerie du dépôt des lois, Paris, An II, pp. 171.

[7] T.K. Conley, M. Brewer-Anderson, Franklin and Ingenhousz: A Correspondence of Interests, Proc. Am. Philos. Soc. 141 (1997) 276–296.

[8] A. Cazin, La chaleur, Bibliothèque des merveilles, Imprimerie Simon Raçon, Paris, 1867, p. 148.

[9] J. Ingen-Housz, Sur la différence de la célérité avec laquelle la chaleur passe à travers les différents métaux, Nouvelles expériences et observations sur divers objets de physique, Théophile Barrois le jeune, Libraire, 1785, pp. 380–390.

[10] B. Thompson, New experiments upon heat, Phil. Trans. R. Soc. 76 (1786) 273–304, https://doi.org/10.1098/rstl.1786.0014.

[11] J.-B. J. Fourier, Analyse des travaux de l'académie royale des Sciences pendant l'année 1822 – Partie mathématique, Mémoires de l'académie royale des sciences de l'institut de France - années 1821 et 1822, tome V, Imprimerie royale, Paris, 1826, pp. 302.

[12] W. Thomson, Mathematical and physical papers, elasticity, heat, electromagnetism – vol. III, C.J. Clay Cambridge University Press warehouse, 1890, pp. 113–260.

[13] J.C. Maxwell, Theory of heat, Longmans, Green and CO., London, 1871, p. 235.

[14] J.B. Biot, Mémoire sur la propagation de la chaleur lu à la classe des sciences mathématiques et physiques de l'institut national, Bibliothèque Britannique, Genève 27 (1804) 310–329.

[15] C.-M. Despretz, Mémoire sur la conductibilité de plusieurs substances solides, in: Annales de chimie et de physique, Imprimerie de Feugueray, Tome XIX. Paris, 1821, pp. 97–106.

[16] G.H. Wiedemann, R. Franz, Ueber die Wärme- Leitungsfähigkeit der Metalle, Ann. Phys. Chem. 89 (1853) 497–531, https://doi.org/10.1002/andp.18531650802.

[17] L.C. Langberg, Ueber die Bestimmung der Temperatur und Wärmeleitung fester Körper, Ann. Phys. Chem. 66 (1845) 1–30, https://doi.org/10.1002/andp.18451420902.

[18] G.H. Wiedemann, Ueber die Leitungsfähigkeit einiger Legirungen für Wärme und Elektricität, Ann. Phys. Chem. 108 (1859) 393–406, https://doi.org/10.1002/andp.18591841103.

[19] L.V. Lorenz, Bestimmung der Wärmegrade in absolutem Maasse, Ann. Phys. Chem. 223 (1872) 429–452.

[20] F. Rozier, Expériences du docteur Black, sur la marche de la chaleur dans certaines circonstances, in: Introduction aux observations sur la physique sur l'histoire naturelle et sur les arts, Le Jay libraire, Paris, 1772, pp. 428–431.

[21] S. Kopperl, J. Parascandola, The development of the adiabatic calorimeter, J. Chem. Educ. 48 (1971) 237–242.

[22] J. Black, Lectures on the elements of chemistry: delivered in the University of Edinburgh – vol. I, John Robinson, Philadelphia, 1807.

[23] A.L. Lavoisier, P.S. Laplace, Mémoire sur la chaleur, Histoire de l'académie royale des sciences, année 1780, Imprimerie royale, Paris, 1784, 355–408.

[24] A.L. Lavoisier, Œuvre de Lavoisier - tome II, Mémoires de chimie et de physique, Imprimerie impériale, Paris, 1862, pp. 724–738.

[25] M. Himbert, A brief history of measurement, Eur. Phys. J. Special Topics 172 (2009) 25–35, https://doi.org/10.1140/epjst/e2009-01039-1.

[26] Le système international d'unités, 8ème édition, Bureau International des Poids et Mesures, Stedi Media, Paris, 2006, ISBN 92-822-2213-6.

[27] J.B.J. Fourier, Suite du mémoire intitulé : Théorie du mouvement de la chaleur dans les corps solides, Mémoires de l'académie royale des sciences de l'institut de France - années 1821 et 1822, tome V, Imprimerie royale, Paris, 1826, 153–246.

