International Journal of Thermophysics, Vol. 26, No. 1, January 2005 (© 2005)
DOI: 10.1007/s10765-005-2370-2

A Novel Comparative Photothermal Method for Measuring Thermal Diffusivity[1]

M. Broussely,[2] A. P. Levick,[2,3] and G. J. Edwards[2]

A novel comparative method has been developed at the National Physical Laboratory (NPL) to measure the thermal diffusivity of semi-infinite samples without *a priori* knowledge of the boundary conditions. It is based on photothermal radiometry, and involves the detection of modulated thermal radiance from a target irradiated by a modulated, focused diode laser beam with a power of 1 W. The technique exploits the fact that the frequency response of the surface temperature modulation scales with thermal diffusivity for a given target geometry (this is a fundamental property of the heat diffusion equation). In the process two samples are measured, one of which is known, and the diffusivity of the second material is derived from scaling the results over frequency. Measurements on samples of platinum and Inconel have shown the validity of the methodology but also raised issues concerning the difficulty of accurate measurements due to surface coatings or roughness.

KEY WORDS: comparative method; laser absorption radiation thermometry (LART); laser; photothermal radiometry; thermal diffusivity.

1. INTRODUCTION

A knowledge of the thermal properties of materials is fundamental in the design of most engineering models where the temperature is a state variable of influence over other properties and therefore over the behavior of any complex system. Thermal diffusivity is among the thermal properties widely measured on prepared samples using various techniques from the Ångström temperature-wave method [1] to the mirage method and the

---

[1] Paper presented at the Fifteenth Symposium on Thermophysical Properties, June 22–27, 2003, Boulder, Colorado, U.S.A.

[2] National Physical Laboratory, Teddington, Middlesex TW11 0LW, United Kingdom.

[3] To whom correspondence should be addressed. E-mail: andrew.levick@npl.co.uk

well-known flash method [2]. Simultaneous measurement of temperature and thermophysical properties such as emissivity and thermal diffusivity and conductivity is the aim of developments of photothermal techniques at the NPL. This paper describes the comparative photothermal method to determine the thermal diffusivity of a sample without knowledge of its boundary conditions or emissivity.

The experimental procedure is to measure the frequency responses of the modulated thermal radiance for known and unknown samples placed in the same environment. A computer algorithm searches for the frequency-scaling factor that gives the closest overlap between the frequency responses. The frequency scaling factor is the ratio of thermal diffusivities $D_{\text{knonwn}}/D_{\text{unknown}}$. Both the amplitude and phase shift of the modulated thermal radiance signal are retrieved via lock-in detection, and either can be used in this technique. For a high sensitivity, the laser modulation frequency must span a regime where the thermal diffusion length $\delta=\sqrt{\frac{2D}{\omega}}$ (D is the thermal diffusivity and ω is the modulation frequency) is comparable with the laser spot size. The overlap between the two scaled responses should be maximized and include the region where there is a transition between spherical and plane thermal-wave propagation. The results presented in this paper are for Inconel 600 and platinum.

The technique has been incorporated into the NPL fiber-optic based laser absorption radiation thermometry (LART) system as part of the ongoing development of a multi-thermal property instrument capable of undertaking *in-situ* measurements of the temperature, thermal diffusivity, thermal conductivity and spectral emissivity of industrial targets, hence the samples should not need any preparation.

2. THEORY AND METHOD

This work involves the development of a scaling method for measuring the thermal diffusivity of materials above 300°C. In photothermal radiometry, a laser is modulated and focused onto a target surface, which induces a small temperature modulation. The corresponding modulation in the thermal radiance is detected. Various thermal properties can, in principle, be deduced from measurements of modulated (ac) and steady (dc) thermal radiances, including temperature, spectral emissivity, thermal diffusivity, and thermal conductivity.

