

A New Transient Hot-Wire Instrument for Measuring the Thermal Conductivity of Electrically Conducting and Highly Corrosive Liquids using Small Samples

J. P. Garnier · J. P. Maye · J. Saillard ·
G. Thévenot · A. Kadjo · S. Martemianov

Received: 19 November 2007 / Accepted: 6 February 2008 / Published online: 8 March 2008
© Springer Science+Business Media, LLC 2008

Abstract The transient hot-wire technique is widely used for measurements of the thermal conductivity of most fluids. However, for some particular liquids such as concentrated nitric acid solutions or similar nitric mixtures, for which the thermal properties are important for industrial or security applications, this technique can be difficult to use, which is essentially due to incompatibility between measurement probe materials and highly electrically conducting and corrosive liquids. Moreover, the possible highly energetic (explosive) character of these liquids requires minimum volume liquid samples, and safety measurement devices and processes. It is the purpose of this paper to report on a new patented instrument, based on tantalum short-hot-wire probe technology, which responds to the above requirements and allows safe automated thermal-conductivity measurements of concentrated acid nitric solutions and similar nitric mixtures for liquid samples less than 2 cm³, with uncertainties better than 5%.

Keywords Corrosive electrically conducting liquid · Nitric acid · Small sample · Thermal conductivity · Transient hot-wire technique

1 Introduction

The transient hot-wire (THW) method has been widely used for measuring the thermal conductivity of materials; for liquids, in particular, this technique has now become a primary method for many applications. It generally involves the measurement of the

J. P. Garnier (✉) · J. P. Maye · A. Kadjo · S. Martemianov
Laboratoire d'Etudes Thermiques, UMR CNRS 6608, ESIP, Université de Poitiers,
40, Avenue du Recteur Pineau, 86022 Poitiers, France
e-mail: jean.philippe.garnier@univ-poitiers.fr

J. Saillard · G. Thévenot
Commissariat à l'Énergie Atomique, DXPL/SMEO/LPC, Centre du Ripault, 37260 Monts, France

temperature response of a thin metallic wire immersed in the liquid and subjected to a step heating power; the thermal conductivity is determined from the theoretical and ideal model of an infinitely long line heat source in an infinite liquid medium, and eventually corrections are taken into account of the non-idealities of the experimental apparatus. In the most favorable conditions, thermal conductivities of liquids can be determined with claimed uncertainties better than 0.5% [1,2].

For electrically conducting liquids, the THW method is not usable with bare metal wires because leakage of electric current and polarization of the liquid at the surface of the wire can occur, leading to uncontrolled errors in the wire temperature and heating-power measurements. For such liquids, the wire must then be electrically insulated by coating it with a thin insulation layer. A number of coating techniques have been employed for this purpose (polyester coating [3], silica coating [4], aluminum-oxide-coated wire [5,6], and tantalum-oxide-coated wire [7–11]). Each coating technique has to be adapted to the wire and liquid types, and to the working (pressure and temperature) conditions. For highly corrosive liquids (molten salts, lithium bromide solutions, acetic and propionic acid+water mixtures, etc.), alternative techniques to coating wires have also been used such as a quartz-coated metallic film sensor [12], lacquered wire in a glass capillary tube [13], or a single glass capillary filled with mercury [14,15] acting as an insulating hot wire. Each electrical insulating technique, coated wire or other method, induces parasitic effects on temperature measurements; these effects have to be evaluated and eventually taken into account. The difficulties to apply the THW method for electrically conducting and highly corrosive liquids have been analyzed by Zhang and Fujii [5] who developed a specific method using a shorter hot wire than those regularly used (length > 150 mm) in classical hot-wire cells. With this transient short-hot-wire (TSHW) method, using a platinum wire 9.2 mm in length and 97 μm in diameter coated with an Al_2O_3 oxide film, the authors claimed to measure thermal conductivities of molten nitrates and carbonates within errors of 3 and 5%, respectively, from 120 cm^3 volume liquid samples. For this previous work, as for most other similar applications, the liquid sample volumes have been chosen large enough to insure the ideal infinite medium condition around the sensor, with no objective of sample miniaturization; these liquid sample volumes are generally larger than 40 cm^3 (e.g., 50 cm^3 in [10] and 80 cm^3 in [7]).

A variant of the classical THW method, using a sinusoidal alternating current, has also been developed [16,17], with the claimed advantage of smaller (13 cm^3) liquid volume samples; the experimental setup has however only been tested for water and glycerin, and the method is said to be not suitable for low thermal conductors.

A particular category of electrically conductive and highly corrosive liquids, called *special* in the present work, is represented by some nitric acid compounds. These technically important liquids can be very energetic and explosive during experiments; so, they have to be usually tested and operated in special containment rooms if the working samples are not sufficiently small. Until now, no attempt had been made to apply the THW method to these *special* liquids for measurements of their thermal properties. For such special liquids, the thermal conductivity had usually only been determined *indirectly* from thermal-diffusivity measurements with a “flash” method [18] similar to those used for solid materials. Unfortunately, for such measurements of thermal diffusivities in liquids, these last ones have to be contained in solid glass

or stainless-steel vessels [18], with associated disadvantages relative to the THW method: larger heat flux transferred to the liquid sample (5 cm^3 minimum volume [18]), uncontrolled heat losses in the vessel wall, and dangerous operational procedures ill-suited for systematic measurements.