[28] J.D. Forbes, Experimental inquiry into the laws of the conduction of heat in bars, and into the conducting powers of wrought iron, Trans. Royal Soc. Edinburgh 23 (1862) 133–146, https://doi.org/10.1017/S0080456800018494.

[29] Collection des papiers du mathématicien Fourier, Théorie de la chaleur, XXVI, Expériences sur le mouvement de la chaleur, 152 feuillets, Bibliothèque nationale de France, 1806 à 1811.

[30] J.D. Forbes, Experimental inquiry into the laws of the conduction of heat in bars. Part II - on the conductivity of wrought iron, deduced from the experiments of 1851, Trans. Royal Soc. Edinburgh 24 (1865) 73–110, https://doi.org/10.1017/S0370164600040918.

[31] J.-C.E. Péclet, Traité élémentaire de physique - Tome 1, Deuxième éd., Malher et Cie libraires, Paris, 1830.

[32] J.-M. Duhamel, Sur la conductibilité intérieure et extérieure de la chaleur dans les corps solides, in: Bulletin des sciences mathématiques, physiques et chimiques, tome XV, Imprimerie Firmin Didot, Paris, 1831, pp. 285–289.

[33] J.-C.E. Péclet, Mémoire sur la détermination des coefficients de conductibilité des métaux pour la chaleur, Comptes rendus hebdomadaires des séances de l'académie des sciences 8 (1839) 627–632.

[34] J.-C.E. Péclet, Traité de la chaleur considérée dans ses applications, Troisième éd., Librairie Victor Masson, Paris, 1860.

[35] A. Berget, Mesure de la conductibilité calorifique du mercure, en valeur absolue, Comptes rendus hebdomadaires des séances de l'académie des sciences 105 (1887) 224–227.

[36] A. Berget, Conductibilité thermique du mercure et de quelques métaux, J. Phys. Theor. Appl. 7 (1888) 503–518.

[37] P.-A. Favre, J.-T. Silbermann, Recherches sur les quantités de chaleur dégagées dans les actions chimiques et moléculaires, Annales de chimie et de physique, troisième série, tome 34, Victor Masson, libraire, Paris, 1852, 357–450.

[38] M. Berthelot, Traité pratique de calorimétrie Chimique, G. Masson éditeur, Paris, 1893.

[39] M. Berthelot, Thermochimie - données et lois numériques, Tome II, Gauthier-Villars et fils, imprimeurs, Paris, 1897.

[40] R.W. Bunsen, Calorimetrische Untersuchungen, Ann. der phys. u. chem. 141 (1870) 1–31.

[41] N. Clément, Cours de chimie appliquée aux arts, Le producteur, journal de l'industrie, des sciences, et des beaux-arts - tome premier, Imprimerie de Lachevardière fils, Paris, 1825, 574–587.

[42] J. Apjohn, The specific heats of the gases as deduced by Dr. Apjohn, compared with the more recent Results of Dr. Suerman, London Edinburgh Philos. Mag. & J. Sci. 13 (1838) 261–273, and 339–350.

[43] H.V. Regnault, Mémoire sur la chaleur spécifique des fluides élastiques, Mémoires de l'académie des sciences de l'institut impérial de France - tome XXVI, Librairie Firmin Didot frères, Paris, 1862, 3–333.

[44] J.D. Everett, Units and physical constants, 2nd ed., Macmillan and co., London, 1886, pp. 87–130.

[45] A.J. Ångström, Ueber das wärmeleitungsvermögen des kupfers und des eisen bei verschiedener temperatur, Ann. Phys. (Berlin) 194 (1863) 423–431.

[46] Procès-verbaux des séances - Comité international des poids et mesures, deuxième série, tome XXII, Gauthier-Villars, imprimeur, Paris, 1950.

[47] T.N. Narasimhan, Thermal conductivity through the 19th century, Phys. Today. 63 (2010) 36–41, https://doi.org/10.1063/1.3480074.

[48] C.H. Lees, On the thermal conductivities of single and mixed solids and liquids and their variation with temperature, Phil. Trans. R. Soc. A 191 (1898) 399–440.

[49] R. Poensgen, Ein technisches verfahren zur ermittlung der wärmeleitfähigkeit plattenförmiger stoffe, in: Mitteilungen über Forschungsarbeiten auf dem Gebiete des Ingenieurwesens, Springer-Verlag, Berlin Heidelberg, 1912, pp. 25–40, https://doi.org/10.1007/978-3-662-02217-7_2.

