Photothermal Technique for in situ Simultaneous Measurement of Thermal properties in addition to Temperature.

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Abstract
The LART (Laser Absorption Radiation Thermometry) is a fibre-optic based instrument developed at the National Physical Laboratory (NPL) to measure temperature independently of target emissivity, reflected radiation from the surroundings and gaseous absorptions. 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 is being extended to measure thermal properties (thermal diffusivity, thermal conductivity and spectral emissivity) with the aim of developing a multi-property LART instrument. It exploits the fact that the frequency response of the surface temperature modulation scales with thermal diffusivity and that the photothermal signal amplitude also depends on the material thermal conductivity. In the process two samples are measured, one of which is known, and the properties of the second material are derived. 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. The Multi LART instrument has large potential for meeting industrial needs for temperature and thermal properties measurements in challenging environments.

1. INTRODUCTION
At NPL, novel techniques based on photothermal radiometry are being developed to measure temperature and thermal properties of targets. The ultimate aim is to produce a “Multi-LART” instrument for in-situ and non-invasive measurement of temperature and thermal properties during industrial processing (e.g. steel manufacture). During the last 10 years, we have developed the LART thermometry method. More recently, we have been developing methods to measure other thermal properties using the same apparatus, including thermal diffusivity, thermal conductivity and spectral emissivity. The methods involve the detection of modulated (ac) and steady-state thermal radiances over a range of laser modulation frequencies and at different wavelengths. This paper describes the new methods, presents initial measurements for Inconel and platinum samples and discusses issues that need to be addressed.

2. THEORY AND METHODS
2.1. Temperature measurement
The following is a simplified theory of the fundamental principles of the Laser Emissivity Free Thermometer technique described as LEFT1 in [3], inspired by previous works [1] and [2]. The photodiode current due to a small, modulated (ac) thermal radiation at wavelength \( \lambda_1 \) caused by photothermal heating by a laser at \( \lambda_2 \) is given by:

\[
I = G \tau_\varepsilon \epsilon_\lambda \frac{P}{K} \left[ \frac{D}{\omega} \right] \Delta \lambda \cos \left( \omega t - \frac{\pi}{4} \right) \frac{2L_0(\lambda_1, T_0)}{\Delta T} \quad (1)
\]

where \( \varepsilon_\lambda \) and \( \tau_\lambda \) the emissivity and optical transmission at \( \lambda_1 \), \( P/\omega \) the power at the frequency \( \omega \), \( \Delta \lambda \) the interference filter bandwidth and \( K \) and \( D \) the thermal conductivity and diffusivity. \( L_0(\lambda_1, T_0) \) is Planck’s function for a black body of temperature \( T_0 \) at \( \lambda_1 \). This relation is only true for a modulation frequency \( \omega \) greater than the cut off frequency \( \omega_0 \) for which the thermal diffusion length equals the laser spot size. The principle is to repeat the photothermal measurement for a laser at \( \lambda_2 \) and detection at \( \lambda_1 \). We see from (1) that the ratio of the two signals \( S_{\lambda_1 \lambda_2} \) and \( S_{\lambda_2 \lambda_1} \) gives (2).

\[
\frac{S_{\lambda_1 \lambda_2}}{S_{\lambda_2 \lambda_1}} = C_{\text{LART}} \frac{L'\left(\lambda_1, T\right)}{L'\left(\lambda_2, T\right)} = C_{\text{LART}} \frac{L'\left(\lambda_1, T\right)}{L'\left(\lambda_2, T\right)} \frac{\epsilon_\lambda}{\epsilon_\lambda} \quad (2)
\]

This ratio varies with temperature but not with target emissivity and line-of-sight transmission factors because these terms cancel in equation (2). \( C_{\text{LART}} \) is the LART calibration coefficient and contains various instrumental parameters. A first measurement is performed for a target of known temperature \( T_0 \) to determine this coefficient for the apparatus configuration. Then the coefficient is used to derive surface temperature from two modulated thermal radiance amplitudes.
Calibration:
\[ C_{\text{LART}} = \frac{S_{\omega,\lambda}}{R_0} \text{ with } R_0 = \frac{\lambda_0^6}{\lambda_0^6} e^{\frac{C_{\omega,\lambda}}{\lambda_0^6}} \]  