This is a comparative method, where the frequency responses due to targets of unknown and known thermal diffusivity are compared. Therefore, it does not require an explicit knowledge of such boundary conditions as the time and space profile of the heating laser beam. Considering a periodic modulated pump laser focused onto an opaque target, one can express the heat diffusion equation for a Fourier component of intensity $P = P\,(x, y, z)\,e^{j\omega t}$ as

$$\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} - \frac{1}{D}\frac{\partial}{\partial t}\right] \Delta T\,(x, y, z, t) = -\frac{\varepsilon}{K} P\,(x, y)\,e^{j\omega t}, \tag{1}$$

where ω is the laser modulation frequency, D is the thermal diffusivity, and ΔT is the temperature modulation. [Note: $P(x, y, z) = P(x, y)$ for an opaque material for which total absorption of the laser occurs at the surface.] In the steady-state condition as $t \to \infty$, the temperature modulation can be expressed as

$$\Delta T\,(x, y, z, t) = \Delta T_0\,(x, y, z)\,e^{j\omega t}, \tag{2}$$

leading to

$$\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} - \frac{j\omega}{D}\right] \Delta T_0\,(x, y, z) = -\frac{\varepsilon}{K} P\,(x, y)\,. \tag{3}$$

An important property of Eqs. (1) and (3) is that the frequency response of heating scales with thermal diffusivity (D) or the time response scales with $\frac{1}{D}$. By setting $\frac{\omega}{D} = \frac{1}{L^2}$ in Eq. (3), the response with respect to L is independent of the material.

In our comparison method, the amplitude of modulated thermal radiance is measured as a function of modulation frequency (i.e., the frequency response) for two targets of known and unknown thermal diffusivity. The frequency and amplitude scaling factors are then determined by fitting the two frequency responses to

$$I^{\lambda_1}_{\lambda_{2,\mathrm{k}}}\,(\omega) = a I^{\lambda_1}_{\lambda_{2,\mathrm{u}}}\,(b\omega) \tag{4}$$

where $I^{\lambda_1}_{\lambda_{2,\mathrm{k}}}$ and $I^{\lambda_1}_{\lambda_{2,\mathrm{u}}}$ are the amplitudes of the modulated thermal radiance for known and unknown targets. a is the amplitude scaling factor due to the difference of emission properties of the sample surface. The equality (Eq. (4)) results in $\frac{\omega}{D_\mathrm{k}} = \frac{b\omega}{D_\mathrm{u}}$, and the thermal diffusivities of the unknown and known targets are thus related by the frequency-scaling factor $b = \frac{D_\mathrm{u}}{D_\mathrm{k}}$.

To achieve good sensitivity, the laser modulation frequencies must span a regime where the thermal diffusion length ($\sqrt{\frac{2D}{\omega}}$) is comparable with the laser spot size or target field diameter (i.e., the intermediate between spherical and plane thermal wave propagation). It is also desirable to maximize the overlap between the scaled modulation frequencies.

The above analysis will be only valid provided the two samples have identical boundary conditions. This is partially satisfied by ensuring that both samples are large compared with the imaged field area. The boundary condition of the sampled surface is given by

$$\frac{\partial T}{\partial z} - \mu T = 0 \quad (z = 0) \tag{5}$$

where μ is the heat loss factor composed of convective and radiative terms. The radiative component of the surface heat loss factor is given approximately by

$$\mu = \frac{4\varepsilon\sigma T^3}{k} \tag{6}$$

where ε is the total hemispherical emissivity and σ is Stefan's constant. With $\varepsilon = 1$, $\sigma = 5.7\,10^{-8}\,\mathrm{W{\cdot}m^{-2}{\cdot}K^{-4}}$, $T = 1000°\mathrm{C}$, and $k = 20\,\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$, for example, the value of μ is equal to $23.2\,\mathrm{m^{-1}}$. At a frequency of 25 Hz and for a sample with a (typical) thermal diffusivity of $3 \times 10^{-5}\,\mathrm{m^2{\cdot}s^{-1}}$, the thermal diffusion factor $\sqrt{\frac{\omega}{2D}}$ is equal to 1618 $\mathrm{m^{-1}}$, and so the surface loss factor is negligible under these conditions.