[50] H.C. Dickinson, M.S. Van Dusen, The testing of thermal insulators, Am. Soc. Refrig. Eng. 3 (1916) 5–25.

[51] M.S. Van Dusen, The thermal conductivity of heat insulators, Trans. Am. Soc. Heating Ventilating Eng. 26 (1920) 385–414.

[52] R.R. Zarr, A history of testing heat insulators at the National Institute of Standards and Technology, ASHRAE Trans. 107 (2001) 661.

[53] J.G. Hust, Glass fiberboard SRM for thermal resistance, NBS Special Publication, 1985, pp. 260–298.

[54] R.R. Zarr, Standard Reference Materials: Glass fiberboard SRM 1450c for Thermal Resistance from 280 K to 340 K, NBS Special Publication, 1997, 260–130.

[55] M.H. Hahn, H.E. Robinson, D.R. Flynn, Robinson line-heat source guarded hot plate apparatus, Heat Transmission Measurements Therm. Insul., ASTM STP 544 (1974) 167–192.

[56] R.R. Zarr, Assessment of uncertainties for the NIST 1016 mm guarded-hot-plate apparatus: Extended analysis for low-density fibrous-glass thermal insulation, J. Res. Natl. Inst. Stand. Technol. 115 (2010) 23–59.

[57] H.C. Dickinson, E.F. Mueller, E.B. George, Specific heat of some calcium chloride solutions between 35 °C and +20 °C, Bull. Bureau Stand. 6 (1909) 379–408.

[58] H.C. Dickinson, N.S. Osborne, An aneroid calorimeter, Bull. Bureau Stand. 12 (1915) 23–48.

[59] H.C. Dickinson, Combustion calorimetry and the heats of combustion of cane sugar, benzoic acid and naphthalene, Bull. Bureau Stand. 11 (1915) 189–257.

[60] F.D. Rossini, The heat of formation of water, J. Res. Natl. Bur. Stand. 6 (1931) 1–35.

[61] F.D. Rossini, The heats of combustion of methane and carbon monoxide, J. Res. Natl. Bur. Stand. 6 (1931) 37–49.

[62] F.D. Rossini, The heat of formation of water and the heats of combustion of methane and carbon monoxide. A correction, J. Res. Natl. Bur. Stand. 7 (1931) 329–330.

[63] EN ISO 6976 - Natural gas - Calculation of calorific values, density, relative density and Wobbe index from composition, ISO, Genève, 2005.

[64] D.C. Ginnings, R.J. Corruccini, An improved ice calorimeter – the determination of its calibration factor and the density of ice at 0 °C, J. Res. Natl. Bur. Stand. 38 (1947) 583–591.

[65] D.C. Ginnings, T.B. Douglas, A.F. Ball, Heat capacity of sodium between 0° and 900° C, the triple point and heat of fusion, J. Res. Natl. Bur. Stand. 45 (1950) 23–33.

[66] D.A. Ditmars, T.B. Douglas, Measurement of the relative enthalpy of pure α -Al_2O_3 (NBS heat capacity and enthalpy standard reference material No. 720) from 273 to 1173 K, J. Res. Natl. Bur. Stand. 75A (1971) 401–420.

[67] Certificate for Standard Reference Material 781, Molybdenum - heat capacity, National Bureau of Standards, Washington, 1977.

[68] Certificate for Standard Reference Material 720, Synthetic sapphire (α - Al2O3), National Bureau of Standards, Washington, 1982.

[69] K.F. Sterrett, D.H. Blackburn, A.B. Bestul, S.S. Chang, J. Horman, An adiabatic calorimeter for the range 10 to 360 K, J. Res. Natl. Bur. Stand. 69C (1965) 19–26.

[70] D.A. Ditmars, S. Ishihara, S.S. Chang, G. Bernstein, E.D. West, Enthalpy and heat capacity standard reference material: synthetic sapphire (α -A1203) from 10 to 2250 K, J. Res. Natl. Bur. Stand. 87 (1982) 159–163.

[71] E.D. West, D.C. Ginnings, An adiabatic calorimeter for the range 30 °C to 500 °C, J. Res. Natl. Bur. Stand. 60 (1958) 309–316.

[72] D.G. Archer, The enthalpy of fusion of gallium, J. Chem. Eng. Data 47 (2002) 304–309, https://doi.org/10.1021/je015532p.

