Historical Evolution of the Transient Hot-Wire Technique

Marc J. Assael · Konstantinos D. Antoniadis · William A. Wakeham

Abstract   The paper attempts to describe the historical evolution of the transient hot-wire technique, employed today for the measurement of the thermal conductivity of fluids and solids over a wide range of conditions. Starting from the first experiments with heated wires in 1780 during the discussions of whether gases could conduct heat, it guides the reader through typical designs of cells and bridges, software employed and theory developed, to the modern applications. The paper is concluded with a discussion of the areas of application where problems still exist, and a glimpse of the technique's future.

Keywords   History · Thermal conductivity · Transient hot wire

1 Introduction

In many papers, Stâlhane and Pyk [1] are considered as the pioneers of the transient hot-wire technique, because in 1931 they employed the technique to measure the thermal conductivity of solids and powders (and some liquids). In some other cases, the work of Haarman [2] in 1971, whose equipment used an automatic Wheatstone bridge to measure the resistance difference of two hot wires, is mentioned as

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one of the first applications of the technique. Although both of these works are of great importance to the development of the modern transient hot-wire instrument, it is the authors' belief, as briefly presented at the 30th International Thermal Conductivity Conference [3], that the roots of the technique extend way back in time, to those first heated-wire experiments in 1780. It is this opinion that will guide the presentation in this work, following first an introduction of the principle of the technique.

The transient hot-wire technique is today a well established, absolute technique [2] for the measurement of the thermal conductivity of gases, liquids, nanofluids, melts, and solids. The two factors that make the technique unique are its wide variety of applications and its very low uncertainty. Indeed, if applied properly, it can achieve uncertainties well below 1 % for gases, liquids, and solids, and below 2 % for nanofluids and melts. With the exception of the critical region and the very low-pressure gas region (which will be discussed separately later), it has been shown that it can be applied successfully to a very wide range of temperatures and pressures.

In the transient hot-wire technique, the thermal conductivity of the medium is determined by observing the rate at which the temperature of a very thin metallic wire increases with time after a step change in voltage has been applied to it, thus creating in the medium a line source of essentially uniform heat flux per unit length that is constant in time. This has the effect of producing a temperature field throughout the medium which increases with time. The thermal conductivity is obtained from the time evolution of the temperature of the wire. We note that the wire acts in a double role: one of a line source of constant heat flux per unit length, and one of a temperature resistance thermometer—provided its material is pure, usually platinum or tantalum. Furthermore, nowadays, to avoid end effects, two wires identical except for their length, are employed. Thus, if arrangements are made to measure the difference of the resistance of the two wires as a function of time, the measurement corresponds to the resistance change of a finite section of an infinite wire (as the end effects being very similar, are subtracted), from which the temperature rise can be determined. Today's instruments employ highly accurate automatic electronic bridges allowing more than 1000 measurements of the transient temperature rise from times less than 1 ms up to 1 s (or 10 s, in the case of solids) coupled with finite element methods to establish a very low uncertainty.

The success of this technique rests upon the fact that by the proper choice of the design parameters it is possible to minimize departures from this model. For the remaining small corrections, full analytical expressions exist. Furthermore, the effect of convective heat transfer can be rendered negligible, while for radiative heat transfer, much more important at higher temperatures, an analytic correction exists even in materials that absorb radiation.

2 Historical

In order to present better insight into the development of the transient hot-wire technique, and in a fashion already adopted previously [3], the discussion is separated into three chronological periods:

(a)   from 1781 to 1888,
(b)   from 1888 to 1971, and
(c)   from 1971 to today.

In the following sections, a typical selection of instruments is presented to demonstrate the evolution of the technique. Certainly this selection does not include all investigators associated with the technique.

2.1 Period from 1781 to 1888

It is the authors' belief that this is the time period when the idea of the hot wire was initially born. To trace the origin of the transient hot wire, one must start with Joseph Priestley in 1781. In his book *Experiments and Observations Relating to Various Branches of Natural Philosophy; with a continuation of the Observations on Air* [4], he wrote "all kinds of acid air conducted heat considerably worse than common air. Alkaline air conducted heat rather better than the acid airs…" He was probably the first one to carry out experiments to measure the "power of gases to conduct heat," i.e., the specific heat capacity, which was unknown at that time. Joseph Priestley in that year became a minister in Birmingham, and he continued his scientific research, and also his theological studies. He expressed his views quite forcibly, and in 1785, his *History of the Corruptions of Christianity* was publicly burned.

Similar experiments were carried out by Count Rumford (Sir Benjamin Thomson) in 1786 [5]. He examined "the conductive power of artificial airs or gases," and while doing so, he stumbled on a completely new mode of heat transfer, convection [5]: "he thus established the universality of the law in relation to all fluids, which, in previous observations and experiments, he had found to exist in gases and vapours, namely, although they carry off the heat from bodies immersed in them, they do it not in consequence of their conducting property, but because, the density of the portions which are in contact with the heated body being rendered less, these portions rise, and are replaced by others, which, being heated in their turn, rise also; and thus a motion continues until the solid, and the fluid in which it is immersed, reach the same uniform temperature." In 1799, Count Rumford unfortunately concluded that "a gas was unable to conduct heat!" He further postulated that "…liquids conduct heat, although far more slowly than the worst conductors among solid bodies, the fact, that air and gases are absolute non-conductors, is established beyond all possibility of cavil" and because of his reputation, this conclusion was not challenged for many years.

Sir John Leslie in *An Experimental Inquiry into the Nature and Propagation of Heat* (1804), wrote [6] about Count Rumford: "A late ingenious experimenter, who by the perspicuity and useful tendency of his writings, is deservedly a favorite of the public, he advanced the paradoxical conclusion that fluids are non-conductors of heat; and this strange assertion, from the celebrity of its author, has been treated certainly with more attention and respect than it otherwise merited… If the proposition, however, be taken in its strict sense, it is more palpably erroneous. Were fluids absolutely incapable of conducting heat, how could they ever become heated?... How could water, for

instance, be heated by the content of warm air? But the question really deserves no serious discussion".