The aim of the present work was the development of a TSHW method adapted to *direct* thermal-conductivity measurements on small ($<2 \text{ cm}^3$) *special* liquid samples. In comparison with the other THW methods previously applied to thermal-conductivity measurements in liquids or even with the “flash” method used in [18] for thermal-diffusivity measurements, this objective corresponds to a significant liquid sample reduction in volume. Moreover, for applications to special liquids as defined previously, the tantalum hot-wire technology has been chosen because tantalum has well-known electrical and thermal properties [19,20], has a higher chemical resistance to corrosion for most concentrated strong acids (nitric, sulfuric, hydrochloric, hydrobromic, etc.) [21], and can be manufactured in thin wires ($25 \text{ }\mu\text{m}$ minimum diameter) that can easily be reduced in diameter by a specific electrochemical treatment and easily insulated from the electrically conducting liquids by a tantalum pentoxide anodic film of controlled nanometric thickness [7,9,22].

2 Principle of the THW Method

The THW method is a transient dynamic technique based on the measurement of the temperature rise of a linear heat source (hot wire) embedded in the test material. For an infinitely long metallic wire (radius: r_0) heated at time $t > 0$ with a constant heat flux q per unit length and immersed in an infinite homogeneous liquid medium (thermal conductivity and diffusivity: λ and a , respectively) with uniform initial temperature T_0 , the instantaneous temperature $T(t)$ of the wire is given by [1]

$$T(t) - T_0 = \Delta T(t) = \left(\frac{q}{4\pi\lambda} \right) \ln \left(\frac{4Fo}{C} \right) \quad (1)$$

where γ is Euler’s constant ($\gamma = 0.5772$) with $C = e^\gamma = 1.781$ and Fo is the Fourier number defined by

$$Fo = \frac{at}{r_0^2} \quad (2)$$

Equation 1 is the analytical solution of an ideal thermal-conductivity model, only valid for $Fo \gg 1$ and over a limited time interval (without convective heat transfer in the liquid medium). In practice, the measured response $E(t)$ of the wire to the temperature increase $\Delta T(t)$ resulting from the Joule effect due to a constant current i is given by

$$e(t) = R(t) i = R_0 (1 + \beta_0 \Delta T(t)) i \quad (3)$$

where $R(t) = R(T)$ is the instantaneous electrical wire resistance (wire temperature: $T(t)$) and β_0 is the wire temperature coefficient (defined for $R(T_0) = R_0$) deduced from an experimental calibration (Sect. 4.1).

Taking account of Eqs. 1 and 3, the thermal conductivity λ can be determined from

$$\lambda = \left(\frac{q R_0 \beta_0 i}{4\pi} \right) \left(\frac{dE(t)}{d(\ln t)} \right)^{-1} \quad (4)$$

where $dE(t)/d(\ln(t))$ is a numerical constant deduced from experimental data for t values that satisfy the condition $Fo \gg 1$ in the absence of thermal convection.

For practical applications of the THW method, and in particular with the miniature hot-wire cells developed in the present work for *special* electrically conductive liquids, the wire and liquid sample dimensions are finite and deviations from the ideal model have to then be evaluated.

3 Experimental Apparatus

The whole experimental apparatus is composed of an electrical measurement system (Sect. 3.3) associated with a specialized stainless-steel vessel (Sect. 3.2) equipped with an independent patented tantalum hot-wire probe (Sect. 3.1).

3.1 Tantalum Hot-Wire Probe

The standard “sensing” element consists of a straight tantalum wire about 15 mm in length (l) and 25 μm in diameter (d) (purity: 99.9%) spot welded at its ends to 1-mm diameter tantalum wires (prongs) partially embedded (Fig. 1) in a 4-mm diameter ceramic rod. This assembly constitutes the hot-wire probe. The tantalum elements (hot wire and prongs), which have to be immersed in *special* liquids, are electrically insulated in situ (after spot-welding of the hot wire on the prongs) with a coating layer of tantalum pentoxide (Ta_2O_5), according to a procedure described in [7]. This coating layer, with a thickness of about 70 nm, is formed by anodization and has proved to be strongly adherent and electrically efficient throughout a series of temperature cycles, with temperatures up to 550 K, for thermal-conductivity measurements in toluene [10].

