

Modeling reflectance and transmittance of quartz-fiber filter samples containing elemental carbon particles: Implications for thermal/optical analysis

L.-W. Antony Chen*, Judith C. Chow, John G. Watson,
Hans Moosmüller, W. Patrick Arnott

Division of Atmospheric Sciences, Desert Research Institute, 2215 Raggio Parkway, Reno, NV 89512, USA

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Abstract

A radiative transfer scheme that considers absorption, scattering, and distribution of light-absorbing elemental carbon (EC) particles collected on a quartz-fiber filter was developed to explain simultaneous filter reflectance and transmittance observations prior to and during thermal/optical analysis for carbonaceous aerosol. The model is applied to study ambient filter samples from the United States and Hong Kong, China, and how they differ from each other and from reference carbon black samples. Most particles in ambient samples deposit into the top half of the filter, resuspended carbon black particles are only found close to the filter surface. Pyrolyzed/charred organic carbon (POC) generated during thermal analysis reduces filter reflectance and transmittance in a fashion that suggests a uniform distribution of POC throughout the filter. When heated in oxygen, most EC evolves earlier than the within-filter charring for certain ambient samples. This shows the different natures of EC, and also results in an inexact optical correction to separate organic and elemental carbon by thermal analysis, especially when the POC/EC ratio is large. Particle absorption in the filter is estimated for comparisons with the EC/POC measurements, suggesting a mass absorption efficiency of $\sim 2.7 \pm 0.2 \text{ m}^2 (\text{gC})^{-1}$ for reference carbon black and $> 15 \text{ m}^2 (\text{gC})^{-1}$ for ambient EC, similar to previous estimates in the literature.

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1. Introduction

Carbonaceous material has been identified as a major component of ambient fine aerosol from remote to urban environments and is involved in various aerosol health, visibility, and climate impacts

* Corresponding author. Tel.: +1-775-674-7028; fax: +1-775-674-7009.

E-mail address: antony@dri.edu (L.-W.A. Chen).

(Vedal, 1997; Watson, 2002; Jacobson, 2001). Carbonaceous material mostly consists of elemental carbon (EC) and organic matter. EC has a chemical structure loosely related to graphite and is emitted directly into the atmosphere during incomplete combustion. EC is non-volatile at ambient conditions, absorbs strongly at visible, near-infrared (IR), and near-ultraviolet (UV) wavelengths, and is sometimes referred to as black carbon (BC). A small quantity of carbonate carbon (e.g., CaCO_3) may be present in some fine particle samples, but carbonate carbon rarely equals the EC content (Chow & Watson, 2002). The rest of carbonaceous material is organic matter that contains a wide range of molecular forms and volatilities. Organic matter can be emitted directly by sources or can be formed in the atmosphere through condensation of low-volatility oxidation products of hydrocarbons. Organic carbon (OC) is the carbon fraction of organic matter. By itself, OC is weakly light-absorbing in the visible region.

Aerosol total carbon (TC), EC, and OC are often quantified by thermal/optical methods (Novakov, 1982; Huntzicker, Johnson, Shah, & Cary, 1982; Cachier, Brémond, & Buat-Ménard, 1989; Chow et al., 1993; Birch & Cary, 1996; Peterson & Richards, 2002) which release carbon collected on a filter (e.g., quartz-fiber) through heating/oxidation and convert it to carbon dioxide (CO_2) or methane (CH_4) for detection. Since EC has low volatility, it is not released without oxygen (O_2) at a temperature below $\sim 700^\circ\text{C}$ and thereby can be separated from OC. Heating in an O_2 -free environment, however, causes certain OC components to pyrolyze and form non-volatile, light-absorbing char that could be mistaken for EC. This bias is corrected by monitoring the reflectance or transmittance of a filter matrix during thermal analyses. Since the pyrolyzed/charred OC (POC) reduces filter reflectance and transmittance, EC is defined as the carbon fraction that evolves after the filter reflectance or transmittance returns to its initial value (the value before thermal treatment). Owing to the complexity of sample/detector configurations, most instruments used for thermal analysis measure reflectance or transmittance, but not both. The charring correction is poorly understood (e.g., Yang & Yu, 2002), and OC and EC remain defined by the method applied rather than in absolute terms. Recent studies show that TC is accurately measured by most methods, but that the OC/EC split depends on the thermal protocol used (Birch, 1998; Chow, Watson, Crow, Lowenthal, & Merrifield, 2001; Schmid et al., 2001). Chow et al. (2001) observed that the NIOSH (1999) thermal optical transmittance (TOT) protocol, heating samples up to $\sim 900^\circ\text{C}$ without O_2 and using transmittance for POC correction, generally yields the same TC but lower EC than the IMPROVE thermal optical reflectance (TOR) protocol (Chow et al., 1993), which is based on reflectance correction and heats samples only to 550°C in an O_2 -free environment.