Measurement:
\[ T = \frac{C_2 \left( \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right)}{\ln \left( R \frac{\lambda_1^6}{\lambda_2^6} \right)} \text{ with } R = \frac{1}{C_{\text{LART}}} \frac{S_{\omega,\lambda}}{S_{\omega,\lambda}} \]  

2.2. Thermal diffusivity

The method compares signals measured on targets of unknown and known thermal diffusivity and does not require an explicit knowledge of the boundary conditions (e.g. laser spot profile).

For a periodic sinusoidal modulated pump laser of power \( P = P(x, y, z) e^{j\omega t} + c.c. \) focused onto a target, the heat diffusion equation for an opaque material can be written:
\[ \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} - \frac{j \omega}{D} \right] \Delta T_0(x, y, z) = -\frac{\varepsilon}{K} P(x, y) \]  

An important property of equation (5) is that the frequency response of heating scales with thermal diffusivity \( D \). By posing \( \omega / D = 1/L^2 \) in equation (5), 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
\[ S_{\omega,\lambda,k}(\omega) = a \cdot S_{\omega,\lambda,k}(b,\omega) \]  

where subscripts \( k \) and \( k \) respectively stand for the known and unknown targets, \( a \) is the amplitude scaling factor and \( b \) is the frequency scaling factor. The thermal diffusivities of the unknown and known targets are thus related by \( b = D_k / D_k \).

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

2.3. Thermal conductivity

Equation (1) showed the expression of the detected modulation at \( \lambda_1 \) for a laser heating at \( \lambda_2 \) (for \( \omega > \omega_0 \)). We can see that the expression is a function of thermal conductivity \( K \). A direct method to determine \( K \) would therefore require the knowledge of all the set-up parameters as well as emissivities. The presented technique is relative and we measure the modulated thermal radiances for two targets of thermal conductivities \( K_k \) (known) and \( K_k \) (unknown). Therefore, taking the ratio \( R \) of the two signal amplitudes gives:
\[ R = \frac{S_{\omega,\lambda,k}}{S_{\omega,\lambda,k}} \frac{e_{\omega,\lambda,k} / K_k \cdot D_k^{1/2} \cdot L'(\lambda_1, T_k)}{e_{\omega,\lambda,k} / K_k \cdot D_k^{1/2} \cdot L'(\lambda_1, T_k)} \]  

Moreover, we note that the measured dc radiance at the two different wavelengths are \( (k_1 \text{ and } k_2 \text{ being the responsivities of detectors at } \lambda_1 \text{ and } \lambda_2) \):
\[ V_{dc,k_1} = e_{\omega,\lambda,k_1} \cdot k_1 \cdot L_0(\lambda_1, T_k) \]
\[ V_{dc,k_2} = e_{\omega,\lambda,k_2} \cdot k_2 \cdot L_0(\lambda_1, T_k) \]
\[ V_{dc,k_1} = e_{\omega,\lambda,k_1} \cdot k_1 \cdot L_0(\lambda_1, T_k) \]
\[ V_{dc,k_2} = e_{\omega,\lambda,k_2} \cdot k_2 \cdot L_0(\lambda_1, T_k) \]

Therefore, considering that the properties \( K_k \) and \( D_k \) are known as well as the thermal diffusivity of the tested material, \( D_0 \) (which can be measured through the thermal diffusivity scaling method (2.2)), the expression for the unknown thermal conductivity becomes:
\[ K_k = \frac{V_{dc,k_1} \cdot V_{dc,k_2}}{V_{dc,k_1} \cdot V_{dc,k_2}} \left( \frac{D_k}{D_k} \right)^{1/2} \frac{S_{\omega,\lambda,k}}{S_{\omega,\lambda,k}} \cdot K_k \cdot C_T \]