[73] D.G. Archer, S. Rudtsch, Enthalpy of fusion of indium: A certified reference material for differential scanning calorimetry, J. Chem. Eng. Data 48 (2003) 1157–1163, https://doi.org/10.1021/je030112g.

[74] A. Cezairlayan, Design and operational characteristics of a high-speed (millisecond) system for the measurement of thermophysical properties at high temperatures, J. Res. Natl. Bur. Stand. 75C (1971) 7–18.

[75] D.A. Ditmars, A. Cezairlayan, S. Ishihara, T.B. Douglas, Enthalpy and heat capacity standard reference material: Molybdenum SRM 781 from 273 to 2800 K, NBS Special Publication, 1977, 260–265.

[76] F. Righini, A. Rosso, Measurement of thermophysical properties by a pulse heating method: platinum from 1000 K to the melting point, High Temp. High Press. 12 (1980) 335–349.

[77] A.S. Dobrosavljevic, K.D. Maglić, Evaluation of a direct pulse heating method for measurement of specific heat and electric resistivity in the range 300–1900 K, High Temp.-High Press. 21 (1989) 411–421.

[78] K.D. Maglić, N.L. Perović, G.S. Vuković, L.P. Zeković, Specific heat and electrical resistivity of niobium measured by subsecond calorimetric technique, Int. J. Thermophys. 15 (1994) 963–972, https://doi.org/10.1007/BF01447106.

[79] A. Cezailayan, M.S. Morse, H.A. Berman, C.W. Beckett, High-speed (subsecond) measurement of heat capacity, electrical resistivity, and thermal radiation properties of molybdenum in the range 1900 to 2800 K, J. Res. Natl. Bur. Stand. 74A (1970) 65–92.

[80] F. Kohlrausch, Über den stationären Temperaturzustand eines von einem elektrischen Strome erwärmten Leiters, Sitzungsber. Königl. Preuss. Akad. Wiss. Berlin. 38 (1899) 711–718.

[81] F. Kohlrausch, Ueber den stationären Temperaturzustand eines elektrisch geheizten Leiters, Ann. Phys. (Berlin) 1 (1900) 132–158, https://doi.org/10.1002/andp.19003060107.

[82] M. Verdet, Théorie mécanique de la chaleur, Tome II, G. Masson Editeur, Paris, 1872, pp. 197–203.

[83] W. Jaeger, H. Diesselhorst, Wärmeleitung, elektricitätsleitung, wärmecapacität und thermokraft einiger metalle, Sitzungsber. Königl. Preuss. Akad. Wiss. Berlin. 38 (1899) 719–726.

[84] W. Meissner, Thermische und elektrische leitfähigkeit einiger metalle zwischen 20 und 373 °abs, Ann. Phys. (Berlin) 352 (1915) 1001–1058, https://doi.org/10.1002/andp.19153521602.

[85] E. Grüneisen, E. Goens, Untersuchungen an metallkristallen. V - Elektrizitäts- und wärmeleitung von ein-und vielkristallinen metallen des regulären systems, Z. Phys. 44 (1927) 615–642, https://doi.org/10.1007/BF01420997.

[86] W. Fritz, H. Poltz, Absolutbestimmung der wärmeleitfähigkeit von flüssigkeiten - Kritische versuche an einer neuen plattenapparatur, Int. J. Heat Mass Trans. 5 (1962) 307–316, https://doi.org/10.1016/0017-9310(62)90020-0.

[87] K.H. Bode, Wärmeleitfähigkeitsmessungen mit dem plattengerät : Einfluss der schutzringbreite auf die messunsicherheit, Int. J. Heat Mass Tran. 23 (1980) 961–970.

[88] U. Hammerschmidt, Thermal conductivity of a wide range of alternative refrigerants measured with an improved guarded hot-plate apparatus, Int. J. Thermophys. 16 (1995) 1203–1211, https://doi.org/10.1007/BF02081288.

[89] W. Jaeger, H. von Steinwehr, Bestimmung des wasserwertes eines berthelotschen kalorimeters in elektrischen einheiten, Verh. Dtsch. Phys. Ges. 2 (1903) 50–59.

[90] S. Sarge, E. Gmelin, G. Höhne, H. Cammenga, W. Hemminger, W. Eysel, The caloric calibration of scanning calorimeters, Thermochim. Acta 247 (1994) 129–168, https://doi.org/10.1016/0040-6031(94)80118-5.

