

**Simultaneous Transmission and Absorption Photometry of Carbon-Black Absorption from Drop-Cast Particle-Laden Filters**

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**S.1. Sample absorptivity**

The conservation of thermal energy for bulk substances can be describe by:

$$m c_p(T) dT/dt = I_o A \beta(T, \lambda) - F(T, T_o) \quad (S1)$$

where the rate of change of sample internal energy is given by the term on the left side of Eq. S1,  $T$  is the sample temperature,  $c_p(T)$  is the sample specific heat capacity at the sample temperature, and  $m$  is the sample total mass (filter and particles, if present). The first term on the right side of the Eq. S1 is the energy absorbed by the sample, where  $I_o$  is the laser beam incident radiation intensity that heats the sample,  $A$  is the sample geometric cross-sectional area,  $\beta(T, \lambda)$  is the sample absorptivity at temperature  $T$  and laser wavelength  $\lambda$ . The heat transfer term,  $F(T, T_o)$ , is defined generically to include arbitrary sample geometries, and represents the sample thermal losses due to conduction through the gaseous medium, substrates, thermocouple wires, convection, and radiation (see Nazarian and Presser (2008)). The parameter  $T_o$  is the initial sample temperature, which in this case is the ambient temperature.

Data acquisition is initiated at the ambient laboratory room temperature. The laser beam aperture is opened and the beam is directed onto the sample, causing the sample temperature to rise (see Regime 1 in Fig. 5) to a perturbed steady-state temperature (represented by Regime 2; generally, the laser power is set to raise the filter temperature only a few degrees above the reference steady-state temperature). The laser aperture is then closed so that the sample temperature relaxes back to the reference steady-state temperature (Regime 3, sample thermal relaxation due to the absence of the probe beam). From Eq. S1, Regimes 1, 2 and 3 can be expressed by:

$$\text{Temperature Rise (Regime 1):} \quad m c_p(T) (dT/dt)_{Reg2} = (I_o A) \beta(T, \lambda) - F(T, T_o) \quad (S2)$$

$$\text{Steady-State Temperature (Regime 2):} \quad (I_o A) \beta(T, \lambda) = F(T, T_o) \quad (S3)$$

$$\text{Temperature Decay (Regime 3):} \quad m c_p(T) (dT/dt)_{Reg3} = -F(T, T_o) \quad (S4)$$

See Nazarian and Presser (2008) for a description of the evaluation of  $F(T, T_o)$ . One can equate different heating regimes to determine the sample absorptivity. Generally, the energy balance

at the steady-state temperature is matched with the temperature decay, and the resulting equation written in terms of  $\beta(T, \lambda)$ .

## S.2. Extinction coefficient

Conservation of electromagnetic radiation is then applied for particle-laden bulk substances (Bohren and Huffman 1983) to approximate the extinction coefficient of the isolated particles by examining both the blank and particle-laden filters. The model entails defining the sample reflectivity,  $\rho$  (fraction of incident radiation intensity reflected from the sample surface including both specular and diffuse components), transmissivity,  $\tau$  (fraction of the incident intensity transmitted through the sample, including specular and diffuse components), and absorptivity,  $\beta$  (fraction of the incident intensity absorbed by the sample), so that (Presser [2012], Presser et al. [2014]):

$$\rho = I_\rho / I_0 \quad (\text{S5})$$

$$\tau = I_\tau / I_0 = (1 - \rho)^2 e^{-\varepsilon d} \quad (\text{S6})$$

$$\beta = I_\beta / I_0 = 1 - \rho - (1 - \rho)^2 e^{-\varepsilon d} \quad (\text{S7})$$

where  $I_0$  is the incident intensity,  $I_\rho$  is the reflected intensity,  $I_\tau$  is the transmitted intensity, and  $I_\beta$  is the resulting intensity absorbed (i.e., not reflected or transmitted) by the sample,  $\varepsilon$  is the extinction coefficient ( $\varepsilon \equiv \alpha + \sigma$  (Bohren and Huffman 1983, Siegel and Howell 1981)),  $\alpha$  and  $\sigma$  are the absorption and scattering coefficients, respectively, and  $d$  is a characteristic path length related to the sample, which for this investigation was the sample (filter) thickness.

