

Consideration of Temperature and Slip Correction for Photothermal Spectrometry

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ABSTRACT

Temperature was considered to estimate the minimum detectable absorption coefficient of aerosol particles from photothermal spectroscopy. Light energy absorbed by subsequent emission from the aerosol results in the heating of the aerosol sample and consequently causes a temperature change as well as changes in thermodynamic parameters of the sample. This thermal effect is the basis of photothermal spectroscopy. Photothermal spectroscopy has several types of techniques depending on how the photothermal effects are detected. Photothermal interferometry traces the photothermal effect, refractive index, using an interferometer. Photoacoustic spectroscopy detects the photothermal effect, sound wave, using a microphone. In this study, it is suggested that the detection limit for photothermal spectroscopy can be influenced by the introduction of a slip correction factor when the light absorption is determined in a high temperature environment. The minimum detectable absorption coefficient depends on the density, the specific heat and the temperature, which are thermodynamic properties. Without considering the slip correction, when the temperature of the environment is 400 K, the minimum detectable absorption coefficient for photothermal interferometry increases approximately 0.3% compared to the case of 300 K. The minimum detectable absorption coefficient for photoacoustic spectroscopy decreases only 0.2% compared to the case of 300 K. Photothermal interferometry differs only 0.5% point from photoacoustic spectroscopy. Thus, it is believed that photothermal interferometry is reliably comparable to photoacoustic spectroscopy under 400 K.

Key words: Photothermal spectroscopy, High temperature, Slip correction, Absorption coefficient, Black carbon

1. INTRODUCTION

Black carbon (BC) is an important object in many areas including climate change and the growth rates of Asian forest tree species (Yamaguchi *et al.*, 2012). Currently, several filter-based instruments such as a Particle Soot Absorption Photometer (PSAP), a Continuous Soot Monitoring System (COSMOS), a Continuous Light-Absorption Photometer (CLAP), an aethalometer and a MultiAngle Absorption Photometer (MAAP) are widely used to measure BC concentration even though they suffer from artifacts associated with the materials of the filter membrane and moisture issues (Shrestha *et al.*, 2014; Kanaya *et al.*, 2013; Reche *et al.*, 2011). A Single Particle Soot Photometer (SP2) as a non-intrusive method is suggested to overcome the issues arisen from the filter-based methods for the characterization of BC. However, the SP2 is also known to be unable to detect loosely packed particles that have very small primary particles even though the particles are black (Gysel *et al.*, 2012). In this situation, a photothermal spectroscopy does provide a filter-free technique as a challenge toward a sensitive measurement of BC via quantification of light absorption. Light energy absorbed by subsequent emission from the aerosol results in the heating of sample and consequently causes a temperature change as well as changes in temperature-related thermodynamic parameters of the sample. PhotoThermal Interferometry (PTI) traces the refractive index change induced by the thermal dissipation of the spectrally absorbed light (Bialkowski, 1996). Recently, image based PTI was also introduced to measure light absorption from absorbing particles (Lee and Kim, 2012). Similarly, PhotoAcoustic Spectroscopy (PAS) measures the sound wave produced due to light absorption, heating of the ambient gas, and subsequent pressure fluctuations detected through microphone. Here, the author considered the effect of temperature in estimating the absorption coefficient of aerosol particles from photothermal spectroscopy. It is suggested that the detection limit of the photothermal spectroscopy can be influenced by the introduction of a slip

correction factor at high temperature environment.

2. METHODS

The basis of photothermal spectroscopy is a photo-induced change in the thermal state of the sample as its name suggested. Photothermal spectroscopy involves thermal effect caused by the optical interaction of airborne samples through energy transfer. The thermal effect finally creates the temperature difference surrounding the airborne samples (Bialkowski, 1996). Thus, it is important to consider the temperature effect during the photothermal process.