Non-standard tantalum-coated hot wires, with diameters as small as 5 μm , and a length $l \approx 1.5$ mm (corresponding to $l/d \approx 300$ instead of $l/d = 600$ for the previous standard probe) have also been manufactured and show the potential of

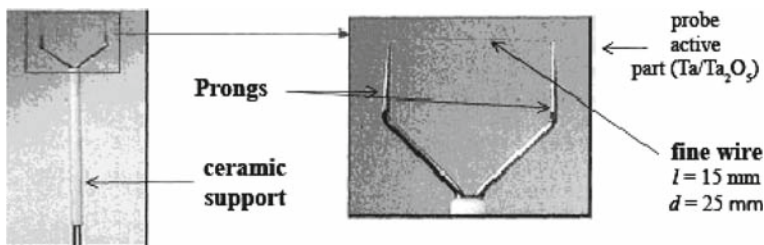


Fig. 1 Tantalum measuring probe

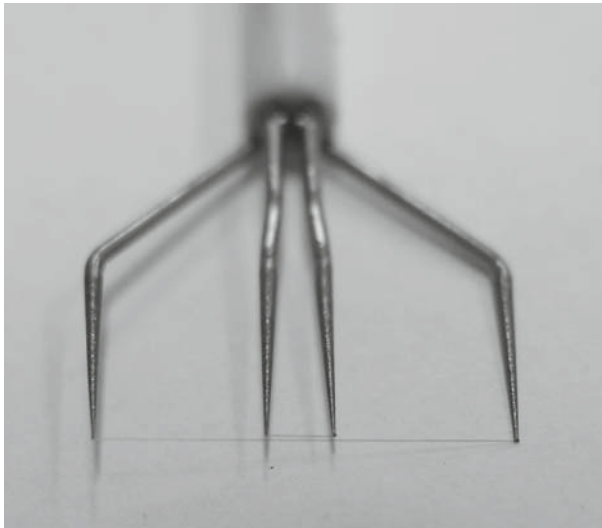


Fig. 2 Two-wire probe

probe miniaturization. These thinner diameter tantalum wires have been obtained from standard manufactured 25- μm wires (minimum available diameters) after a controlled electrochemical diameter reduction using a specific acid mixture and procedure.

In fact, most tantalum probes used for our thermal-conductivity measurements are made of two parallel tantalum wire probes (Fig. 2) which allow quasi-simultaneous thermal-conductivity and thermal-diffusivity measurements with the same liquid sample. This last type of probe, which associates a standard ($d = 25 \mu\text{m}$) and a non-standard ($d \approx 5 \mu\text{m}$) tantalum wire, is described in a recent patent [23], and the corresponding original method of thermal-diffusivity measurements will be presented in a future paper.

3.2 Measuring Cell

The cell is composed of a stainless-steel vessel of 2 cm³ volume with the tantalum wire probe mounted on the top with a Teflon gasket. The cell is designed to work in the 0.1 to 1 MPa pressure range and the 0 to 80°C temperature range with the vessel immersed in a liquid thermostated bath at a controlled temperature. The cell is also designed to allow easy filling and removal of the liquid in the vessel which includes, for this purpose, two specific liquid ports.

Figure 3 shows the patented [23] measuring cell (perspective view (Fig. 3a) and vertical section (Fig. 3b)); on Fig. 3, the following key parts (with the corresponding reference numbers) can be observed:

- inferior (4) and superior (6) parts of the cell
- chamber for the studied liquid sample (8)
- measuring probe (14, 60)

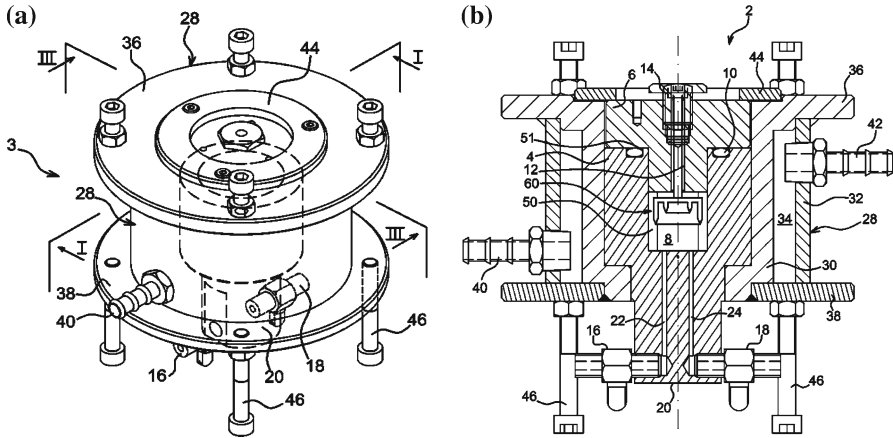


Fig. 3 Patented measuring cell [26]: (a) perspective view and (b) vertical cross section according to the plan I-I of Fig. 3a. Key parts: inferior (4) and superior (6) parts of the cell, chamber for the studied liquid sample (8), measuring probe (14, 60), input and output for the studied liquid (16, 18), and input and output for the thermostatic liquid (40,42)

- input and output for the studied liquid (16, 18)
- input and output for the thermostatic liquid (40,42)

3.3 Measurement System

A block diagram of the electrical measuring system is shown in Fig. 4. It is composed of the measuring probe, a source meter (Keithley 2400), a nanovoltmeter (Keithley 2182), and a microcomputer which links and controls the two meters.