[91] K.-H. Schönborn, W. Hemminger, Determination of the enthalpy of fusion of indium by direct comparison with Joule heats, Thermochim. Acta 69 (1983) 127–136, https://doi.org/10.1016/0040-6031(83)85071-0.

[92] K. Raetz, Determination of the heat of fusion of bismuth with heat flux DSC, Thermochim. Acta 151 (1989) 323–331, https://doi.org/10.1016/0040-6031(89)85362-6.

[93] W. Hemminger, K. Raetz, Bestimmung der Schmelzwärme von Zinn und Indium mit einem Dynamischen Wägestrom-Differenzcalorimeter, PTB Mitteilungen 99 (1989) 83–88.

[94] E. Griffiths, New specific heat apparatus, P. Phys. Soc. Lond. 33 (1921) 355–361, https://doi.org/10.1088/1478-7814/33/1/333.

[95] J.H. Awbery, E. Griffiths, The thermal capacity of pure iron, Proc. R. Soc. A 174 (1940) 1–15, https://doi.org/10.1098/rspa.1940.0001.

[96] E. Griffiths, The thermal conductivity of materials employed in furnace construction, Trans. Faraday Soc. 12 (1917) 193–204, https://doi.org/10.1039/TF9171200193.

[97] E. Griffiths, G.W. Kaye, The measurement of thermal conductivity, Proc. R. Soc. A 104 (1923) 71–98, https://doi.org/10.1098/rspa.1923.0095.

[98] F.H. Schofield, The thermal and electrical conductivities of some pure metals, P. Phys. Soc. Lond. *A* 107 (1925) 206–227, https://doi.org/10.1098/rspa.1925.0016.

[99] E.H. Ratcliffe, Thermal conductivities of fused and crystalline quartz, Brit. J. Appl. Phys. 10 (1959) 22–25, https://doi.org/10.1088/0508-3443/10/1/306.

[100] D. Salmon, The NPL 610 mm guarded hot plate / heat flow meter standard apparatus for thick insulations, in: Thermal Conductivity, Technomic, Lancaster, PA, 1994, pp. 834–843.

[101] I. Williams, R. Shawyer, Certification report for a Pyrex glass reference material for thermal conductivity between -75 °C and 195 °C - CRM039, Report EUR 13358 EN, 1991.

[102] S. Quin, G. Venuti, F. de Ponte, A. Lamberty, Certification of a resin-bonded glass fibre board for thermal conductivity between - 10 °C and + 50 °C - IRMM-440, Report EUR 19572 EN, 2000.

[103] D. Salmon, The NPL high temperature guarded hot-plate, in: Thermal Conductivity, Technomic, Lancaster, PA, 1996, pp. 431–441.

[104] A. Perot, Organisation et outillage du laboratoire d'essais du conservatoire des arts et métiers, Mémoires de la Société des ingénieurs civils de France 1 (1905) 738–753.

[105] C. Féry, Nouvelle bombe calorimétrique, Journal de Physique Théorique et Appliquée 2 (1912) 550–556, https://doi.org/10.1051/jphystap:019120020055001.

[106] A. Boyer-Guillon, Le laboratoire d'essais du conservatoire national des arts et métiers: Section des essais de machines, La Houille Blanche 1 (1909) 2–5.

[107] A. Boyer-Guillon, Manière de mesurer les pertes de chaleur des enveloppes calorifuges. Quelques résultats d'essais faits au laboratoire, Bulletin du laboratoire d'essais du Conservatoire, National des Arts et Métiers 7 (1906).

[108] R. Biquard, Sur un procédé de mesure du coefficient de conductibilité thermique des corps peu conducteurs, in: Comptes rendus hebdomadaires des séances de l'académie des sciences, Gauthier-Villars imprimeur-libraire, Paris, 1910, pp. 268–270.

[109] R. Biquard, The efficiency of various methods of insulating refrigerated rooms. Experiments on thermal conductivity, in: Proceedings of the 2nd International Congress of Refrigeration, Vienna, Austria, October 6–8, 1910, 299–300.

[110] E.A. Allcut, Heat insulation as applied to buildings and structures, Proc. Inst. Mech. Eng. 128 (1934) 195–251, https://doi.org/10.1243/PIME_PROC_1934_128_013_02.