Forty-four years later, the discussion about conduction in gases was still going on, when Sir William Robert Grove presented an interesting communication. The communication was illustrated by an experiment, in which it was shown, that a platinum wire, rendered incandescent by a voltaic current, was cooled far below the point of incandescence when immersed in an atmosphere of hydrogen gas. Sir William Robert Grove wrote [7,8]: "This was found not to be due to specific heat, nor to the conducting powers of the gases. Convection did not explain the fact; and considerable difficulty was found, upon examination, to exist, if it was attempted to refer it to the greater mobility of the particles of hydrogen gas, the tightest known, than of either oxygen, nitrogen, or carbonic acid. It was found that this peculiar property also belonged, but to a less extent, to all the compounds of hydrogen and carbon." It is worthwhile noting that experiments with heated wires in gases started to become common in this era.

Some years after, in 1861, Professor Gustav Magnus reported in Poggendorf's Annalen [9], immediately being translated into English and appearing in full in the Philosophical Magazine [10]: "A platinum wire is less strongly heated by a galvanic current when surrounded by hydrogen than when it is in atmospheric air or any other gas. It cannot be doubted that hydrogen conducts heat, and that in a higher degree than all other gases." We note that more experiments with heated wires in gases have started to appear in the literature.

Nevertheless, the debate about conduction in gases had not seen its end yet. John Tyndall, in his 1863 book *Heat Considered as a Mode of Motion*, writes [11]: "Rumford denied the conduction of gases, though he was acquainted with their convection. The subject of gaseous conduction has been recently taken by Prof. Magnus of Berlin, who considers that his experiments prove that hydrogen gas conducts heat like a metal… Beautiful and ingenious as these experiments are (referring to experiments performed by Magnus and Grove), I do not think they conclusively establish the conductivity of hydrogen…. Theories are indispensable, but they sometimes act like drugs upon the mind. Men grow fond of them as they do of dram-drinking, and often feel discontented and irascible when the stimulant to the imagination is taken away." John Tyndall proceeded to describe the following two experiments. By employing a voltaic current, he raised the temperature of the platinum wire shown in Fig. 1, and while it was in vacuum, until it glowed. Subsequently, he let air in. This resulted in the disappearance of the glow. He attributed this effect to heat carried away from the wire by convection. He then repeated the same experiment with air and then with hydrogen. The fact that he needed much more voltaic current in order to get it to glow in hydrogen, he attributed to the higher conductive power of hydrogen.

The gas conduction debate ended in essence with the wide acceptance of the groundbreaking paper of James Clerk Maxwell [12,13] on the *Illustrations on the Dynamic Theory of Gases* and his calculation of a theoretical value of the thermal conductivity of a gas. In the same paper, he also showed the dependence of the thermal conductivity on temperature and pressure. Furthermore, two years later, Rudolf Julius Emanuel Clausius in his papers *On the Conduction of Heat by Gases* [14,15] backed up Maxwell's theories, showing that the thermal conductivity increased with temperature and was independent of pressure when the gas was ideal.

Fig. 1 Hot wire employed
by Tyndall [11]

Ten years later, in 1872, Josef Stefan [16,17] with his experimental expertise
(he is well known for the fourth power temperature to radiation law), set out to
defy Maxwell's words. He thus measured the thermal conductivity of air with an
instrument he called "diathermometer," shown in Fig. 2. Since this is one of the
first instruments to measure the thermal conductivity of gases, it is worthwhile giv-
ing a small description of its use here. The apparatus consisted of two concentric
cylinders made of sheet brass separated from each other radially by 2 mm with the
same distance between the pairs of top and bottom surfaces. The inner cylinder (1)
was equipped with a short tube of the same metal (2) that extends upwards. A glass
tube (3) was cemented into this metal tube and forms the manometer connection.
The glass tube (3) was mounted in a cork (4) which was inserted into a chamber (5)
of the same metal. The glass tube was not in contact with the metal of the cham-
ber to avoid conduction. This whole was then mounted in an outer metal vessel (6)
so as to achieve the concentric cylinder configuration desired with minimal thermal
coupling between the two vessels. The upper surface of the outer metal chamber
(6) carried also a stopcock (7) to allow filling the annular space with a gas while
the lower end of the outer cylinder carries a further valve. The apparatus included
a mercury manometer connected to the glass tube. Observations of the level of the
mercury in the tube permitted monitoring of the pressure of the gas in the inner
cylinder.

Having gained a lot of experience from his previous experiments, Stefan developed
an equation to describe heat transfer in the concentric cylinder arrangement. The con-
cept of the experiment was that the entire apparatus was first equilibrated in air, and
the inner cylinder filled with air and then sealed. The entire cell was then immersed
in an ice/water mixture at time $t = 0$, and the pressure observed over time as heat
conduction across the annular region and at the ends of the cylinder between the outer
cylinder and the inner takes place with heat flowing from the inner cylinder to the

Fig. 2 Diathermometer
of Stefan [16]
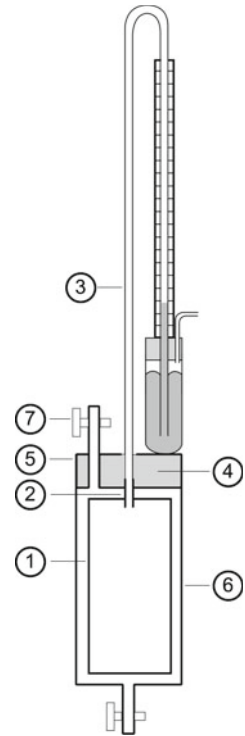
outer. This causes the mean temperature of the gas in the annular space to decrease
and the pressure of the gas to diminish.