Using Wien approximation:
\[ C_T = \frac{L_0(\lambda_1, T_k) - L_0(\lambda_2, T_k)}{L_0(\lambda_1, T_k) - L_0(\lambda_2, T_k) \cdot L'(\lambda_1, T_k) = \left( \frac{T_k}{T_k} \right) \cdot \frac{\lambda_1^6}{\lambda_2^6}} \]

Note that if both sample surfaces have precisely the same temperature the correction factor \( C_T \) equals 1. However, we observed that even a small difference of temperature can have a significant effect on the calculated result.

2.4. Spectral emissivity: combining LART and standard radiometry.

As the temperature of the surface has been measured independently of its emissivity by LART, only a dc thermal radiance measurement is required to
deduce the spectral emissivity of the target surface at the wavelength detected. The conditions are that the detection instrument must be calibrated first on a black body and that the surface is freely emitting, with no reflection of background radiations affecting the measurement.

\[ V_{dc,\lambda} = \varepsilon_1 \cdot k_1 \cdot L_0 (\lambda_1, T) \]  

(11)

\( k_1 \) is determined by calibration and \( L_0 \) is calculated from the temperature measured beforehand by LART.

### 2.5. Measurements needed

#### 2.5.1. Calibration

Initially, the instrument is calibrated. The detectors coefficients \( k_1 \) and \( k_2 \) are obtained by measurements on a blackbody of known temperature. The LART \( C_{LART} \) calibration coefficient is obtained by measuring a modulated thermal radiation on a reference target surface of known temperature for a given modulation frequency and for both configurations \( S_{\omega \lambda_1} \) and \( S_{\omega \lambda_2} \).

#### 2.5.2. Measurements

The following measurements are made on the actual targets:

- Modulated thermal radiations detected at \( \lambda_1 \) and \( \lambda_2 \) for a modulated heating with a laser of wavelength \( \lambda_2 \) and \( \lambda_1 \) respectively over a range of frequencies. The range of frequency (typically from 1 to 1000 Hz) has to be chosen according to the laser spot size so that it includes the case where this spot is of the same size as the thermal diffusion length. This has to be performed for two targets, one of which is of known thermal conductivity and diffusivity.

- A dc thermal radiation measurement detected on each of the two materials and with both detectors (at \( \lambda_1 \) and \( \lambda_2 \)). Care has to be taken to ensure that radiation is emitted purely from the target surface without reflected background radiation. A tube of specular inner surface (or ‘light-pipe’) may be used.

The set of modulated (ac) measurements includes the measurements needed for the determination of the temperature by LART method and thus the frequencies used for LART calibration must be included in that series. The LART measurements can be carried out separately so these values can be averaged over a longer time for the specified frequencies, thus reducing uncertainty on the surface temperature.

### 3. EXPERIMENTAL SETUP

The fibre optic LART instrument is described in detail in [3]. We utilise two lasers for the photothermal heating (a diode pumped Nd:YAG at \( \lambda_2 = 1320 \) nm and a solid state diode laser \( \lambda_1 = 840 \) nm), both providing 1 Watt of power and intensity modulated. Two photodiodes are employed (Si and InGaAs) in conjunction with band-pass interference filters to detect thermal radiation at wavelengths \( \lambda_1 \) and \( \lambda_2 \). An optical fibre light guide transmits laser radiation to the target and thermal radiation from the target onto the photodiodes. The optical head consists of a concave spherical mirror and the end of the fibre light guide, both mounted in a steel tube so the end facet of the fibre and the target lie at two conjugate points of the mirror.