The source meter can supply and measure very precisely the voltage or current by means of a four-wire technique. The precision of the sourcing current in the working range (0–100 mA) is 0.034% of the reading + offset. Because of the limited

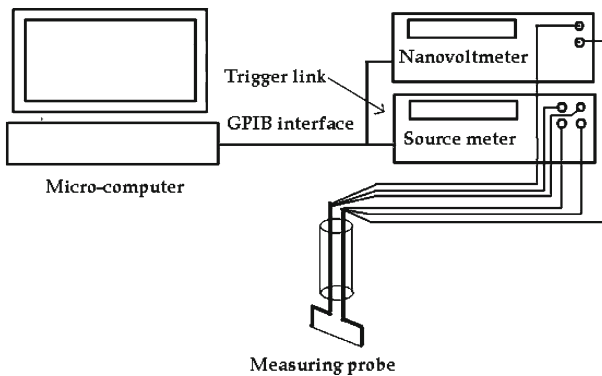


Fig. 4 Block diagram of the measuring system

measurement capabilities of the meter, it was necessary to add a nanovoltmeter to ensure better precision. On the (0–100 mV) range, the resolution of this meter is 10 nV and the uncertainty over one year is better than 30 ppm of reading. The speed of acquisition of the source meter and nanovoltmeter can vary, depending on the choice of the integration time NPLC (number of power line cycles). To provide the best signal-to-noise ratio, the NPLC value is often chosen corresponding to a 20-ms sampling period and typically an acquisition frequency of 10 Hz. The two meters are connected to a microcomputer via a GPIB interface. A LabView[®] program (National Instruments), specifically written for this application, controls the meters and reads the data.

4 Experimental Results

4.1 Probe Calibration

As observed by other researchers [11], tantalum is not usually utilized in the field of resistance thermometry and the experiments confirm that the temperature coefficient β_0 can vary slightly with manufacturer, probably because of impurities. So, each probe has to be calibrated before thermal-conductivity measurements are initiated.

An example of probe calibration (electrical resistance R versus temperature T) is shown in Fig. 5 for T between 0 and 25°C; this calibration confirms the excellent linearity (assumed in Eq. 3) between R and T in this temperature range, with a temperature coefficient value $\beta_0 = 3.37 \times 10^{-3} \text{K}^{-1}$; it can be noted that, for a given tantalum wire, this β_0 value is not changed by the anodic oxidation process to form the Ta_2O_5 oxide layer, the nanometric thickness of which can easily be determined from electrical resistance measurements [22].

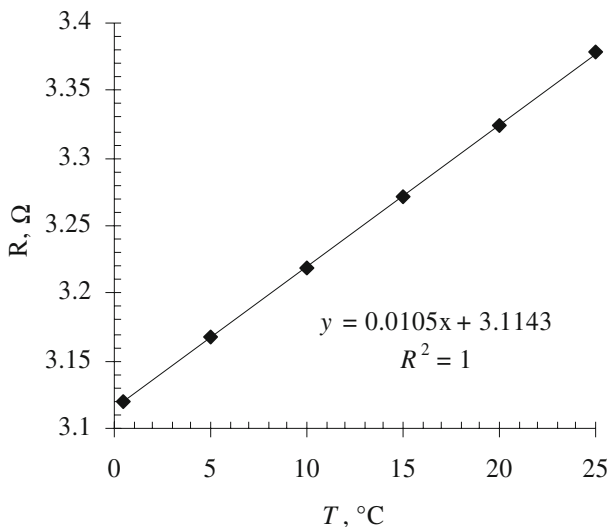


Fig. 5 Probe calibration versus temperature

4.2 Results

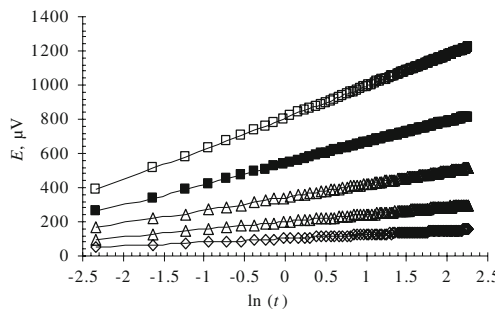
Preliminary validation experiments have been carried out with measurements of the thermal conductivity of water and toluene, liquids most commonly used as Refs. [1, 9, 11, 24] and also of Galden[®] liquid, a dielectric perfluorinated liquid with a lower thermal conductivity. The results of these experiments are presented in the following sections. An original application of the method to thermal-conductivity measurements in pure nitric acid is then presented and discussed.

4.2.1 Water

The water used for thermal-conductivity measurement is ultra-pure, with an electrical conductivity $\rho = 8.2 \text{ M}\Omega \cdot \text{cm}$. Figures 6 and 7 show, for water at 0 and 25°C, respectively, at 0.1 MPa and for various values of the electrical current i (80, 70, 60, 50, and 40 mA), typical curves used for the determination of the thermal conductivity from Eq. 4, with the corresponding measured λ values. On these figures, E represents the potential difference between the potential at unspecified and initial times.