During the course of the experiment, in a time dt, the amount of heat transferred
between the two cylinders when the temperature difference between them was ΔT,
was

$$dQ = \frac{\lambda A \Delta T}{d} dt, \tag{1}$$

where d is the radial separation of the two cylinders and A, in Stefan's derivation, is
the mean (effective) surface area for conduction. In that time, the same amount of heat
was lost by the inner cylinder as its temperature diminishes by dT which amounts to

$$dQ = -MC_m dT, \tag{2}$$

in which M is the mass of the cylinder and C_m is the heat capacity of the material.
Stefan then assumes that the heat loss from the air held in the inner cylinder is negligi-
ble by comparison and that the effect of heat loss through the upper glass manometer
tube, which is indeed a small effect, and thus we have the equation,

$$MC_m dT = -\lambda A (T - T_0) dt/d \tag{3}$$

subject to the initial condition $T = T_a$ at $t = 0$. Solving the above differential equation and assuming that the temperature of the inner cylinder is equal to the mean temperature of the gas within it, the pressure of the gas will reflect that temperature. Thus, it follows that if the pressure of the gas at the start of the experiment in the equilibrium situation was p_0 and it is p_1 when the entire cell reaches equilibrium with the ice water at $0\,°C$, then

$$\frac{p - p_1}{p_0 - p_1} = \exp\left[-\frac{\lambda A t}{M C_m d}\right] \tag{4}$$

From which it follows that, given measurements of the pressure of the gas in the inner cylinder over time, one can deduce the thermal conductivity of the gas without a knowledge of the initial pressure in the system but only with a knowledge of the geometry of the cell and the mass of the cylinder and its heat capacity.

This final value of the thermal conductivity of air reported by Stefan departs from recent and agreed values at approximately the same temperature by 3 %. In his second paper published in 1875 [17], Stefan extended his studies to the thermal conductivity of other gases using a similar technique as that which had been so successful for air. As a result of extensive measurements, Stefan reports the ratio of the thermal conductivity of a series of gases to the thermal conductivity of air near ambient conditions (a temperature of $10\,°C$) is assumed here. Table 1 contains the results of his determination of these ratios determined directly using the result of Eq. 4. The same table reports the values of the thermal conductivity for each gas evaluated from the base value of the thermal conductivity of air reported above and determined by Stefan as well as the best estimates for the gases using modern methods. The values are seen to be remarkably similar in most cases; the differences are usually a matter of a few percent at most.

All these discussions and experiments with heated wires in a sense prepared the ground for the work of Schleiermacher [20]. Following the work of Stefan and his predecessors, Schleiermacher set out to measure the thermal conductivity of gases by using a platinum hot wire (probably this is the first real hot-wire instrument). The instrument, shown in Fig. 3, was composed of a horizontal platinum wire of 0.4 mm diameter and 32 cm length, placed in the center of a glass cylinder of 2.4 cm diameter and kept taut by a metallic spring. Potential leads were soldered at points A and B.

Table 1 Thermal conductivity of some gases measured by Stefan [17]

Gas	$\lambda_{gas}/\lambda_{air}$ Stefan	λ_{gas} (mW · m^{-1} · K^{-1}) Stefan	λ_{gas} (mW · m^{-1} · K^{-1}) Literature
Air	1.000	24.7	23.9 [18]
Oxygen	1.018	25.1	25.5 [19]
Nitrous oxide	0.665	16.4	14.5 [18]
Carbon monoxide	0.981	24.2	24.9 [19]
Carbon dioxide	0.642	15.8	16.2 [19]
Ethylene	0.752	18.6	16.8 [18]
Methane	1.372	33.9	32.8 [19]
Hydrogen	6.718	166.0	172.5 [19]

Fig. 3 Schleiermacher's hot wire instrument [20]

Table 2 Thermal conductivity of some gases measured by Schleiermacher [21]

Gas	λ_{gas} (mW · m^{-1} · K^{-1})	
	Schleiermacher	Literature
Air	23.5	23.9 [18]
Hydrogen	171.5	172.5 [19]
Carbon dioxide	13.7	16.2 [19]
Mercury vapor (500 K)	7.75	7.9 [22]

The resistance of the portion of the wire between points A and B was obtained by measuring the voltage and the current through it. The temperature inside the glass was obtained from the resistance of the wire, while the temperature outside was registered by a wound resistance thermometer. Equilibrium was reached in minutes. The thermal conductivity, λ, of the gas was obtained from the expression,

$$\lambda = A \frac{q}{(T_1 - T_2)}, \tag{5}$$

where T_1 and T_2 are the inside and outside temperatures, q is the heat per unit length supplied, and A is a constant obtained from the geometry of the instrument or by measuring other gases of known thermal conductivity. This instrument was employed for measurements up to 1000 °C [21]. Some typical values measured around room temperature (except in the case of mercury vapor) are shown in Table 2. The differences from literature values are less than 5 %.