Several different optical fibre configurations were investigated for the thermal property measurement methods reported here. The first light guide is a fibre bundle that splits into five branches; two branches are single fibres (diameter 200 \( \mu \)m) used to transmit laser radiation, three are smaller bundles (each fibre has a diameter of 100 \( \mu \)m). The detection is carried out either through one of the single fibres (configuration A) or one of the fibre bundles (configuration B). In the configuration A, the main fibre bundle end can also be coupled to a extension single fibre (diameter 1 mm) that transmits both laser emission and thermal radiations to and from the optical head (configuration C). The second light guide investigated is a fused fibre coupler where the laser and detecting fibres (diameter 100 mm) are fused into one single fibre (configuration D). In configurations A and B we have to slightly defocus the laser spot to create an overlap between the heated and detected areas. Measurements were made for Inconel and platinum samples heated inside a tube furnace.

### 4. RESULTS AND DISCUSSION

#### 4.1. Temperature measurements

Over the last 10 years, the principles of the LART method have been demonstrated for various targets. The Figure 2 shows results for platinum and Inconel targets, presenting two materials of very different emissivity heated at the same temperature [3]. Lower emissivity of platinum results in weaker signal and
increased uncertainties but the average temperature is not significantly affected by the big emissivity change.

![Graph showing temperature deviations](image)

**Figure 2**: LART temperature results on Inconel and Platinum

When employed only for temperature measurement, the LART instrument can be easily set-up for \( \omega > \omega_c \); it becomes more complex when the instrument has to simultaneously measure other properties. A certain number of “on site” temperature measurements have been undertaken, including of silicon wafers in a Chemical Vapour Deposition apparatus, silicon carbide pellets inside an NMR magnet or melted RF levitated metal drops. These experiments demonstrated that LART can be employed in real world applications.

### 4.2. Multi-property results

The sample used here is an Inconel rod with a hole to fit a small platinum rod. It is placed at the end of a tube furnace to suppress any emission and reflection originating from the furnace tube that would add to the detected dc radiance. The presented results are for a surface temperature of 941°C.

#### 4.2.1. Thermal diffusivity

The ratios obtained for platinum and oxidised Inconel with configurations A, B, and C were measured to be 5.55 ±0.37, 5.5 ±1 and 3.6 ±0.6 respectively, compared to a literature value of 4.26 ±0.55. The random uncertainties here were calculated by Monte Carlo analysis of the effect of random signal noise on the fitted ratio.

There is considerable variation in the thermal diffusivity ratio when different optical configurations are used. This is not yet fully understood, but may be due to effects associated with the oxide layer on the Inconel sample.

![Graph showing amplitude responses](image)

**Figure 3**: Amplitude responses for configuration A

![Graph showing amplitude results](image)

**Figure 4**: Inconel and platinum amplitude results (set-up C)

When measuring at small scales (< 1 mm) the effect of the oxide layer (with thickness of the order of 100 µm) may become significant. Furthermore, we have found that the shape of the frequency responses is sensitive to the optical configuration. For a semi-infinite and opaque target, the responses should be flat at low modulation frequencies (3D behaviour) and roll-off towards \( \sqrt[3]{\omega} \) variation at high frequencies (1D behaviour). We have found that this is usually the case, but not always. In Figure 4, the roll-off for inconel is not obvious but the response tends towards \( \sqrt[3]{\omega} \). In figure 3 the roll-off has a more complex shape and does not follow \( \sqrt[3]{\omega} \) at high frequency. This unexpected behaviour is mainly due to a bad or complex overlap of the laser spot and detection areas. Superficial layers (roughness, oxide) can also cause unexpected result at high frequencies (see Inconel high frequencies end of the plot, figure 3).
The uncertainty displayed is based on the standard deviation of all the data. A Monte Carlo method is implemented to calculate the subsequent uncertainty on the resulting $\frac{D_t}{D_n}$ value after the curve fitting. It does not include the influence of all the possible experimental systematic errors caused by target distance (laser spot size), orientation, targeted area surface condition, and surface temperature.