3. EXPERIMENTAL SETUP

A schematic diagram of the LART apparatus used to measure thermal diffusivity is shown in Fig. 1a. A diode laser of wavelength 840 nm (λ_1) is used with a standard LART detection system: an InGaAs photodiode (LG products GAP 3000), a silicon flat filter and an interference filter centered at $\lambda_2 = 1320$ nm (NBP-1320). The silicon flat filter strongly attenuates any back-scattered laser radiation at 840 nm, thus protecting the photodiode from damage, while transmitting thermal radiance at 1320 nm. The optical head consists of a concave spherical mirror and the end facet of a fiber bundle, both mounted in a steel tube with an end-window for protection from dust (see Fig. 1b). The imaging is configured so the end facet of the fiber bundle and the target lie at two conjugate points of the mirror. By moving the end facet along the optical axis of the mirror, the target distance can be readily adjusted. The use of a mirror gives the advantage of no chromatic aberration. The optical fiber bundle is made up of 130 fibers, each with a core diameter of 100 μm (except two that have a diameter of 200 μm and positioned at the center of the bundle) and made from enhanced infrared transmitting silica. It splits into five branches at the other end. Three branches are smaller bundles, and two are the 200 μm single fibers. For this experiment we use only these two single fibers, one

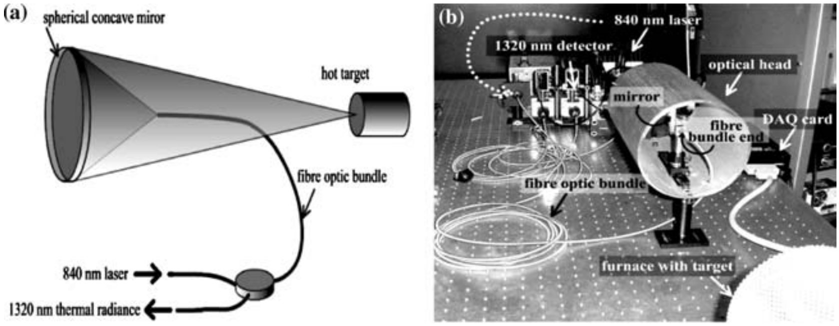

Fig. 1. Experimental apparatus; (a) LART thermal diffusivity measurement setup and (b) photo of the LART setup.

for the laser transmission and the other one to carry out the detection, with an optical configuration to get a magnification of two. Moreover, the optical head has to be slightly defocused so that the modulated temperature area will be imaged onto the fiber carrying the radiation to the detector; the exact focus position has to be avoided.

The data acquisition (DAQ) computer comprises a National Instruments PXI DAQ system and a SCC-2345 acquisition device. The photodiode signal is fed into a SCC-AI06 input module. This module comprises a low-pass multi-pole filter with a cut-off frequency 10 kHz. A high pass RC filter ($C = 0.22\,\mu F$ and $R = 22\,M\Omega$) is inserted before this input to subtract any dc signal without affecting significantly the measured modulated signal amplitude even at frequencies as low as 0.4 Hz. The reference TTL square wave from the laser modulation is fed into a feedthrough module SCC-FT01. The A–D channels are sampled at 50 kHz during a minimum of six periods, giving digitized waveform arrays. Amplitudes and phases are computed from the thermal radiance and TTL digitized waveform arrays using a software phase sensitive detection algorithm. The software is written in National Instruments LabView$^{\mathrm{TM}}$. To allow statistical estimations, *e.g.,* standard deviation, a set of ten consecutive measurements is taken for each frequency. For each sample a series of readings is taken for each chosen frequency in a given range. Typically, 45 frequencies uniformly spaced on a logarithmic scale between 0.5 and 1000 Hz. Each reading comprises the amplitude and phase shift (average and standard deviation over the 10 measurements for each frequency).

The acquisition system filters induce frequency-dependent phase shifts which are determined by an independent experiment. An infrared LED driven by a function generator is positioned in front of the fiber end (the optical filters have been removed from the detector). The signal phase shift (due to the system) is measured with respect to the driving sine wave. These measurements are used to correct the phase-shift results from the thermal diffusivity experiments. The results are then scaled either manually or through a curve-fitting algorithm written in Matlab®.