Knowing both  $\beta$  and  $\tau$  from experimental measurements, the reflectivity,  $\rho$ , is derived from the radiation balance equation:  $\rho = 1 - \beta - \tau$ , and rearranging Eq. S6 lead to:

$$\varepsilon = -\frac{1}{d} \ln \left[ \frac{\tau}{(1 - \rho)^2} \right] \quad (\text{S8})$$

where for fibrous filters  $I_\rho = I_r + I_{bs}$ , for which  $I_r$  represents the reflected light intensity from the filter surface and  $I_{bs}$  denotes the unobstructed backscattered light intensity past the filter front surface due to the embedded particles/fibers. Thus,  $\rho$  represents all sources of reflected light.

The extinction coefficient for the blank filter, coated filter, and isolated particles is  $\varepsilon_i = \alpha_i + \sigma_i$ , where  $\alpha_i$  and  $\sigma_i$  are the absorption and scattering coefficients, respectively, and the subscript  $i = s$  (substrate),  $ps$  (particle-laden substrate), and  $p$  (particles only). It is assumed that the absorptivity and transmissivity of the particle-laden filter are composed of the sum of the individual contributions by the blank filter and isolated particles, and thus are represented by:

$$\beta_{ps} = \beta_p + \beta_s \quad (\text{S9})$$

and

$$\tau_{ps} = \tau_p \cdot \tau_s = e^{-A_{ps}^*} = e^{-(A_p^* + A_s^*)} \quad (\text{S10})$$

where  $A^*$  is the exponent of the transmission law which considers both the absorption and scattering coefficients ( $A_i^* = \varepsilon_i d = -\ln(\tau_i)$ ,  $i = s, ps, p$ ). To evaluate the extinction coefficient of the particle-laden filter, one must consider the contribution from both the blank filter and the isolated particles. For the blank filter, surface reflections and absorptivity are both considered (i.e.,  $\rho_s, \beta_s$ , and  $\alpha_s \neq 0$ ), and thus  $\tau_s + \beta_s + \rho_s = 1$ . For the isolated particles case, surface reflection from the particles is considered negligible (i.e.,  $\rho_p = 0$ , since the isolated particles are not characterized with a bulk surface, as assumed with the filter, but by randomly dispersed aerosol of particles), and thus  $\tau_p + \beta_p = 1$ . For the particle-laden filter case, it can be shown, after substituting Eq. S6 into Eq. S10 for  $\tau_{ps}$ ,  $\tau_p$ , and  $\tau_s$ , and rearrangement of terms, that  $\varepsilon_{ps}$  will be of the form (see Presser et al. (2017)):

$$\varepsilon_{ps} = \varepsilon_p + \varepsilon_s + \frac{1}{d} \ln \left[ \frac{(1-\rho_{ps})^2}{(1-\rho_s)^2} \right] \quad (\text{S11})$$

where the last term on the right is defined as  $\varepsilon_{ps}'$ . Also,  $\rho_{ps} = \rho_s - (1-\tau_p)(1-\tau_s) = \rho_s - \beta_p(\beta_s + \rho_s)$ , which is derived after substitution into the radiation balance equation for the particle-laden filter and rearrangement of terms. The above expression indicates that as the particle loading becomes lighter or heavier (as when comparing the different filters), both the particle absorption and filter fiber/particle scattering will affect  $\varepsilon_{ps}'$  in a nonlinear fashion, which is considered to account for absorption enhancement and shadowing effects.

### S.3. Polydispersion of spherical particles

A normalized lognormal probability distribution function, assumed to represent the polydispersion of particles sizes coating the filter, is given by:

$$P(D) = \frac{1}{\sqrt{2\pi} \sigma_g D} \exp \left\{ \frac{-[\ln(D/D_g)]^2}{2 \sigma_g^2} \right\} \quad (\text{S12})$$

where  $D_g$  is the geometric mean diameter and  $\sigma_g$  is the geometric mean standard deviation. The procedure of Dobbins et al. (1966) is used to evaluate the terms in Eq. 5, where  $\bar{C}_j$  ( $j = ext, sca, abs$ ) are the mean extinction, scattering, and absorption cross sections, respectively,  $\bar{Q}_j$  ( $j = ext, sca, abs$ ) are the mean extinction, scattering, and absorption efficiencies, respectively,  $\bar{C}_v$  is the volume fraction,  $D_{30}$  is the volume mean diameter, and  $D_{32}$  is the volume-to-surface area diameter (Sauter mean diameter), and are defined by:

$$\bar{C}_j = \frac{\pi}{4} \int_0^\infty Q_j[x, m_r(\lambda)] P(D) D^2 dD \quad (\text{S13})$$