2.2 Period from 1888 to 1971

In the previous time period, the hot wire was developed as a technique for measuring the thermal conductivity of gases. During the period from 1888 to 1971, the transient hot wire evolves as a full instrument for measuring the thermal conductivity of fluids and solids. Weber [23,24] investigated the sources of errors involved in the determination of the thermal conductivity of gases by the method of Schleiermacher, and proposed a modified form of apparatus in which the errors resulting from convection are greatly reduced. Although many similar instruments were developed, the main novelty of the instrument shown in Fig. 4, is that it is placed vertically, probably for the first time. A 0.40 mm diameter platinum wire of 54.5 cm length was employed and placed inside a 2.3 cm diameter glass tube. The wire was employed as a four-terminal resistance bridge, and was kept taut by a spring at the bottom of the vessel. With this

Fig. 4 Hot-wire instrument
proposed by Weber [23,24]

Table 3 Thermal conductivity
of some gases measured
by Weber [23]

Gas	λ_{gas} (mW · m^{-1} · K^{-1})	
	Weber	Literature
Argon	16.1	17.3 [19]
Helium	144	150 [19]
Neon	45.5	48.2 [19]
Hydrogen	174	172.5 [19]
Nitrogen	23.7	24.9 [19]
Oxygen	24.1	25.5 [19]
Carbon dioxide	16.4	16.3 [19]
Nitrous oxide	14.7	14.5 [18]
Methane	30.1	32.7 [19]

improved form of apparatus, measurements were made of the thermal conductivity of a number of gases shown in Table 3. The values obtained are only a few parts per hundred away from the values accepted today.

However, the first "transient" hot-wire instrument was proposed by Stâlhane and Pyk in 1931 [1], in order to measure the thermal conductivity of solids and powders (and some liquids); see Fig. 5. The hot wire is wound around a tube with a thermometer inside. Constantan wire was chosen because of its very low temperature coefficient
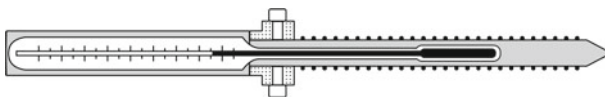

Fig. 5 Transient hot-wire instrument employed by Stâlhane and Pyk [1]

of resistance. The whole rod was simply immersed in the powder, which was held at constant temperature. They further investigated the relationship between the time and temperature rise, for a fine straight wire subjected to a step change in the heat input to the wire. They found that for a short interval after the initiation of the step change, the following empirical relation holds for the temperature difference, ΔT:

$$\Delta T = \frac{Aq}{\lambda} \ln \left(\frac{r_o^2}{t} + B \right). \tag{6}$$

Here q is the heat per unit length, r_o is the wire radius, and t is the time. Constants A and B were obtained from fluids of known thermal conductivity.

Eucken and Eglert in 1938 [25] improved the design of Stâlhane and Pyk, and designed an absolute transient hot-wire instrument for low temperatures. They employed a cross-like arrangement; see Fig. 6, where the 0.1 mm diameter platinum wire was in the middle of the cross, two wires at its side served as potential leads and the remaining two, as support wires. The temperature was obtained from the wire's resistance. The wire was held under tension by employing a small spring on its top. With this instrument, they measured, among others, the thermal conductivity of benzene and glycerin down to $-78\,°C$, and of carbon dioxide and ammonia down to $-104\,°C$.

van der Held and van Drunen in 1949 and van der Held et al. 1953 [26,27] employed a 0.3 mm diameter manganese wire, and a 0.1 mm diameter copper/constantan thermocouple both placed in a narrow capillary with both ends fused into the wall of a glass vessel (see Fig. 7). Liquid is placed between the capillary and the glass vessel. In this way, the thermal conductivity of aggressive liquids could be measured. The glass vessel is placed in a Dewar flask for a steady temperature.

They preferred to use a thermocouple to record temperatures instead of recording the resistance of the wire, as the later would involve high temperature rises and complicated recorders and bridges. Hence, a Moll-galvanometer was employed, and the light spot was registered photographically. They also made many corrections for the wire thickness and the presence of the glass and employed times in the region of 20 s to 50 s. They thus measured the thermal conductivity of many fluids (hydrocarbons, alcohols, acids, etc.) with a quoted uncertainty of 2 %.

van der Held and van Drunen did a lot of theoretical work. They derived the empirical expression of Stâlhane and Pyk by solving the Fourier equation, and they further advanced it to the well known "ideal solution" as

$$\Delta T = \frac{q}{4\pi\lambda} \left[\ln \frac{4at}{r_o^2} - 0.5772\dots \right], \tag{7}$$

or for two distinct times,

$$\Delta T_1 - \Delta T_2 = \frac{q}{4\pi\lambda} \ln \left(\frac{t_2}{t_1} \right), \tag{8}$$

Fig. 6 Transient hot-wire
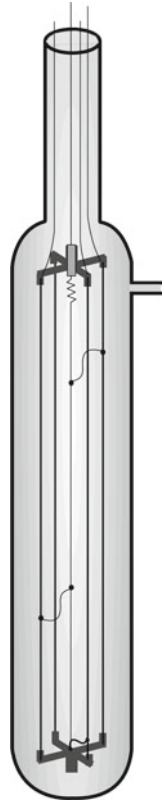instrument of Eucken
and Eglert [25]

Fig. 7 Transient hot-wire
instrument of van der Held
and van Drunen [26]

Thermocouple

Hot-Wire

where α is the thermal diffusivity of the medium. Thus, absolute measurements could be performed. They also investigated the time period over which measurements could be performed and indicated that at higher times, the influence of convection becomes very important.

de Vries [28] designed a transient hot-wire sensor for measuring the thermal conductivity of solids. The 0.1 mm diameter hot wire, made of enameled constantan, was folded and placed inside a glass capillary of 0.4 mm outside diameter. Outside the capillary, a fine monel gauze formed a socket of 1.4 mm diameter. The glass capillary and an additional thermocouple were introduced into a gauge cylinder, and the empty space is filled with paraffin wax. The whole sensor had a length of 10 cm. The resistance was measured with a sensitive dc Wheatstone bridge, and times of 3 min were employed. Daily trends in moisture content of soil reflected on the measurement of the thermal conductivity.