[111] L. Heyberger, Sur les procédés de mesure du coefficient de conductibilité calorifique des matériaux peu conducteurs de la chaleur, Bulletin du Laboratoire d'Essais mécaniques, physiques, chimiques et de machines du Conservatoire National des Arts et Métiers, Librairie Polytechnique Ch., Béranger, 1927.

[112] L. Heyberger, Le coefficient K de transmission globale de la chaleur à travers une paroi, Bulletin du Laboratoire d'Essais 15 (1946) 158.

[113] C. Meyer, La mesure des propriétés thermophysiques dans la chaîne BNM grandeurs thermiques, Bulletin du Bureau National de Métrologie 99 (1995) 55–63.

[114] J.-C. Rousselle, A guarded hot plate apparatus for measuring the thermal conductivity from -80 to +100 °C, Therm. Conductivity, NBS Spec. Publ. 302 (1968) 513–520.

[115] R. Doussain, Influence du mode de construction des plaques chauffantes à anneau de garde et de l'isolation latérale sur la mesure de la conductivité thermique des matériaux isolants, Heat Transfer: Non-stationary heat transfer through walls, measurement of thermal conductivity, heat transfer with two phase refrigerants, pergamon press, The international institute of refrigeration (1971) 289–299.

[116] H. Ziebland, Certification report on a reference material for the thermal conductivity of insulating materials between 170 K and 370 K - Resin-bonded glass fibre board (BCR No 64), Report EUR 7677 EN, 1982.

[117] R. Doussain, Méthodes et matériaux de référence pour la mesure de la conductivité thermique, Bulletin du Bureau National de Métrologie 18 (1974) 12–25.

[118] T.W. Watson, D.R. Flynn, H.E. Robinson, Thermal conductivity and electrical resistivity of Armco iron, J. Res. Natl. Bur. Stand. 71 C (1967).

[119] W.J. Parker, R.J. Jenkins, C.P. Butler, G.L. Abbott, Flash method of determining thermal diffusivity, heat capacity, and thermal conductivity, J. Appl. Phys. 32 (1961) 1679–1684, https://doi.org/10.1063/1.1728417.

[120] R. Doussain, H. Le Bodo, Thermal diffusivity of germanium, gallium arsenide and cadmium telluride over the temperature range 80 K - 900 K, Laser Induced Damage Opt. Mater., NBS Spec. Publ. 435 (1975) 98–106.

[121] J.A. Cape, G.W. Lehman, Temperature and finite pulse-time effects in the flash method for measuring thermal diffusivity, J. Appl. Phys. 34 (1963) 1909–1913, https://doi.org/10.1063/1.1729711.

[122] R.D. Cowan, Pulse method of measuring thermal diffusivity at high temperatures, J. Appl. Phys. 34 (1963) 926–927, https://doi.org/10.1063/1.1729564.

[123] K.B. Larson, K. Koyama, Correction for finite-pulse-time effects in very thin samples using the flash method of measuring thermal diffusivity, J. Appl. Phys. 38 (1967) 465–474, https://doi.org/10.1063/1.1709360.

[124] B. Hay, J.-R. Filtz, J. Hameury, L. Rongione, Uncertainty of thermal diffusivity measurements by laser flash method, Int. J. Thermophys. 26 (2005) 1883–1898, https://doi.org/10.1007/s10765-005-8603-6.

[125] B. Hay, J.-R. Filtz, J. Hameury, G. Davée, O. Enouf, Thermal diffusivity measurement of ceramic coatings at high temperature using front face and rear face laser flash methods, Int. J. Thermophys. 30 (2009) 1270–1282, https://doi.org/10.1007/s10765-009-0560-z.

[126] B. Hay, J. Hameury, N. Fleurence, P. Lacipiere, M. Grelard, V. Scoarnec, G. Davee, New Facilities for the Measurements of High-Temperature Thermophysical Properties at LNE, Int. J. Thermophys. 35 (2014) 1712–1724, https://doi.org/10.1007/s10765-013-1400-8.

[127] V. Scoarnec, J. Hameury, B. Hay, A new guarded hot plate designed for thermal conductivity measurements at high temperature, Int. J. Thermophys. 36 (2015) 540–556, https://doi.org/10.1007/s10765-014-1794-y.