The samples are an Inconel 600 rod of 36 mm diameter with a hole to insert a platinum rod of 8 mm diameter, both being originally finely polished. We also used an Inconel sample with an oxide layer of the order of 100 μm at the time of the experiment. The series of experiments were carried out with the rods placed in a tube furnace, in atmosphere, and the polished Inconel sample got progressively oxidized while heated at about 875°C. One aim of the developed instrument is to be insensitive enough to small scales so that measurements do not need any sample preparation; we will see that the surface condition can have a strong influence on the photothermal measurements, especially regarding the phase shift.

4. EXPERIMENTAL RESULTS

4.1. Exploitation of Results by Amplitude and Phase Frequency Scaling

As already mentioned, the laser modulation frequencies must cover a range where the thermal diffusion length $\delta = \sqrt{\frac{2D}{\omega}}$ is comparable with the laser spot size and target field diameter. There is a cut-off frequency where the response is transitional from three-dimensional (3D) to 1D behavior. The sensitive part of the amplitude frequency response corresponds to this roll-off, and it is the principal part of the data to scale. Using an algorithm of curve fitting written on Matlab®, we can scale both the amplitude and phase-shift results in frequency. The results shown here are for Inconel 600 and platinum (of purity 99.9%) samples maintained at 875 °C with the target surface positioned at 191.5 mm from the optical head, the focus distance being 187.5 mm. We observe that at certain frequencies the data are biased by effects due to parameters other than the thermal diffusivity (e.g., change of slope at high frequencies for the amplitude response). The biased data are discarded before proceeding to the curve fitting. The results of figure Fig. 2 give a ratio of $\frac{D_k}{D_u} = 5.55\,(\pm 0.37)$ for an $a = 0.0323$. We observe that the platinum amplitude presents a second change of slope at frequencies over 200 Hz caused by uncertainties on the very low signal itself due to the low emissivity of the polished platinum sample.

Concerning the phase, as there is no equivalent to the amplitude coefficient a, the phase shift should only vary on the frequency scale as a function of the thermal diffusivity. Figure 3a shows that part of the data cannot be scaled, because there are additional physical effects than thermal diffusion through a homogeneous material. For an ideal case at

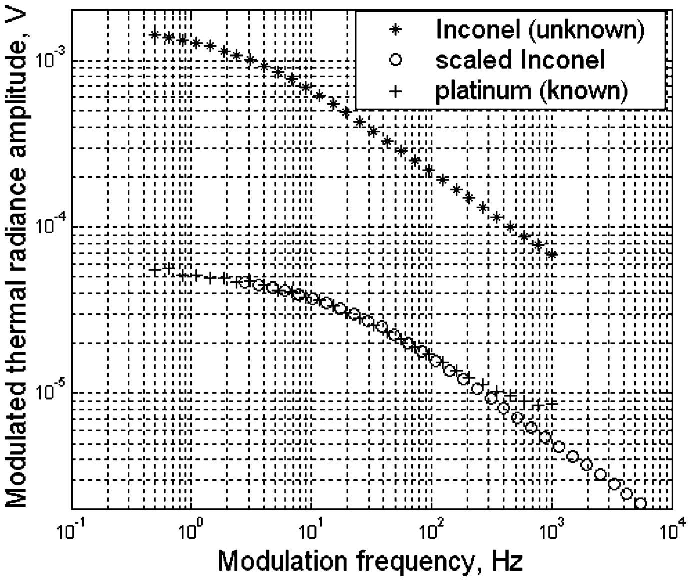

Fig. 2. Scaled amplitude response, $\frac{D_k}{D_u} = 5.55$ and $a = 0.0323$.