Gillam et al. [29] in 1955 employed the ideas of Stålhane and Pyk, and of Eucken and Englert, to produce a simpler apparatus of lower uncertainty, 0.3 % for liquids and solids (of low melting point—melted solid, like liquid was poured into the glass and solidified there, see Fig. 8). They also employed a 0.1 mm platinum wire with potential leads. The temperature was obtained from the wire's resistance, and an optimized Kelvin bridge was employed to record accurately the resistance change. Times recorded were between 1 s and 60 s.

New instruments are now characterized (a) by a wire with potential leads, (b) by a temperature rise that is obtained from the resistance of the wire, (c) by times up to 1 min while (d) new electronic bridges just appear. More instruments were developed; Grassman and Straumann [30] in 1960 published a transient hot-wire instrument for gases and solids, and Haupin [31], an instrument for solids in which a thermocouple

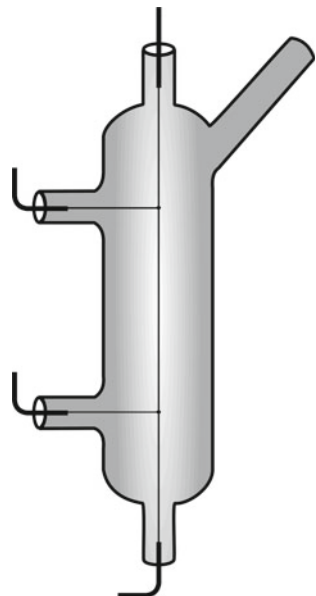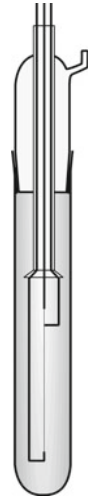**Fig. 8** Transient hot-wire instrument of Gillam et al. [29]

Fig. 9 Transient hot-wire
instrument of Turnbull [32]

with its junction placed in the middle of the sample is heated with alternating current
acting both as a heat source and thermometer.

Turnbull [32], in 1962, measured the thermal conductivity of molten salts in the
liquid and solid states, and of organic silicates. In Fig. 9, the transient hot-wire instru-
ment employed for organic silicates is shown. The sample was held in a borosilicate
glass cell. A 0.1 mm diameter platinum wire, of 10 cm length, immersed in the sam-
ple, was heated by direct current connected in a three-lead Wheatstone bridge. The
rate of rise of the wire temperature was found by reading the bridge galvanometer
deflection at intervals of 3.3 s or by means of a fast-response potentiometric recorder.
The thermal conductivity was obtained through Eq. 7, and an absolute uncertainty of
3 % was quoted.

A four-terminal transient hot-wire instrument was also employed by Horrocks and
McLaughlin [33] in 1963 for measuring the thermal conductivity of liquids, with an
absolute quoted uncertainty of 0.25 %. They used a 60 µm diameter platinum wire of
15 cm length, annealed for an hour. Platinum potential leads were placed about 1 cm
from the ends, and a platinum spring at the top prevented wire sagging. In their work,
Horrocks and McLaughlin performed a full analysis of the corrections attributed to the
(a) finite wire diameter, (b) boundary medium, and (c) finite wire length, and a study of
convection and radiation effects. It should also be mentioned that they employed a time
scale for measurements at about 10 s, limited by the electronics available for timing.

In 1964, Mittenbühler [34] used a heating wire of one metal with a thermocouple
welded to the heating wire in the form of a cross in order to measure the thermal con-
ductivity of solids. An ac or dc power supply can be employed, and the temperature
rise generated by a known heating power is used to determine the thermal conductivity.
The developed method formed the basis of methods for a German [35] and a European
[36] standard in use today.

Four years later, in 1968, Burge and Robinson [37] proposed another four-termi-
nal transient hot-wire instrument for gases employing lower times. The line source
consisted of a 0.7 mm diameter, 20.6 cm length wire. Around it tightly wrapped was a
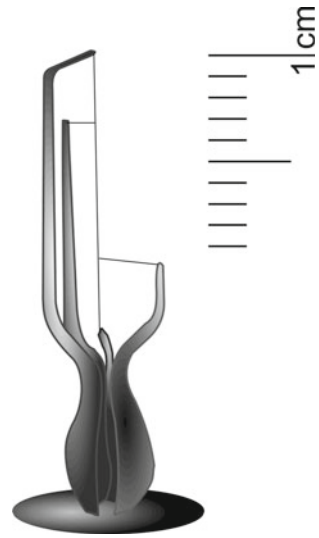
0.02 mm nickel temperature sensing coil. A three-element copper–constantan thermo-couple recorded the gas temperature. The resistance change was recorded by a camera attached to an oscilloscope connected to a dc resistance bridge. Times were limited to 0.27 s, and the temperature rise never exceeds 10 °C. The thermal conductivity of He, Ne, Ar, and their mixtures was measured. Hayashi et al. [38] also employed a four-terminal transient hot-wire instrument, but to measure the thermal conductivity of solids up to 1200 °C.

The year 1971 is the year of changes. Davis et al. [39] proposed a very small 6.2 μm diameter and 1.3 cm length platinum transient hot wire (see Fig. 10). Measurement times of 1 s to 10 s were employed. Instead of photographing galvanometer spots or using chart recorders, a digital voltmeter (HP 2402A, 40 measurements/s) was employed to record the change in voltage because of the change in resistance, coupled to a precision frequency generator. The temperature change was calculated from the wire's resistance. For electrically conducting fluids, they used a thin metal film evaporated on a quartz rod. The quartz substrate rod was 1.25 mm long and had a diameter of 0.025 mm. The length of the sensing platinum film was 0.51 mm. The film was in contact with both ends with gold-plated portions of the quartz rod. The resistance of the sensor was about 6 Ω. This was employed as a relative instrument.