2.1 PhotoThermal Interferometry (PTI)

Photothermal interferometry traces the refractive index change induced by the thermal dissipation of the spectrally absorbed light. If we assume that the variation of the refractive index along the pathlength is uniform, phase shift ($\Delta\phi$) between a probe beam and a pump beam for the photothermal interferometry system is given as follows (Sedlacek, 2006).

$$\Delta\phi = \frac{2\pi l}{\lambda} \cdot \frac{n-1}{T_0} \cdot \frac{\alpha P_{exc}}{4\pi a^2 \rho C_p f} \quad (1)$$

In equation (1), l is the pathlength of the measuring volume, λ is the wavelength of the probe and pump beams, n is the refractive index of air, T_0 is the temperature of the airborne sample, α is the absorption coefficient of airborne sample, P_{exc} is the power of excitation laser, a is the pump beam radius, ρ is the density of air, C_p is the specific heat of air, and f is the modulation frequency of the excitation beam.

The phase difference corresponding to the induced change in the refractive index caused by the temperature change is detected at two photodiodes as power outputs and is linear to the difference between the signal detected in photo-diode 1 and photo-diode 2 (Moo-semüller *et al.*, 1997). Thus, the signal-to-noise-ratio (SNR) of the power can be written as follows.

$$SNR = \sqrt{\frac{\eta \lambda_{probe} P_0}{hc \Delta f}} \Delta\Phi_i \quad (2)$$

When the SNR is equal to 1, the minimum detectable change of the phase shift can be expressed as

$$\Delta\phi_{min} = \sqrt{\frac{hc \Delta f}{\eta P_0}} \quad (3)$$

In equation (3), Δf is the detection bandwidth, λ is the wavelength of the probe beam (He-Ne laser, 632 nm),

P_0 is the power of the probe laser, h is Planck's constant, $h\nu$ is the photon energy of the probe laser and η is the detector efficiency. Then, the minimum detectable absorption coefficient (α_{min}) can be derived from (1) and (3) as follows.

$$\alpha_{min} = \frac{2a^2 \rho C_p f \lambda T_0}{(n-1) l P_{exc}} \sqrt{\frac{hc \Delta f}{\eta P_0}} \quad (4)$$

The excitation laser beam radius (a), modulation frequency (f), the wavelength of probe beam (λ), the pathlength of the measuring volume (l), the power of the excitation laser (P_{exc}), the detection bandwidth (Δf) and the power of the probe laser (P_0) can be assumed to be constant since the parameters are fixed at once the experimental setup is determined. The refractive index of air n does depend on the temperature, which is the principle of the PTI. In other words, the relationship between the refractive index and the temperature was already considered to derive the minimum detectable absorption coefficient. Therefore, the refractive index was not considered in the estimation of minimum detectable absorption in terms of temperature. Then, the minimum detectable absorption coefficient depends only on three thermodynamic properties, the density (ρ), the specific heat (C_p) and the temperature (T_0).

This simplifies the expression for the minimum detectable absorption coefficient as below.

$$\alpha_{min} \sim \rho C_p T_0 \quad (5)$$

The density and the specific heat are functions of the temperature and can be easily formulated from 300 K to 400 K. The author used thermodynamic properties listed in the National Institute of Standards and Technology (NIST) database (<http://webbook.nist.gov/chemistry/>).

2.2 PhotoAcoustic Spectroscopy (PAS)

Similar to photothermal interferometry, photoacoustic spectroscopy measures the sound wave produced due to the consequence of light absorption, heating of the ambient gas, and subsequent pressure fluctuations detected through microphone. In other words, PAS detects the pressure of the acoustic wave created by the heating of the airborne sample using an alternating laser. In more detail, the laser beam power is modulated at the resonance frequency of the sample chamber. Then, the sound is produced due to the airborne sample heating by light absorption, and subsequent pressure fluctuations allow for a standing acoustical wave in the resonator. The induced pressure depends directly on the optical absorption coefficient as below, so that the detection of pressure allows us to mea-

sure the light absorption (Moosemüller *et al.*, 1997).

$$\alpha = \frac{P}{P_0 Q} \cdot \frac{cL}{C} \left[\left(\frac{L}{2R} \right)^2 + 0.39 \right]^{-\frac{1}{2}} \quad (6)$$

In equation 6, α is the absorption coefficient, P is the pressure induced by acoustic wave, P_0 is the laser power, Q is the quality factor of the resonance cell, c is the speed of ambient sound, L is the length of the cylindrical cell, C is a constant having a value of 0.25 for air, and R is the radius of the cylindrical cell.