high frequencies (hence, a thermal diffusion length much smaller than the laser spot size) we should get a monodimensional behavior, that is, a phase lag of −45° at the surface. But as the δ decreases it approaches the order of magnitude of thin layers (coating, oxide, etc.) or roughness of the surface. The consequence is seen on the phase results of Fig. 3b. In addition to that are numerical errors due to the modulation frequency approaching the digital sample rate of the acquisition system, weaker signal causing higher noise, and also errors due to the filters in the acquisition system the effect of which is difficult to correct accurately at high frequencies. As for the scaling of the amplitude response, only the scalable data points have to be taken into account for the curve fitting and the phase shift is preponderantly sensitive to thermal diffusivity for frequencies lower than about 2 or 3 times the roll-off frequency. The ratio gives

$$\frac{D_k}{D_u} = 5.66\,(\pm 0.11) \quad \text{(Fig. 3b)}.$$

This value is to compare with a reference ratio of 4.26 ± 0.55 obtained from the NPL laser flash thermal diffusivity measurement of the Inconel 600 ($(5.84 \pm 0.3) \times 10^{-6}\,\mathrm{m}^2 \cdot \mathrm{s}^{-1}$) and the platinum literature results [5]. A difference of more than 20% is not satisfactory. However, we have

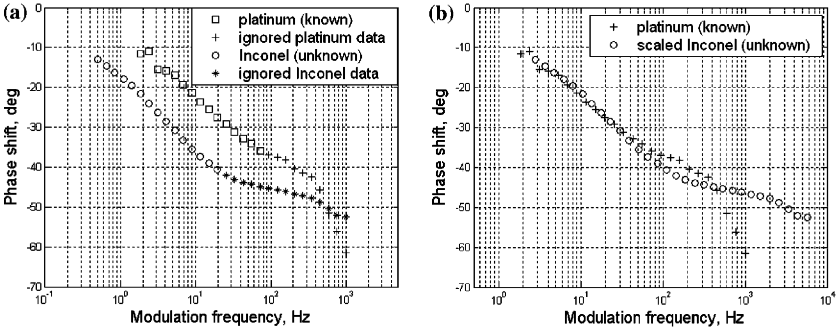

Fig. 3. Scaled phase shift for Inconel and platinum; (a) phase shift responses, data used and ignored and (b) scaled phase response, $\frac{D_k}{D_u} = 5.66$.

obtained responses expected from the photothermal and heat diffusion theory. Moreover, the same method has been implemented at NPL with a Cassegrain optical bench and the scaling results for the same samples were within 1% from the laser flash value ([6]). The method, although validated, proves more difficult to apply with our fiber optic apparatus.

4.2. Discussion on Uncertainties

The error displayed in parentheses is determined as follows. A random uncertainty applies to all data and is monitored by the standard deviation on each series of ten consecutive readings. A Monte Carlo method using those standard deviations is implemented to calculate the subsequent uncertainty on the resulting $\frac{D_k}{D_u}$ value after the curve fitting. The following results show that such a value of uncertainty can take an unrealistically small value, meaning that the corresponding curve fitting was very insensitive to the recorded standard deviation (random noise) of each data point. This obtained value is not satisfactory as it does not take into account the consequences of the uncertainties on all the experimental parameters of influence such as the target distance (laser spot size), orientation, targeted area surface condition, and surface temperature. The effect on the amplitude and phase shift results can be evaluated experimentally or sometimes theoretically. On the other hand, the effect on the cut-off frequency and hence on the thermal diffusivities ratio is very difficult and its experimental determination would be very time consuming.

4.3. Influence of Oxide Layer on the Inconel Sample

The experiments carried out have raised issues concerning various unaccounted for effects on the exploitation of results, particularly due to the target surface conditions. These issues add complication to the method and need to be well understood. Figure 4 shows the frequency response data for an oxidized Inconel sample compared to the same sample after surface polishing. The target is placed within one millimeter from the on-focus position and at 900°C. The signal level (Fig. 4a) is lower due to a decrease in the emissivity. However, a second effect becomes apparent when translating the second amplitude response to the level of the first. At higher frequencies, the slope changes and the normalized amplitude is higher for the oxidized surface than for the polished one. The phase shift response (Fig. 4b) starts identically but diverges with frequency, and the oxidized sample response presents a sudden rise at lower frequencies and with a smaller absolute phase value. The oxide layer (and possibly a rougher surface) causes this behavior at high frequencies (see Refs. 3 and 4 for previous work on the effect of surface layers). Because the surface is relatively rough, it rapidly becomes oxidized. The third curve in Fig. 4 corresponds to the same sample after being held at 900°C for 7 h. Even here we can observe slight changes at high frequencies in addition to the small difference of amplitude due to the emissivity change.