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 5 shows the frequency response data for an oxidized Inconel sample compared to the same sample after surface polishing. The target is placed within one mm from the on-focus position and at 900°C. The signal level on the polished surface is lower due to a lower emissivity. However, a second effect becomes apparent when scaling the second amplitude response to the level of the first. The slope changes at higher frequencies, with a higher signal for the oxidised surface than for the polished one. The oxide layer (and possibly a rougher surface) causes this behaviour at high frequencies (see Refs. [5] and [6] for previous work on the effect of surface layers). The third curve in Fig. 5 corresponds to the same sample after being held at 900°C for 7 hours, getting gradually oxidised again. Even here we can observe slight changes at high frequencies in addition to the small difference of amplitude due to the emissivity change.

This shows that some physical parameter, linked to the surface of the sample and other than the diffusivity, affects the modulated thermal radiance. This point is to be analysed more in detail at NPL on samples with known grown oxide layer thickness.

### 4.2.2 Thermal conductivity

The modulation frequency must be high enough to satisfy the condition $\omega > \omega_c$ so that the thermal diffusion length is significantly smaller than the laser spot size. On the other hand, the frequency must not be so high that the signal amplitude decreases to the point where the signal to noise ratio is too low (the signal amplitude varies as $\omega^{-1/2}$). However, the thermal conductivity measurement should not be affected by the choice of the modulation frequency. This characteristic is used to validate the method by spanning a range of frequencies from 1Hz to 300 Hz in order to check the invariability of our result with the frequency.
Moreover, the choice of the wavelength of the laser source should not have any influence on the result either and the two lasers (1320 nm and 840 nm) can be used indifferently (Figure 4). As shown in equation (1), the theoretical slope of the responses should be following a $\omega^{-\frac{1}{2}}$ function; the dash lines on the plot are validating this statement. As expected, the ratio of Inconel over platinum amplitude responses is constant for $\omega > \omega_c$ and unchanged whichever wavelength is used.

The result should be independent of the wavelength used for the detection. The plots corresponding to the assumption of the same temperature on both sample surfaces show a difference between using $\lambda_1$ and using $\lambda_2$. The two plots of corrected results are matching very well and this tends to validate our evaluation of the temperature difference between the targets.

The thermal conductivity obtained is not in good agreement with the NPL reference value and 25% difference is observed. Since the samples used for each study might differ only slightly it is not easy to tell the reason for this difference. The presence of an oxide layer on the Inconel sample surface could also have an influence in the measurements. Nevertheless, this provisional result is still assessing the method and proves promising in the development of the LART multi-properties instrument.

4.2.3. Spectral emissivity results

Emissivity has the simplest principle but is the most difficult to get experimentally with precision because the surface absolute temperature has to be measured very accurately during the calibration. Moreover, even a small offset in the dc measurement due to extraneous radiation can lead to significant errors.

A reference target using a heat pipe furnace liner is about to be tested, providing a better knowledge of the surface temperature by conventional techniques as well as a freely emitting surface at the edge of the tube furnace. We expect to overcome the described causes of errors with this target and soon include spectral emissivity to our results.

5. CONCLUSION

Comparative methods for thermal properties measurements in addition to temperature have been integrated into the NPL optical fibre emissivity free radiation thermometer instrument: the LART.

This work aims to develop a portable, self-aligned, robust “Multi LART” instrument capable of measuring temperature and thermal properties non-invasively and in-situ, for use in industrial process applications. This is a very challenging task, and this paper presents the principles and initial results for “Multi LART”. 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.

Further work will be carried out to improve the instrumentation, and understand and reduce the measurement uncertainties, including the modelling of the frequency responses for various surface conditions and optical configurations. Also, for calibration, thermal conductivity and spectral emissivity measurements, a heat pipe based reference target will provide a surface of known absolute temperature and free of extraneous reflected radiation.

One of the main limitations for this instrument is the high cost of the two high power lasers. Even though the price per Watt of lasers has not followed the microprocessor improvements trend, new high power diode lasers are now covering wavelength ranges of 780-1000 nm and 1300-1700 nm for a considerably lower price than equivalents a decade ago, giving LART more credit as an upcoming temperature and thermophysical properties measurement device.

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REFERENCES