McLaughlin and Pittman [40,41] (continuing the work of Horrocks and McLaughlin [33]) proposed a very interesting transient hot-wire instrument with a 25 μm diameter and 15 cm length platinum wire, with a weight under it. The instrument was designed to operate from 100 K to 450 K and up to 10 MPa pressure. The cells and the vessel were made of stainless steel, and an elaborate temperature enclosure was employed to attain a temperature stability of 1 mK · h^{-1}. The measurement time was between 1 s and 20 s. They also employed a digital voltmeter to record the change in voltage because of the change in resistance. The temperature change was calculated from the wire's resistance. They also analytically examined the ideal solution and the following corrections to it: (a) temperature-dependent fluid properties, (b) finite wire

diameter, (c) finite conductivity wire, (d) wall effects, (e) interfacial thermal resistance, (f) time-dependent heat-source power, (g) end effects, and (h) initial fluid temperature distribution.

The most important changes in 1971 are attributed to the work of Haarman [42,43]. His equipment used an automatic Wheatstone bridge to measure the resistance difference of two wires. The two wires were identical except for their length. Hence, end effects were subtracted. The bridge was also equipped with an electronic potential comparator. The bridge was capable of measuring the time required for the resistance of the hot wire to reach six predetermined values, with the aid of high-speed electronic switches and counters. This new bridge made possible a tenfold reduction in the duration of each experimental run, eliminated completely the effects arising from convection, and reduced greatly other time-dependent errors. In essence, the work of Haarman introduced high precision electronics in the determination of the resistance of the wire and thus the temperature rise, allowing higher precision and much lower uncertainties.

2.3 Period from 1971 to Today

The period of 1971 to today is characterized by two major events:

(a) The pioneering work of Haarman (use of two wires, faster electronic bridge, experimental time of seconds), and
(b) The use of a full theory as presented in a paper by Healy et al. [44]. The measurements are described by an ideal solution which is followed by a series of corrections:
  – Effects eliminated entirely (convection),
  – Corrections rendered negligible (finite diameter of the wire, Knudsen effects, radiation, viscous heating, compression work), and
  – Remaining corrections (end effects, finite heat capacity of the wire, outer boundary corrections, and variable fluid properties).

Hence, together with the advances in electronics, a full theory exists that enables absolute measurements of low uncertainty. This was the start of a new series of transient hot-wire instruments. As the majority of these new instruments were developed by groups that cooperated through research projects, very similar instruments appeared. Hence, they will be presented all together. Most of the current transient hot-wire groups originated from, or were connected to:

– J. Kestin (Brown University, USA) or
– W.A. Wakeham (Imperial College and Southampton University, UK).

Such groups are:

– C.A. Nieto de Castro (Lisbon University) and J.M.N.A. Fareleira (Instituto Superior Tecnico, Portugal),
– M.J. Assael (Aristotle University, Greece),
– R.A. Perkins and H.M. Roder (NIST, USA),
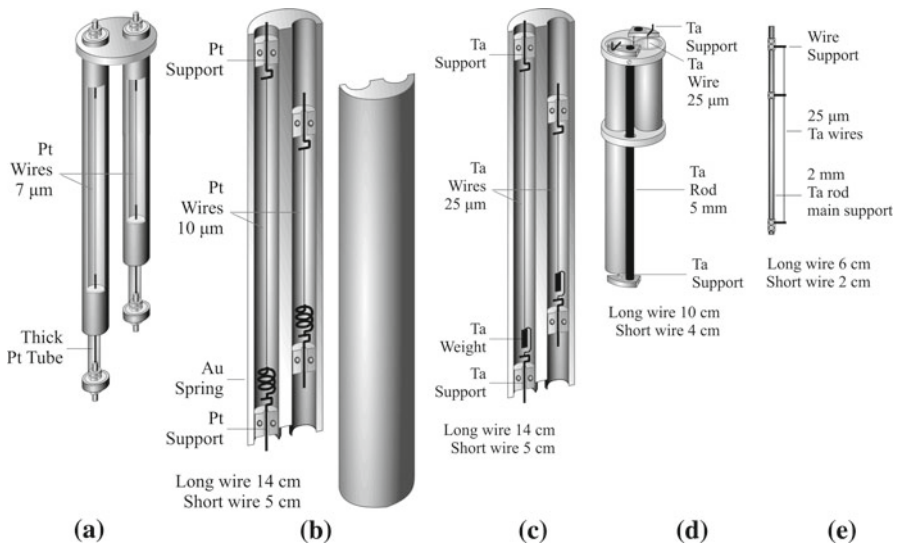– A. Nagashima and Y. Nagasaka (Keio University, Japan),

Fig. 11 Some transient hot-wire instruments for fluids

and more recently

– J. Wu (Jiaotong University, China),
– E. Vogel (Rostock University, Germany).

Figure 11 shows some characteristic typical changes that the transient hot wire has undergone since 1971. Design (a) refers to two 7 µm diameter platinum wires, fixed at both ends. These were Wollaston processed wires, i.e, they were initially drawn covered by silver. Once in place, the silver was chemically dissolved and the wire was annealed. Such wires were employed for gases [45] and liquids [46], but they were soon abandoned as they became slack during heating. Upon heating, the wires expand and thus they must move laterally through the fluid even if by only a few tens of micrometers. This is enough to add a convective contribution to the heat transfer.

Design (b) was a logical improvement step [47–49]. The gold spring ensured that the wires were always taut. The Wollaston processed wires were also substituted by 10 µm diameter wires. An alternative arrangement was to introduce a weight. The cells shown in (c) include a weight, and this worked very well for the measurement of the thermal conductivity of liquids [50].