The transmittance and reflectance correction can lead to different results since transmittance depends on absorption and forward scattering through the particle–filter matrix while reflectance is dominated by backscattering of the filter surface with particle deposit. Since EC and OC determined by thermal/optical methods have been widely used in linking emission, ambient concentration, and radiative effects of carbonaceous aerosol (e.g., Watson, 2002), the potential measurement biases represent substantial uncertainties in current emission inventories and radiative forcing models. The objective of this work is to model filter reflectance and transmittance based on a radiative transfer scheme that considers the material distribution within a filter. Modeled results are compared with measurements of resuspended carbon black and ambient samples using both reflectance and transmittance to evaluate the influence of POC on the OC/EC split. This study also estimates the EC mass absorption efficiency on a quartz-fiber filter.

2. Experimental

Fig. 1 shows the configuration used for thermal/optical carbon analysis that is carried out by: (1) liberating carbon compounds at different temperature and oxidation environments from a small sample punch taken from a quartz-fiber filter, (2) converting these compounds to CO_2 by passing the evolved carbon through a manganese dioxide (MnO_2) oxidizer at 912°C , (3) reducing the CO_2 to CH_4 by passing the flow through a nickel catalyst methanator at $\sim 440^\circ\text{C}$, and (4) quantifying the CH_4 by flame ionization detector (FID). The carrier gases are pure He or He/ O_2 (typically 98% He and 2% O_2). Parameters in step 1, including temperature and O_2 mixing ratio, can be adjusted for various thermal protocols. Transit through the oxidation and reduction ovens in Fig. 1 both delays the arrival of the evolved carbon at the detector with respect to the optical detectors and broadens the carbon peak.

A He/Ne laser beam (632 nm wavelength) is directed toward the exposed side of the filter via a quartz light pipe. Direct forward and backward scattering of the radiation is detected by identical photodetectors on both sides of the filter to measure reflectance and transmittance throughout the analysis. Neutral density films (Wratten Gelatin, Kodak, Rochester, NY) of known optical properties placed in the optical path demonstrate the large and linear dynamic range of the photodetectors. Reflectance (R) and transmittance (T) are defined as the ratios of reflected and transmitted laser signals from a sample relative to the corresponding detector output with no sample present. For blank quartz-fiber filters (Pallflex 7202, Pall Laboratory, Ann Arbor, MI), the average R and T are found to be $\sim 1.9 \times 10^{-2}$ and $\sim 4.5 \times 10^{-3}$, respectively, and vary by $< 5\%$ from filter to filter. Considering that quartz fibers do not absorb strongly in the visible region, R and T are relatively small and $1 - R - T$ is close to one. Only small fractions of the reflected laser light are detected because of the limited detection angle.

Carbon black (RS683, Cabot Corp., <http://www.cabot-corp.com>), used here as a reference material, consists of quasi-spherical particles manufactured by the incomplete combustion of a heavy

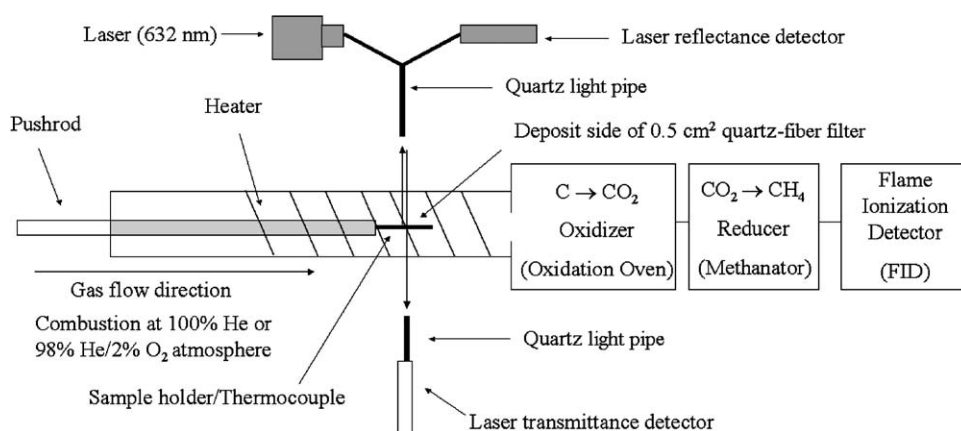


Fig. 1. Schematic diagram of the DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic, Inc., Calabasas, CA). The sample holder is open on top and bottom to minimize interference with the transmittance measurement. The carrier gas flows above and below (not through) the sample. The thermocouple is installed near the sample holder to characterize the filter temperature.

aromatic feedstock in a hot flame of preheated air and natural gas. The particles collide and fuse together in the combustion zone of the reactor to form aggregates. The median diameter of the aggregates is specified as ~ 56 nm by the manufacturer but they may agglomerate to larger particles during storage. To deposit carbon black particles onto quartz-fiber filters, the reference material is first resuspended in a chamber designed to segregate dried and sieved granular material into specified size fractions (Chow et al., 1994). A pulsed air jet injects carbon black particles into the chamber, where they are turbulently mixed with filtered air. The air is then sampled by 47 mm diameter Pallflex quartz-fiber filters downstream of a $2.5\ \mu\text{m}$ size-selective impactor. Thermal/optical analysis (TOR and TOT) of the samples indicates little charring during heating and more than 95% EC content.