[128] R. Zarr, W. Guthrie, B. Hay, A. Koenen, Collaborative guarded-hot-plate tests between the Laboratoire national de métrologie et d'essais and the National Institute of Standards and Technology, Metrologia 54 (2017) 113–128, https://doi.org/10.1088/1681-7575/aa4e55.

[129] N. Fleurence, B. Hay, G. Davée, A. Cappella, E. Foulon, Thermal conductivity measurements of thin films at high temperature by modulated photothermal radiometry at LNE, Phys. Status Solidi A 212 (2015) 535–540, https://doi.org/10.1002/pssa.201400084.

[130] R. Razouk, B. Hay, M. Himbert, A new in situ electrical calibration system for high temperature Calvet calorimeters, Rev. Sci. Instrum. 84 (2013) 094903, https://doi.org/10.1063/1.4821876.

[131] R. Razouk, B. Hay, M. Himbert, Uncertainty assessment of enthalpy of fusion measurements performed by using an improved Calvet calorimeter, Metrologia 52 (2015) 717–729, https://doi.org/10.1088/0026-1394/52/5/717.

[132] R. Razouk, O. Beaumont, B. Hay, A new accurate calorimetric method for the enthalpy of fusion measurements up to 1000 °C, J. Therm. Anal. Calorim. 136 (2019) 1163–1171, https://doi.org/10.1007/s10973-018-7772-z.

[133] F. Haloua, B. Hay, J.-R. Filtz, New french reference calorimeter for gas calorific value measurements, J. Therm. Anal. Calorim. 97 (2009) 673–678, https://doi.org/10.1007/s10973-008-9701-z.

[134] F. Haloua, E. Foulon, A. Allard, B. Hay, J.R. Filtz, Traceable measurement and uncertainty analysis of the gross calorific value of methane determined by isoperibolic calorimetry, Metrologia 52 (2015) 741–755, https://doi.org/10.1088/0026-1394/52/6/741.

[135] J. Hameury, Determination of uncertainties for emissivity measurements in the temperature range 200–800 °C, High Temp.-High Press 30 (1998) 223–228.

[136] J. Hameury, B. Hay, J.-R. Filtz, Measurement of infrared spectral directional hemispherical reflectance and emissivity at BNM-LNE, Int. J. Thermophys. 26 (2005) 1973–1983, https://doi.org/10.1007/s10765-005-8609-0.

[137] J. Hameury, B. Hay, J.-R. Filtz, Measurement of total hemispherical emissivity using a calorimetric technique, Int. J. Thermophys. 28 (2007) 1607–1620, https://doi.org/10.1007/s10765-007-0213-z.

[138] L. Ramiandrisoa, A. Allard, B. Hay, S. Gomés, Uncertainty assessment for measurements performed in the determination of thermal conductivity by scanning thermal microscopy, Meas. Sci. Technol. 28 (2017) 115010, https://doi.org/10.1088/1361-6501/aa8892.

[139] L. Ramiandrisoa, A. Allard, Y. Joumani, B. Hay, S. Gomés, A dark mode in scanning thermal microscopy, Rev. Sci. Instrum. 88 (2017) 125115, https://doi.org/10.1063/1.5002096.

[140] T. Baba, T. Arai, A. Ono, Laser beam profile measurement by a thermographic technique, Rev. Sci. Instrum. 57 (1986) 2739, https://doi.org/10.1063/1.1139035.

[141] T. Arai, T. Baba, O. Akira, Thermographic investigation of laser flash diffusivity measurement, High Temp. High Press. 19 (1987) 269–273.

[142] T. Baba, M. Kobayashi, A. Ono, J.H. Hong, M.M. Suliyanti, Experimental investigation of the nonuniform heating effect in laser flash thermal diffusivity measurements, Thermochim. Acta 218 (1993) 329–339, https://doi.org/10.1016/0040-6031(93)80433-B.

[143] M.M. Suliyanti, T. Baba, A. Ono, Thermal diffusivity measurements of pyroceram 9606 by the laser flash method, Therm. Conductivity 22 (1994) 80–91.

[144] N. Taketoshi, T. Baba, A. Ono, Development of a thermal diffusivity measurement system with a picosecond thermoreflectance technique, High Temp. High Press. 29 (1997) 59–66.

[145] A.N. Shchukarev, Tests on the heat value of fuel by the method of combustion in compressed oxygen [in Russian], Nauchn. Khim.-Tekh, Leningrad, 1928.