Equation 6 can be expressed in another way as below.

$$\alpha = P \cdot \frac{1}{P_0} \cdot \frac{A_{res}}{\gamma - 1} \cdot \frac{\pi^2 f_0}{Q} \quad (7)$$

In equation 7, A_{res} is the cross sectional area of the resonator, γ is the specific heat ratio for air and f_0 is the resonance frequency. Parameters other than γ can be assumed constant, therefore, the absorption coefficient α depends on only one thermodynamic property, the specific heat ratio (γ) of air. As shown above, absorption coefficients for the PTI and the PAS are dependent on thermodynamic properties.

2.3 Slip Correction

As far as the author knows, there have been no photothermal spectroscopy research which considers temperature higher than room temperature. In addition, the author investigated the different behavior of PTI and PAS for the high temperature environment condition by considering the slip correction factor. Mean free path of the air molecules increases in the high temperature condition, resulting in an environment where the collision between molecules and airborne samples slip. In this case, the specific heat is thought to be reduced due to the active movement of particles. Thus, we can model the specific heat as proportional to the slip correction factor to the negative power. It is modeled that the relative specific heat is proportional to $C_c^{-1/3}$ (model 1), $C_c^{-1/2}$ (model 2) and C_c^{-1} (model 3), where C_c is the slip correction factor. The simplest slip correction factor was used as below (Hinds, 1999).

$$C_c = 1 + \frac{2\lambda}{d} \left(1.257 + 0.4e^{-\frac{0.55d}{\lambda}} \right)$$

The author made comparison of relative minimum detectable absorption coefficient between PTI and PAS on the assumption that the reference aerosol size is monodisperse at $d_p=100$ nm and the reference temperature is 300 K.

3. RESULTS AND DISCUSSION

First, the relative minimum detectable absorption

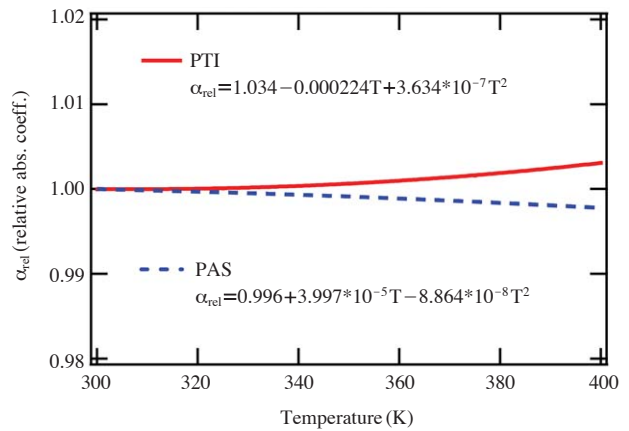


Fig. 1. Relative minimum detectable absorption coefficients for PTI (Photothermal Interferometry) and PAS (Photoacoustic Spectroscopy) at different temperature higher than room temperature without considering a slip correction factor.

coefficient without considering the slip correction factor was estimated. For the case of PTI, when the temperature of the environment is 400 K, the relative minimum detectable absorption coefficient increases approximately 0.3% higher than the case of 300 K as can be seen in Fig. 1. For the case of photoacoustic spectroscopy, the relative minimum detectable absorption coefficient was estimated only 0.2% less than the case of 300 K. Thus, it is believed that the photothermal interferometry is comparable to the photoacoustic spectroscopy under 400 K. The deviation of 0.3% for the PTI at the temperature of 400 K is probably due to enhanced molecular interaction between the airborne samples and air at the elevated energy state. The equations of polynomial fitting for both cases were presented in the Fig. 1. Extrapolation using these equations allows us to estimate the discrepancy between photothermal interferometry and photoacoustic spectroscopy. The discrepancy was calculated to be approximately 30% for the temperature of 2000 K, which is common in combustion study.