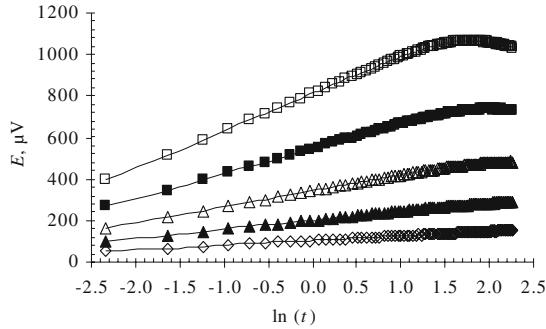
It should be noted that the appearance of free convection can easily be detected during the experimental run, when the observed voltage as a function of $\ln(t)$ departs from linearity. An analysis of these figures shows that an increase in the i values leads to an earlier onset of convection according to the fact that, with higher currents, the temperature rises more rapidly, with maximum wire heating (for $i = 80 \text{ mA}$) of about 2.7°C (with negligible radiative heat transfer). In addition, from Figs. 6 and 7, it appears that, for a given current, the beginning of free convection is slightly dependent on the water temperature due to the influence of the water viscosity, which decreases with increasing temperature.

The measured values of thermal conductivity ($\lambda = 0.56 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 0°C and $\lambda = 0.60 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 25°C) are in good agreement with those ($\lambda = 0.609 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 25°C) found in other studies [9]. The well-known increase of thermal conductivity with the water temperature is observed along with a quasi-independence



i (mA)	80	70	60	50	40
$\lambda(\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$	0.557	0.559	0.560	0.558	0.550

Fig. 6 Transient responses of the hot wire in water at 0°C for $i = 80, 70, 60, 50,$ and 40 mA ($\square, \blacksquare, \triangle, \blacktriangle, \diamond$) and corresponding measured λ values



i (mA)	80	70	60	50	40
λ (W · m ⁻¹ · K ⁻¹)	0.607	0.601	0.602	0.604	0.603

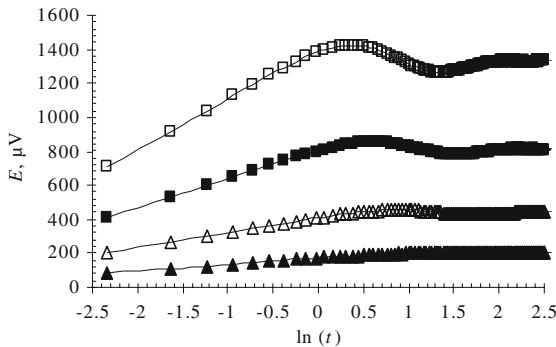
Fig. 7 Transient responses of the hot wire in water at 25°C for $i = 80, 70, 60, 50,$ and 40 mA ($\square, \blacksquare, \triangle, \blacktriangle, \diamond$) and corresponding measured λ values

of the measured thermal conductivity with the current value in the range from 40 to 80 mA. The uncertainty of these measured values is discussed in Sect. 4.3.

4.2.2 Toluene

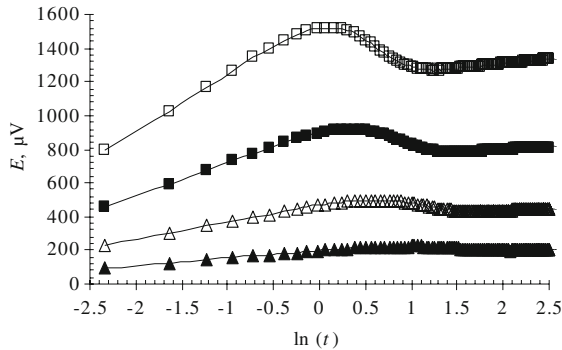
The second reference liquid used for these preliminary validation tests is toluene from Merck with 99.9% purity. The results of the experiments carried out for the determination of the thermal conductivity of toluene are presented in Figs. 8 and 9 at 0 and 25°C, respectively.

These figures give, for different current values (60, 50, 40, and 30 mA), the measured λ values at 0°C ($\lambda = 0.142$ W · m⁻¹ · K⁻¹) and 25°C ($\lambda = 0.135$ W · m⁻¹ · K⁻¹), respectively. One notes that these values are in good agreement with those found in



i (mA)	60	50	40	30
λ (W · m ⁻¹ · K ⁻¹)	0.141	0.141	0.142	0.142

Fig. 8 Transient responses of the hot wire in toluene at 0°C for $i = 60, 50, 40,$ and 30 mA ($\square, \blacksquare, \triangle, \blacktriangle$) and corresponding measured λ values



i (mA)	60	50	40	30
λ ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	0.136	0.135	0.135	0.135

Fig. 9 Transient responses of the hot wire in toluene at 25°C for $i = 60, 50, 40,$ and 30 mA (□, ■, △, ▲) and corresponding measured λ values

the literature ($\lambda = 0.13855 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 0°C and $\lambda = 0.13087 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 25°C) in [25] and ($\lambda = 0.131 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 25°C) in [9]. The differences (2–3%) between measured and reference values might be due to both model errors (use of a short wire as heat source) and measurement errors (Sect. 4.3), rather than convective phenomena which can easily be detected from the E [$\ln(t)$] responses.