According to the phase results, it seems that even the low frequency part of the phase shift plot has moved, which might be interpreted as an apparent change in thermal diffusivity. However, this shows that some physical parameter, linked to the surface of the sample and other than the diffusivity, affects the modulated thermal radiance amplitude and phase.

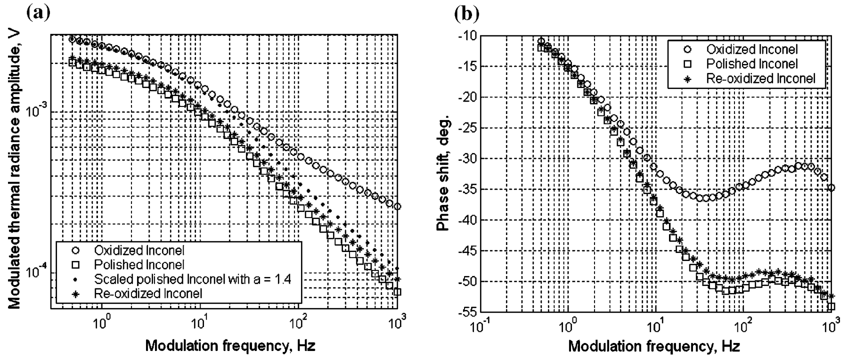

Fig. 4. Oxidized, polished, and re-oxidized Inconel sample at 900°C; (a) Inconel's amplitude response and (b) Inconel's phase shift response.

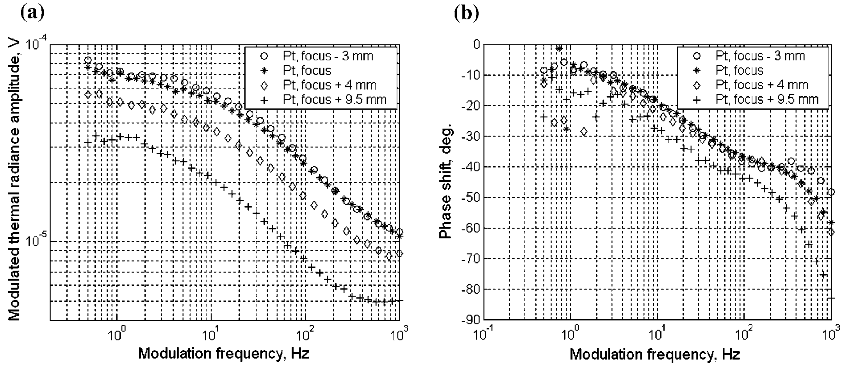

Fig. 5. Influence of distance on platinum sample's response; (a) amplitude and (b) phase shift.

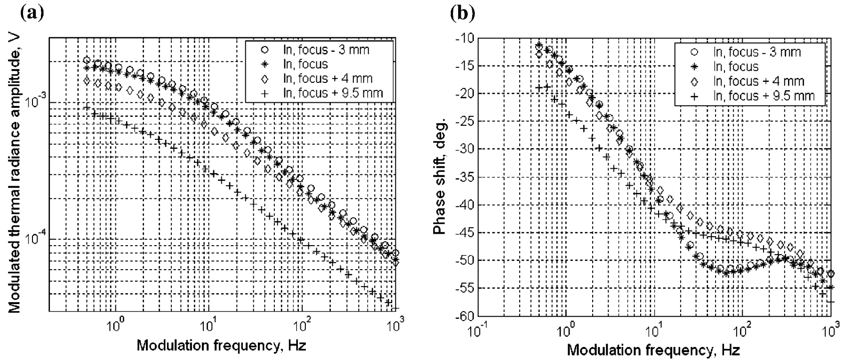

Fig. 6. Influence of distance on Inconel 600 sample's response; (a) amplitude and (b) phase shift.