The author showed the relative minimum detectable absorption coefficients for PTI estimated using different models of slip correction factor in Fig. 2. The relative minimum detectable absorption coefficients relative to that calculated with $T=300$ K were reduced as temperature increased. When it is assumed that the heat capacity is proportional to the slip correction factor to the $-1/3$ (model 1), the relative minimum detectable absorption coefficient decreased about 7.5% when the temperature was 400 K. For the case of model 2 and 3, the relative minimum detectable absorption coefficients were reduced by 11% and 21%, respectively. The equations for linear regression fitting were imbedded

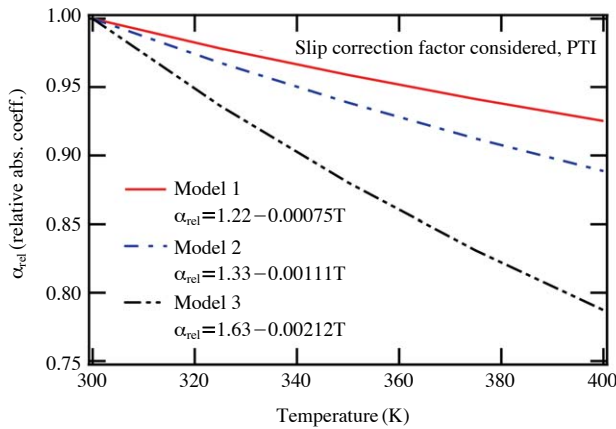


Fig. 2. Relative minimum detectable absorption coefficient estimated by PTI (Photothermal Interferometry) for different models of slip correction factor.

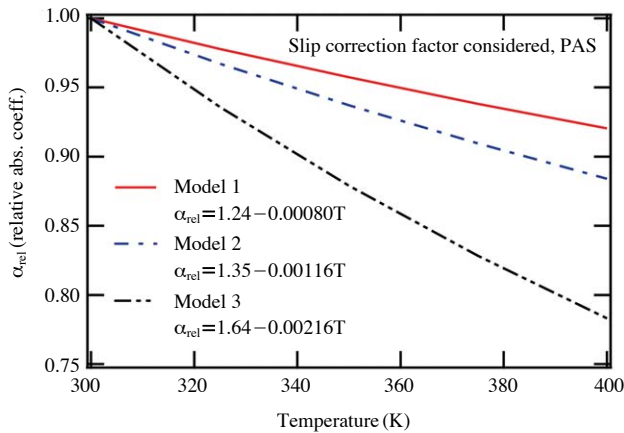


Fig. 3. Relative minimum detectable absorption coefficient estimated by PAS (Photoacoustic Spectroscopy) for different models of slip correction factor.

in Fig. 2. These equations could be used to estimate the relative minimum detectable absorption coefficient for the temperatures higher than 400 K. Extrapolation using these equations allows us to estimate the deviation from the relative minimum detectable absorption coefficient at 300 K for the photoacoustic spectroscopy. The relative minimum detectable absorption coefficients at 2000 K, which is a typical example of combustion study, were calculated to be approximately 31%, 49% and 78% for the model 1, 2 and 3, respectively.