The same general conclusions concerning the appearance of free convection and the influence of liquid temperature on thermal-conductivity values presented previously for water are the same for toluene, with maximum wire heating of about 4.6°C for $i = 60$ mA.

4.2.3 Galden® HT90

Galden® is a generic trade mark of perfluorinated liquids principally used as cooling dielectric liquids. Their precise names follow a nomenclature HTXX where XX is a number increasing with molar mass.

Figures 10 and 11 show experimental curves used for the determination of the thermal conductivity of Galden®HT90 (from Solvay, with a reported value $\lambda = 0.07 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 25°C) at 0°C ($\lambda = 0.066 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) and 25°C ($\lambda = 0.060 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$), respectively, with currents i from 30 to 60 mA. The same general conclusions concerning the onset of free convection and the influence of liquid temperature on thermal-conductivity values presented previously for water or toluene are similar for Galden®HT90, with maximum wire heating of about 7.4°C for $i = 60$ mA.

For such a liquid where the thermal conductivity is lower than that of water or toluene (factor of about 10 in comparison with water), it can be observed that, for given i values, maximum wire heatings are greater and conductive linear time ranges are shorter than the same parameters for either water or toluene; this λ dependence is general

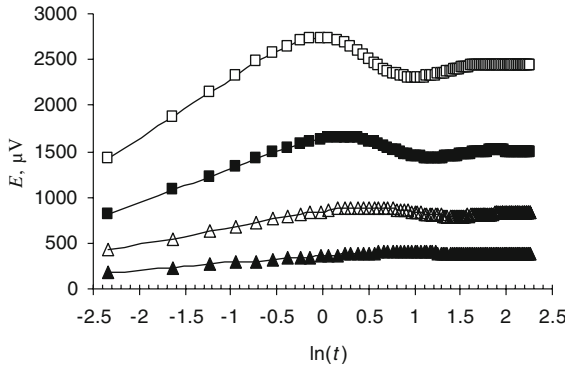


Fig. 10 Transient responses of the hot wire in Galden[®] HT90 at 0°C for $i = 60, 50, 40,$ and 30 mA ($\square, \blacksquare, \triangle, \blacktriangle$) and corresponding measured λ values

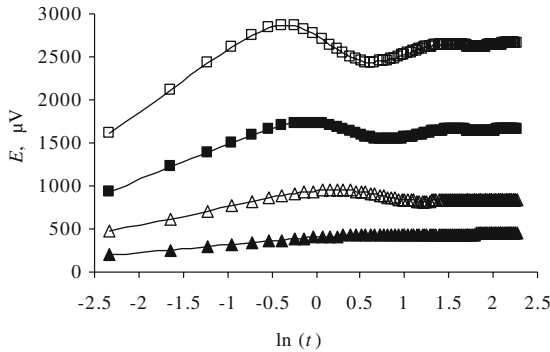
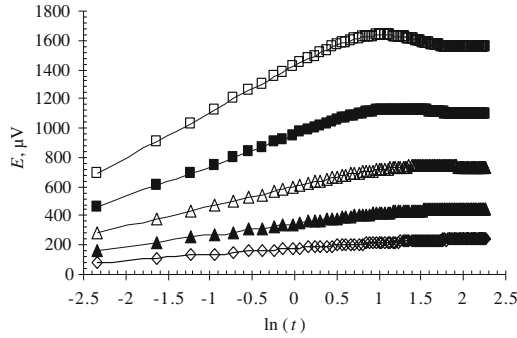


Fig. 11 Transient responses of the hot wire in Galden[®] HT90 at 25°C for $i = 60, 50, 40,$ and 30 mA ($\square, \blacksquare, \triangle, \blacktriangle$) and corresponding measured λ values

and easily explained from heat transfer regimes (conductive + convective) around the wire.

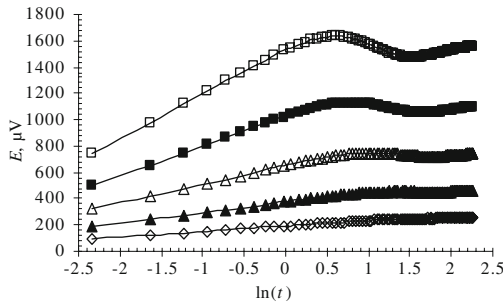
4.2.4 Nitric acid

Nitric acid is very commonly used in industrial chemistry, in particular, for fabrication of many propellants. The lack of physical properties’ knowledge, such as thermal conductivity and thermal diffusivity, often results in its very oxidative and corrosive properties. However, some thermal-conductivity values of nitric acid, with concentrations up to 50%, were published by Van Der Held et al. [13] in 1949 from experiments with a lacquered wire embedded in a glass capillary tube; the thermal-conductivity