[146] B.N. Oleinik, O.A. Sergeev, V.D. Mikina, Metrological investigations in thermochemistry and thermophysics, Meas. Tech. 12 (1969) 1216–1222, https://doi.org/10.1007/BF00994817 [Translated from Izmeritel'naya Tekhnika 9, 38-41 (1969)].

[147] S.V. Lipin, Communications of the VIMS to the Eighth General Conference on Weights and Measures [in Russian], VIMS 130, Standartgiz, Moscow, 1933.

[148] Comptes rendus des séances de la huitième conférence générale des poids et mesures réunie à Paris en 1933, Librairie-Imprimerie Gauthier-Villars, Paris, 1934, pp. 64–65.

[149] V.S. Uskov, B.N. Oleinik, Benzoic acid for calorimetric evaluations, Meas Tech 7 (1964) 229–231, https://doi.org/10.1007/BF01408993 [Translated from Izmeritel'naya Tekhnika 3, 31-33 (1964)].

[150] V.D. Mikina, B.N. Oleinik, Yu.I. Aleksandrov, K.A. Khrustaleva, Calorific value of benzoic and succinic acids, Meas. Tech. 17 (1974) 700–702, https://doi.org/10.1007/BF00812392 [Translated from Izmeritel'naya Tekhnika 5, 35-37 (1974)].

[151] Y.I. Aleksandrov, V.P. Varganov, S. Sarge, Design and Study of Gas Calorimeter for Absolute Measurements of the Combustion Heat of Natural Gas, Russ. J. Appl. Chem. 74 (2001) 1534–1538, https://doi.org/10.1023/A:1013717504838 [Translated from Zhurnal Prikladnoi Khimii 74, 1489-1493 (2001)].

[152] Y.I. Aleksandrov, V.I. Belyakov, V.P. Varganov, S. Sarge, Method for measuring the combustion heat of natural gas with isothermal calorimeter, Russ. J. Appl. Chem. 74 (2001) 1539–1545, https://doi.org/10.1023/A:1013769521676 [Translated from Zhurnal Prikladnoi Khimii 74, 1494-1499 (2001)].

[153] O.A. Sergeev, I.M. Frenkel, V.I. Kulagin, Precision equipments developed at the All-Union Metrology-Research Institute for measuring the specific heats of solids, Meas. Tech. 17 (1974) 706–708, https://doi.org/10.1007/BF00812394 [Translated from Izmeritel'naya Tekhnika, 5, 39-40, 1974].

[154] I.M. Frenkel, O.A. Sergeev, State primary standard of the solid bodies' specific heat in the range of 273.15 to 700 °K, Meas. Tech. 18 (1975) 545–551, https://doi.org/10.1007/BF00817507 [Translated from Izmeritel'naya Tekhnika 4, 45-49 (1975)].

[155] Yu. A, Kirichenko, B. N. Oleinik, T.Z. Chadovich, New Scientific-Research Investigations in Metrology. Thermal Measurements [in Russian], 1, Izdatelstvo Standartov, Moscow, 1964.

[156] O.A. Sergeev, L.I. Filatov, I.M. Frenkel, Instrument "lambda" with direct readings of thermal conductivity, Meas. Tech. 14 (1971) 1031–1033, https://doi.org/10.1007/BF00983035 [Translated from Izmeritel'naya Tekhnika 7, 35-37 (1971)].

[157] Y.A. Kirichenko, Measurements of temperature conductivity by the method of radial temperature waves in a cylinder, Meas. Tech. 3 (1960) 406–410, https://doi.org/10.1007/BF00976310 [Translated from Izmeritel'naya Tekhnika 5, 29-32 (1960)].

[158] R.S. Gorozhanina, A.Y. Freedman, A.B. Shaievitch (translated by M.C. Selby), NBS special publication 260-30, Standard Samples Issued in the USSR (a translation from the Russian), 1971, pp. 10–11.

[159] J.-R. Filtz, J. Wu, C. Stacey, J. Hollandt, C. Monte, J. Hameury, B. Hay, M. Villamañan, E. Thurzo-Andras, S. Sarge, A european roadmap for thermophysical properties metrology, Int. J. Thermophys. 36 (2015) 516–528, https://doi.org/10.1007/s10765-014-1807-x.