$$\bar{Q}_j = \frac{4 \bar{C}_j}{\pi \int_0^\infty P(D) D^2 dD} \quad (\text{S14})$$

$$\bar{C}_v = \frac{\pi}{6} N \int_0^\infty P(D) D^3 dD \quad (\text{S15})$$

$$D_{lm}^{l-m} = \frac{\int_0^\infty P(D) D^l dD}{\int_0^\infty P(D) D^m dD} \quad (\text{S16})$$

where  $l, m = 0, 1, 2, 3 \dots n$ ,  $Q_j$  ( $j = ext, sca, abs$ ) are the differential extinction, scattering, and absorption efficiencies for a specific particle (output from the Lorenz-Mie calculation (Wiscombe 1979)), respectively,  $x$  is the size parameter ( $= \pi D/\lambda$ ), and  $m_r(\lambda)$  is the complex refractive index ( $= n_r + ik$ ). Note that  $x$  is used in the Lorenz-Mie calculation to determine  $Q_j$ . Equations S13 – S16 are transformed into simpler expressions by defining  $z \equiv \ln(D/D_g)/\sqrt{2} \sigma_g$  before integrating over all particle sizes.

## Nomenclature

$A$	sample geometric cross-sectional area ( $\text{m}^2$ )
$A^*$	exponent of the transmission law
$C$	cross section ( $\text{m}^2$ )
$C_v$	volume fraction
$c_p(T)$	specific heat capacity ( $\text{J g}^{-1} \text{K}^{-1}$ )
$d$	characteristic path length through the sample, filter thickness (m)
$D$	diameter (m)
$D_g$	geometric mean diameter (m)
$D_{30}$	volume mean diameter (m)
$D_{32}$	volume-to-surface area mean diameter (Sauter mean diameter) (m)
$dT/dt$	sample temperature derivative ( $\text{K s}^{-1}$ )
$F(T, T_o)$	heat transfer term (W)
$I_o$	light intensity incident on the filter front side ( $\text{W m}^{-2}$ )
$I_p$	reflected intensity ( $\text{W m}^{-2}$ )
$I_\tau$	light intensity transmitted through the filter ( $\text{W m}^{-2}$ )
$I_\beta$	absorbed intensity by the sample ( $\text{W m}^{-2}$ )
$I_r$	reflected light intensity from the filter surface ( $\text{W m}^{-2}$ )
$I_{bs}$	unobstructed backscattered light intensity past the filter front surface ( $\text{W m}^{-2}$ )
$k$	imaginary part of the complex refractive index
$m$	mass (g)
$m_r$	refractive index ( $=n + ik$ )
$n$	total number of points
$n_r$	real part of the complex refractive index
$N$	number concentration (particles $\text{m}^{-3}$ )
$P(D)$	probability distribution function (m)
$t$	time (s)
$T$	sample temperature (K)
$T_o$	initial (laboratory) sample temperature (see Fig. 5) (K)
$Q$	efficiency
$x$	size parameter ( $= \pi D/\lambda$ )
$z$	defined nondimensional expression

## Greek symbols

$\alpha$	absorption coefficient ( $\text{m}^{-1}$ )
$\beta(T, \lambda)$	spectral hemispherical absorptivity (absorbed fraction of the incident radiation intensity)
$\varepsilon$	extinction coefficient ( $\text{m}^{-1}$ )
$\varepsilon'$	portion of the sample extinction coefficient attributed to filter effects ( $\text{m}^{-1}$ )
$\lambda$	wavelength (m)

$\rho$	spectral hemispherical reflectivity (reflected fraction of the incident radiation intensity)
$\rho_{eff}$	effective mass density ( $\text{g m}^{-3}$ )
$\sigma$	scattering coefficient ( $\text{m}^{-1}$ )
$\sigma_g$	geometric mean standard deviation
$\tau$	spectral hemispherical transmissivity (transmitted fraction of the incident radiation intensity)

### Subscripts

<i>abs</i>	absorption
<i>ext</i>	extinction
<i>I</i>	incident
<i>i</i>	index representing <i>s</i> , <i>ps</i> , and <i>p</i>
<i>j</i>	index representing <i>ext</i> , <i>sca</i> , and <i>abs</i>
<i>l,m</i>	index
<i>p</i>	particles
<i>ps</i>	particles and substrate (filter)
<i>Reg_</i>	regime
<i>s</i>	substrate (blank filter)
<i>sca</i>	scattering

### Superscripts

—	mean value
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