<i>i</i> (mA)	80	70	60	50	40
λ (W·m ⁻¹ ·K ⁻¹)	0.321	0.320	0.319	0.317	0.321

Fig. 12 Transient responses of the hot wire in pure nitric acid at 0°C for *i* = 80, 70, 60, 50, and 40 mA (□, ■, △, ▲, ◇) and corresponding measured λ values



<i>i</i> (mA)	80	70	60	50	40
λ (W·m ⁻¹ ·K ⁻¹)	0.321	0.322	0.321	0.322	0.323

Fig. 13 Transient responses of the hot wire in pure nitric acid at 25°C for *i* = 80, 70, 60, 50, and 40 mA (□, ■, △, ▲, ◇) and corresponding measured λ values

values of concentrated nitric acid at 10% and 50% presented by these authors are, respectively, 0.552 W · m⁻¹ · K⁻¹ and 0.412 W · m⁻¹ · K⁻¹. Moreover, they show a linear dependence of thermal conductivity with the nitric acid concentration.

Figures 12 and 13, for five current values (80, 70, 60, 50, and 40 mA), show the transient responses of the hot wire in pure nitric acid at 0 and 25°C, respectively, with maximum wire heating less than 3.9°C for *i* = 80 mA and 1°C for *i* = 50 mA. The median values of the thermal conductivity are 0.319 W · m⁻¹ · K⁻¹ at 0°C and 0.322 W · m⁻¹ · K⁻¹ at 25°C. These values are in good agreement with the values given in [13] for lower concentrations, taking into account the linear dependence observed by the authors.

4.3 Uncertainties

Many authors have established the different corrections to be taken into account for thermal-conductivity determination by the hot-wire technique [1,3,26] when there are deviations from the ideal state, namely, finite wire length and radius, finite container, etc. These corrections δT_i (following the nomenclature used by [1]) applied on the measured temperature ΔT_W of the wire, can be written in the following form:

$$\Delta T = \Delta T_W(t) + \sum_i \delta T_i \quad (5)$$

where ΔT is the theoretical temperature difference with regard to the ideal case.

The corrections can often be calculated or are generally small enough to be neglected if sufficient experimental precautions are taken. For the patented apparatus used (cell and probe), the length-to-diameter ratio ($l/d = 600$) and the minimum distance between wire and cell wall are large enough to eliminate significant errors. Moreover, for the liquids and wire heatings used, Knudsen effects, compressive work, or radiative transfer are negligible. As discussed previously (Sect. 4.2.1), the appearance of parasitic convective heat transfer around the wire can easily be experimentally detected (and therefore eliminated for λ determination); the appearance of free convection is clearly dependent on the liquid and wire heating (see Figs. 6–13). In fact, for short hot wires like those used for the present experiments, the main error for λ determination is coming from the conductive heat transfer between the ends of the finite wire and the supporting prongs; a theoretical analysis of this error has been made in [27], with an upper limit of the relative value given by

$$\varepsilon = \frac{r_0}{l} \sqrt{(\lambda_1/\lambda) \ln(4at_e/r_0^2 C)} \quad (6)$$

where λ_1 is the thermal conductivity of the wire, λ and a are the liquid thermal conductivity and thermal diffusivity, respectively, t_e is the measurement time, r_0 is the wire radius, and $C = 1.781$ (Sect. 2).

According to [7], the upper limit of the calculated error is less than 4% for the present experiments, depending on liquid properties. The instrumental uncertainties are negligible, as seen in Sect. 3.3. The length of the wire appears indirectly in Eq. 4 by the value of q , the heat flux per unit length; the uncertainty in its determination leads to an additional uncertainty of less than 1% for wire lengths greater than 10 mm.

In conclusion, the total uncertainty in the thermal-conductivity absolute measurement is less than 5%, depending on fluid properties, the worst case corresponding to lower thermal conductivity in liquids. A smaller uncertainty could be obtained with the use of reference liquids (water, toluene, etc.) and relative measurements with the same probe.

4.4 Discussion

From these experimental results, it can be deduced that

- The maximum temperature rise ΔT_{\max} of the sensor wire is less than 7.5°C for all the linear zones of the response $E(\ln(t))$ which are presented for different liquids and current intensities i .
- The time range (t_{\min}, t_{\max}) of the linear zone is dependent on the liquid and sensitivity to the current i , with t_{\max} decreasing with increasing values of i (early appearance of convection).
- The λ values, calculated from the regression equation of the linear zones are well validated with published values and are not meaningfully sensitive to i values, over the tested i ranges. These results show that any of the tested i values is suitable, because of the sufficiently small wire temperature rises and sufficiently large time ranges (t_{\min}, t_{\max}) observed.
- For thermal-conductivity measurements in pure nitric acid, a current i less than 50 mA (with the total heat released in the wire $Q \leq 10^{-2}$ J) associated with 25- μm diameter tantalum wire probe leads to a wire heating of less than 1°C with an uncertainty less than 5% on the λ value.