This point should be analyzed more in detail to complete the validation of the scaling photothermal method.

4.4. Influence of Target Distance (Laser Spot Size)

Both Inconel and platinum samples were measured with different distances between the optical head and the sample surface. The results in amplitude and phase shift are shown in figures Figs. 5 and 6. Defocusing the image of the fiber end has the effect of increasing the laser spot size and consequently the cut-off appears at a lower frequency. The phase shift response then moves toward the lower frequencies when the distance increases. Also, the signal weakens which induces higher uncertainties on the numerical determination of the phase shift values (see Fig. 5b).

Table I. Ratio Values for Different Target Distances. Platinum/Inconel at 875°C

Position of target	$\frac{D_{\mathrm{Pt}}}{D_{\mathrm{In}}}$ from amplitude data	$\frac{D_{\mathrm{Pt}}}{D_{\mathrm{In}}}$ from phase data	Laser flash value
Focus – 3 mm	5.32 ± 0.15	5.95 ± 0.08	4.26 ± 0.55
Focus	6.27 ± 0.21	7.59 ± 0.1	4.26 ± 0.55
Focus + 4 mm	5.55 ± 0.37	5.66 ± 0.11	4.26 ± 0.55
Focus + 9.5 mm	5.4 ± 0.57	5.4 ± 0.21	4.26 ± 0.55

Table I shows the fitted results for four different positions of the optical head. The values obtained for the focus tend to confirm the need to slightly defocus the optical head. The other values, except for the phase fitting result for the "focus −3 mm" position, seem satisfactory considering the random uncertainty budget.

5. CONCLUSION

A comparative method for thermal diffusivity measurements has been integrated into the NPL optical fiber LART instrument. This apparatus provides more flexibility of use, is self aligned, and can be easily transported for on-site measurements. Experiments were carried out on two materials with different properties. The responses obtained, both in amplitude and in phase, are in agreement with photothermal theory and should allow reaching the scaling objective. However, the results were not in good agreement with the value obtained by the laser flash method at NPL, a difference of 20% being observed. The same method, implemented with an optical Cassegrain system has previously shown thermal diffusivity results agreeing very well with the laser flash value. These results were presented at the ICPPP 2002 [6]. Moreover, several issues arose pertaining to the sensitivity of the results to the surface conditions of the target: roughness and superficial layer (oxide, coating). We could also observe that low diffusivity materials present a roll-off in the frequency response at very low frequencies, rendering the measurement long, imprecise, and sometimes impossible.

A significant sensitivity study is needed for this present setup to assess a realistic interval of confidence to apply on the thermal diffusivity results with respect to uncertainties on such parameters as the target distance, orientation, surface condition, homogeneity, temperature, etc.

This work represents a new step in the design of the LART Multi, a fiber optic instrument aiming to simultaneously measure temperature, spectral emissivity, thermal diffusivity and thermal conductivity without a knowledge of the heat source boundary conditions.

ACKNOWLEDGMENTS

This work was carried out as part of the Thermal Metrology Programme funded by the National Measurement System, United Kingdom Department of Trade and Industry.

REFERENCES

1. M. A. Ångström, *Philos. Mag.* **25**:130 (1863).
2. W. J. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abott, *J. Appl. Phys.* **32**:1679 (1961).
3. H. G. Walther, *J. Appl. Phys.* **89**:5 (2001).
4. J. A. Garcia, L. Nicolaides, P. Park, A. Mandelis, and B. Farahkbahsh, *Anal. Sci.* **17**:s89 (2001).
5. Y. S. Touloukian, ed., *Thermophysical Properties of Matter: The TPRC Data Series*, Thermophysical Properties Research Center, Purdue University (IFI/Plenum, New York, 1970–1977).
6. K. Lobato, A. Levick, and G. Edwards, *Rev. Sci. Instrum.* **74**:615 (2003).