In 1982, in order to measure the thermal conductivity of electrically conducting liquids, Alloush et al. [51] proposed that the wires be made from tantalum. Tantalum upon oxidation, forms a thin layer of tantalum pentoxide which is an electrical insulator. A small correction to the calculated temperature should be applied [52]. The cells shown at (c), the weights, and all electrical connections are made of tantalum and were consequently anodized in situ. This arrangement worked excellently [53,54], and it is still used today. Designs (d) and (e) are more recent and are based on the tantalum idea. However, instead of a weight, the wire supports are also made of tantalum, so they expand similarly to the wire when the temperature rises [55,56]; hence, the wire

is always kept taut. Also in design (e) the wires are much shorter and are placed one over the other [56].

One of the main problems arising in applying the technique to solids is the inevitable contact resistance between the samples or between the sample and the wire. Today, there are three transient hot-wire standard test methods for the measurement of the thermal conductivity of solids:

– the American 1999 ASTM C1113-99 Resistive Transient Hot-Wire test method [57],
– the European 1998 EN 993-14 Cross-Array Transient Hot-Wire test method [37], and
– the European 1998 EN 993-15 Parallel Transient Hot-Wire test method [58].

In the case of the resistive mode of the transient hot-wire method [57], a pure platinum wire is placed between two solid specimens of the material and a constant electrical current is applied to it. The wire acts as both a heat source and as a temperature recorder. However, the heating wire is usually 0.35 mm to 0.50 mm in diameter, with a length of about 20 cm, resulting in a resistance of about 0.1 Ω to 0.2 Ω, which in turn requires high operating power. The large power and the low resistance can easily produce larger uncertainties. Moreover, the use of a single wire instead of two enhances the errors associated with the end effects of the wire. Another point that should be added is that, in this resistive form of the transient hot-wire method, only a segment of the temperature versus time curve is used instead of the whole curve, in order to obtain the thermal conductivity. Hence, the choice of this "segment" affects the uncertainty of the method, which is also affected by the appearance of contact resistance when the wire is embedded in the solid. The contact resistance still exists even if powders are employed.

On the other side, in the parallel or the cross-array mode of the transient hot-wire instrument, instead of the wire acting both as sensor and a thermometer, a thermocouple is placed usually 1.5 cm from the heating platinum wire to register the temperature [37,58]. However, the errors that exist in the resistive mode of the hot wire, also appear in this one.

Therefore, in order to overcome the difficulties arising from the contact resistance and the end effects of the wire, the experimental setup with two tantalum wires was adjusted for the measurement of solids and melts. Two recent designs can be seen in Fig. 12. In order to avoid air gaps, in design (a) [59], the two wires are placed inside a soft silicone layer which is squeezed between the two solids. In this way, the contact is excellent. By obtaining the temperature rise from the wire's resistance measurement, at very short times the properties of the silicone layer are first obtained, and then at longer times the properties of the solid. The absolute uncertainty achieve in this way is about 1 %, and the technique is only hindered in temperature by the melting temperature of the soft silicone layer.

Design (b) is based on the same idea, but here the wire is placed between soft alumina layers which are consequently fired under pressure to become solid [60]. This arrangement worked very well for measurements of the thermal conductivity of molten metals at high temperatures; Peralta-Martinez et al. [61] reported such measurements for molten mercury, gallium, tin, and indium up to 750 K.
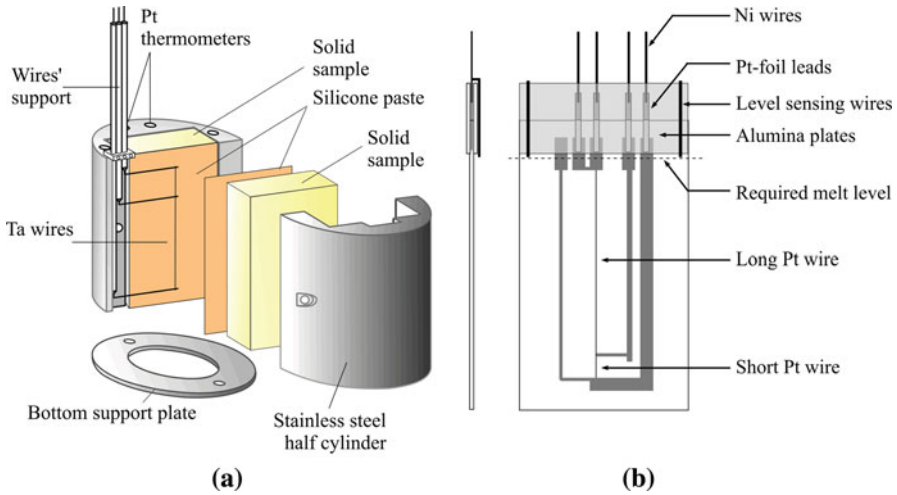
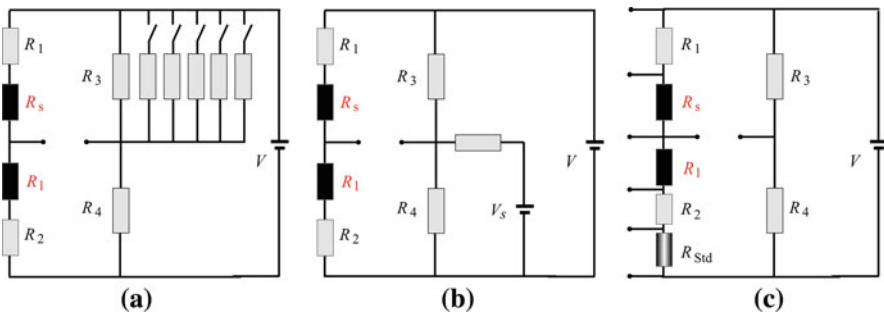**Fig. 12** Some transient hot-wire instruments for solids

Fig. 13 Typical automatic bridge designs

In order to accurately measure the resistance of the wires, electronic bridges were developed rapidly following the advances in electronics and computers. An excellent series of bridges was developed in Imperial College by M. Dix, and these are shown in Fig. 13 as an example. Design (a) was employed in the 1970s [45–48]. Upon reaching equilibrium, the resistances in the upper right arm were introduced automatically one at a time and thus six equilibrium points, i.e., six wire resistances, were obtained in one run. In order to be able to obtain more resistance measurements at one run, design (b) was employed in the 1980s and 1990s [62,63]. In this design, instead of changing the resistances of the upper right arm, the voltage of the lower right arm was changed to predetermined, by a computer, values. Hence, about 64 resistance measurements were obtained in 1 s. In design (c), employed after 2000 [64], voltages are registered continuously. Wire resistances are calculated from the known standard resistance (R_{Std}).