Similar to the case of PTI, the relative minimum detectable absorption coefficients estimated for PAS were reduced as temperature increased. Fig. 3 shows that the relative minimum detectable absorption coefficient decreased about 8% when the temperature was 400

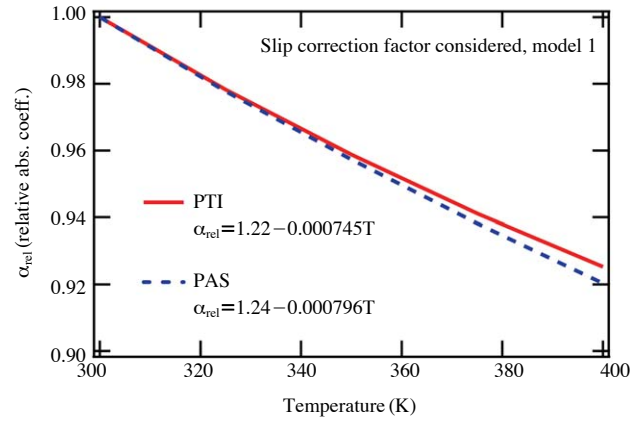


Fig. 4. Comparison of relative minimum detectable absorption coefficients between PTI and PAS for the model 1.

K for the model 1 case. The trend for the model 2 and 3 is very similar to the case of PTI. The equations for linear regression fitting were imbedded in Fig. 3. These equations could be used to estimate the relative minimum detectable absorption coefficient for the temperatures higher than 400 K. Extrapolation using these equations allows us to estimate the deviation from the relative minimum detectable absorption coefficient at 300 K for the photoacoustic spectroscopy. The relative minimum detectable absorption coefficients at 2000 K were calculated to be approximately 48%, 61% and 84% for models 1, 2 and 3, respectively.

Both PTI and PAS use optical heating to obtain relevant signals. During the optical interaction, the thermal energy is absorbed into the volume of particles which depends on d_p^3 . Airborne samples that spectrally absorb light dissipate heat radially. If slip between molecules and particles takes place, the specific heat could decrease since the particles can move actively under the condition of reduced drag, resulting in a fast heat transfer. This implies that the specific heat can be decreased. Thus, it is appropriate that specific heat can be modified by the slip correction factor to the $-1/3$. Fig. 4 shows that slip correction factor up to 400 K, the relative minimum detectable absorption coefficients for both the PTI and the PAS are maintained almost same and decreased linearly to the temperature. The relative minimum detectable absorption coefficients decreased only by 8% up to the temperature of 400 K. Therefore, both the PTI and the PAS can be applied up to this temperature without considering the slip correction if the error of 8% is assumed to be acceptable. However, slip correction needs to be considered in environments higher than 400 K. The equations for linear regression fitting were imbedded in Fig. 4. These equations could be used to estimate the relative minimum

detectable absorption coefficient for the temperatures higher than 400 K. Extrapolation using these equations shows that the relative minimum detectable absorption coefficient for the photothermal interferometry is 17% point higher than that for the photoacoustic spectroscopy at 2000 K.

4. CONCLUDING REMARKS

As far as the author knows, this research investigated the temperature effect on the PAS and PTI technique for the first time. The PAS is comparable to the PTI up to $T=400$ K from room temperature. When considering slip correction, the relative minimum detectable absorption coefficients using PAS were also comparable to those using PTI up to $T=400$ K. The detection limit of the photothermal interferometry can be affected by the slip correction factor in the environment higher than room temperature. The minimum detectable absorption coefficient for the photothermal interferometry depends only on some thermodynamic properties such as the density, the specific heat and the temperature. Without considering the slip correction, when the temperature is 400 K, the relative minimum detectable absorption coefficient for the photothermal interferometry increased approximately 0.3%. The relative minimum detectable absorption coefficient for the photoacoustic spectroscopy decreased 0.2%. The difference of the minimum detectable absorption coefficient between the photothermal interferometry and the photoacoustic spectroscopy is only 0.5% points. Thus, it is believed that photothermal interferometry is reliably comparable to photoacoustic spectroscopy under 400 K. At a temperature of 2000 K, however, the relative minimum detectable absorption coefficient for the photothermal interferometry deviated approximately 30% from that for the photoacoustic spectroscopy. Therefore, it is believed that more detailed research needs to be done to elucidate which technique is reliable.

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