5 Conclusion

The TSHW method and the associated apparatus presented in this paper, with an original short ($l < 15$ mm) anodized thin ($d < 25$ μm) tantalum wire probe and a miniaturized measurement cell, has proved to be suitable for measuring the thermal conductivity of reference liquids such as toluene and water, with liquid sample volumes smaller than 2 cm^3 and with absolute estimated uncertainties better than 5%. For other liquids, better absolute accuracies can be obtained (if necessary) from relative measurements in relation with reference liquids, whose thermal conductivities are known with uncertainties less than 0.5% from classical long-wire THW methods [2] using larger liquid samples.

This TSHW method has been successfully tested for highly corrosive and electrically conducting concentrated nitric acid solutions, for which minimum liquid sample volumes and safe experimental procedures are required. This method is now used by CEA, in place of an indirect “flash method” [18], for thermal-conductivity measurements in such liquids. In practice, for this purpose, the probe used is a patented [26] two parallel tantalum wire probe which allows quasi-simultaneous independent measurements of thermal conductivity and thermal diffusivity. The direct measurement of this last property is realized according to an original method which requires the use of two parallel wires and will be described in a future paper.

As demonstrated for concentrated nitric solutions, this method and its associated patented apparatus are also usable, with similar accuracies, for all liquids compatible with the tantalum hot-wire probe technology.

References

1. J.J. Healy, J.J. de Groot, J. Kestin, *Physica* **82C**, 392 (1976)
2. S.G.S. Beirao, M.L.V. Ramires, M. Dix, C.A. Nieto de Castro, *Int. J. Thermophys.* **27**, 1018 (2006)
3. Y. Nagasaka, A. Nagashima, *J. Phys. E: Sci. Instrum.* **14**, 1435 (1981)
4. E. Yamasue, M. Susa, H. Fukuyama, K. Nagata, *J. Cryst. Growth* **234**, 121 (2002)
5. X. Zhang, M. Fujii, *Int. J. Thermophys.* **21**, 71 (2000)
6. H. Fukuyama, T. Yoshimura, H. Yasuda, H. Ohta, *Int. J. Thermophys.* **27**, 1760 (2006)
7. A. Alloush, W.B. Gosney, W.A. Wakeham, *Int. J. Thermophys.* **3**, 225 (1982)
8. K. Kawamata, Y. Nagasaka, A. Nagashima, *Int. J. Thermophys.* **9**, 317 (1988)
9. M.L.V. Ramires, J.M.N.A. Fareleira, C.A. Nieto de Castro, M. Dix, W.A. Wakeham, *Int. J. Thermophys.* **14**, 6 (1993)
10. M.L.V. Ramires, C.A. Nieto de Castro, J.M.N. Fareleira, W.A. Wakeham, *J. Chem. Eng. Data* **39**, 186 (1994)
11. R.A. Perkins, M.L.V. Ramires, C.A. Nieto de Castro, *J. Res. Natl. Inst. Stand. Technol.* **105**, 255 (2000)
12. P.S. Davis, F. Theeuwes, R.J. Bearman, R.P. Gordon, *J. Chem. Phys.* **55**, 4776 (1971)
13. E.F.M. Van Der Held, F.G. Van Drunen, *Physica XV* **10**, 865 (1949)
14. J.G. Bleazard, A.S. Teja, *J. Chem. Eng. Data* **40**, 732 (1995)
15. R.M. DiGuilio, R.J. Lee, S.M. Jeter, A.S. Teja, *ASHRAE Trans.* **96**, 702 (1990)
16. A. Griesinger, K. Spindler, E. Hahne, *Heat Mass Transfer* **32**, 419 (1997)
17. A. Griesinger, W. Heidemann, E. Hahne, *Int. Comm. Heat Mass Transfer* **26**, 451 (1999)
18. D. Roy, CEA Report (1997)
19. S.M. Cardonne, P. Kumar, C.A. Michaluk, H.D. Schwartz, *Int. J. Refract. Met. Hard Mater.* **13**, 187 (1995)
20. N.D. Milosevic, G.S. Vukovic, D.Z. Pavicic, K.D. Maglic, *Int. J. Thermophys.* **20**, 1129 (1999)
21. F. Cardarelli, P. Taxil, A. Savall, *Int. J. Refract. Met. Hard Mater.* **14**, 365 (1996)
22. D.A. Vermilyea, *Acta Metall.* **1**, 282 (1953)
23. G. Thevenot, J. Saillard, J.-P. Maye, J.-Ph. Garnier, *EP 1724572 A1*, European Patent Office (2006)
24. W.A. Wakeham, M. Zalaf, *Fluid Phase Equilib.* **36**, 183 (1987)
25. H. Watanabe, *Int. J. Thermophys.* **18**, 2 (1997)
26. X.-G. Liang, *Meas. Sci. Technol.* **6**, 467 (1996)
27. P.G. Knibbe, *Int. J. Heat Mass Transfer* **29**, 463 (1986)