The accurate measurement of the resistance of the wires over very short times allowed the technique to extend to much lower times. As a consequence, during the last decade the analytic "ideal solution" described previously, was substituted by the
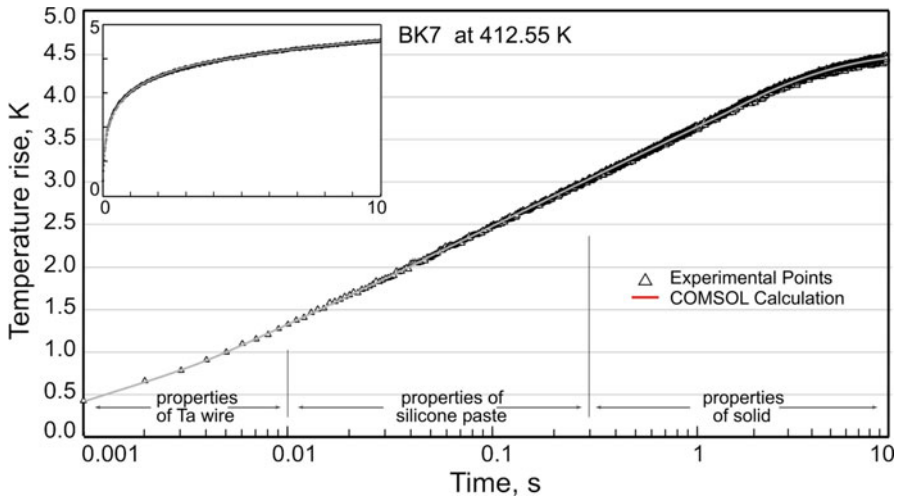
Fig. 14 Measurement of the thermal conductivity of BK7 at 412.55 K

use of finite element analysis in the measurement procedure. Solving the differential heat conduction equation by a numerical method in place of an analytic solution allows us to use the method for more complex geometries than originally envisaged such as those set out in the description of the technique for solids and molten metals. Hence, the finite element solution is used in order to exactly represent the geometry of the measurement sensors and to ameliorate the accuracy of the measurements. The use of finite elements followed the development of the software technology. Thus, in the beginning, the mesh of the geometry was created by software developed in the Fortran programming language while today it can be easily done with finite element packages (Comsol, Ansys, etc.) [64].

Finally, we ought to close this section with a good example of a transient hot-wire instrument. The arrangement (a) in Fig. 12, together with the automatic electronic bridge (c) in Fig. 13, was employed [64] to measure the thermal conductivity of BK7 solid at 412.55 K and ambient pressure. 1000 measurements between 0.001 s and 10 s are shown in Fig. 14. The first part of the curve is related to the properties of the tantalum wire, the second part refers to the silicone paste, and the last part to the properties of the solid. Full agreement of the COMSOL calculated values with the experimental temperature rise values, over five orders of magnitude in time, is observed. Thus, the heat transfer model developed for the description of the hot-wire sensor is entirely consistent with the practical operation of the sensor over a time range of five orders of magnitude as the heat pulse transmits through four different materials. Following the uncertainty analysis described elsewhere [59], it is possible to assert that the uncertainty in thermal conductivity of the solid determined by this technique is better than 1 %.

3 Are There Still Problems?

Regardless of the successful application of the transient hot-wire technique in the measurement of the thermal conductivity of gases, liquids, melts, nanofluids, and solids,

over very wide ranges of temperature and pressure, there are still some areas where the technique cannot be applied.

(a) In the case of the critical region, the technique cannot be applied as it requires a temperature rise of a few kelvins. The changes in the physical properties of the fluid near critical conditions are just too large, with either temperature or even height of the measurement cell.

(b) The case of the low pressure dilute gas region, however, is a region where measurements seem to systematically deviate from expectations. It has recently been shown [65] that although viscosity measurements at very low pressure and up to high temperatures agree very well with calculated results employing the best available potentials, this does not happen for thermal conductivity. It has further been shown [65] that this small deviation seems to increase with the molecule complexity or polarity. Although the deviations might be small for engineering purposes, their origin still remains of great scientific interest.

(c) In the case of thin films, the technique cannot be applied for measurements of low uncertainty because the thickness of the sensor is comparable to the thickness of the sample and heat losses occur.

4 The Future?

It is the authors' belief that the technique will further expand into more areas of application:

(a) Low-pressure gas region. As already stated, this is a region where the measurements performed by this technique do not seem to agree with theoretical predictions, for unknown reasons. So this is a region that certainly needs to be clarified. It is an important problem to be solved for the industrially important fluid steam.

(b) The high-temperature region for solids. The application of the silicone paste eliminated the contact resistance problems. However, silicone paste has a temperature limit of around 550 K. Hence, other materials need to be found, if the technique is to be applied in this way to higher temperatures.

(c) The application of the transient hot-wire technique to the measurement of the thermal conductivity of thin films still shows many difficulties that have to be overcome in order to achieve measurements of low uncertainty.

(d) Wires will become shorter and instruments much smaller. The continuous developments in electronics and particularly MEMS will surely result in more clever applications based on the transient hot-wire technique.

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