Twenty ambient samples from the Interagency Monitoring of PROtected Visual Environments (IMPROVE) network (IMPROVE, 2000), ranging from remote to suburban environments in the United States (13 sites) and 18 samples from suburban to urban areas in Hong Kong, China (three sites), were submitted to thermal/optical analysis. The IMPROVE network uses pure Pallflex quartz filters as specified above while the Hong Kong study used quartz filters that contain 5% borosilicate glass as a binder (QM-A, Whatman, Ann Arbor, MI).

Samples were first heated to 550°C in a pure helium atmosphere, according to the IMPROVE thermal protocol to release OC, and then heated to 800°C in a 98% He/2% O_2 atmosphere to remove EC and POC (Chow et al., 1993, 2001). At 550°C in the He atmosphere, O_2 was not introduced until the FID signal returned to nearly zero.

3. Radiative transfer model

A two-flux approach (K–M theory, Kubelka & Munk, 1931) dealing with a uniform plane layer of material that both absorbs and scatters radiation is extended to treat non-uniform layers to model R and T prior to and during carbon analysis. Fig. 2 illustrates the modeled quantities in a filter of thickness D . The distance from the laser-incident surface is z . Incident radiation intensity is denoted by I_0 ; downwelling (I_+) and upwelling radiation (I_-) within the filter are functions of z . The incident radiation is attenuated in the filter through scattering (σ_s) and absorption (σ_a). The K–M theory assumes that radiation is totally diffuse in accordance with the Lambert cosine law. In the carbon analyzer, however, the incident radiation is a direct laser beam (not diffuse) and only a fraction of the scattered radiation is detected. The cross section of backscattering into a solid angle receivable by the reflectance detector is indicated by $\beta\sigma_s$, and σ_{ATN} represents the light attenuation coefficient. Both $\beta\sigma_s$ and σ_{ATN} are functions of z . By assigning $I'_+ = I_+/I_0$, $I'_- = I_-/I_0$, and $z' = z/D$, the K–M theory can be simplified to

$$\frac{dI'_+}{dz'} = -\sigma'_{\text{ATN}} I'_+, \quad (1)$$

$$-\frac{dI'_-}{dz'} = \beta\sigma'_s I'_+ - \sigma'_{\text{ATN}} I'_-, \quad (2)$$

where $\sigma'_{\text{ATN}}(\sigma_{\text{ATN}} \times D)$, $\beta\sigma'_s(\beta\sigma_s \times D)$, and $\sigma'_a(\sigma_a \times D)$ are dimensionless, referred to as generalized attenuation, backscattering, and absorption coefficients, respectively. (Note: Eq. (1) defines σ'_{ATN} ; $\sigma'_{\text{ATN}} = \sigma'_s + \sigma'_a$ only if multiple scattering can be neglected.)

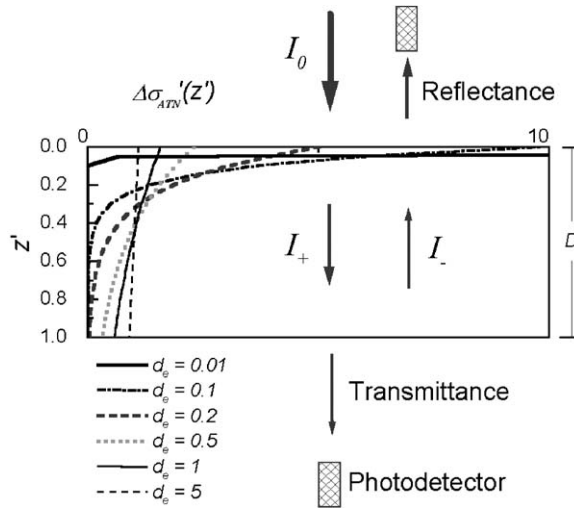


Fig. 2. Schematic diagram for radiative transfer through a particle-laden filter of thickness D . ($\Delta\sigma'_{\text{ATN}}(z')$) indicates the exponential distribution of material with an absorption optical depth ($\tau_{\text{ATN,p}}$) of 1 at various penetration depths. I_0 is the incident radiation intensity; I_+ and I_- indicate downwelling and upwelling radiation intensities within the filter, respectively; z' is the fractional distance from the filter top; d_e is the effective particle penetration depth.

For a blank quartz-fiber filter, σ'_{ATN} and $\beta\sigma'_s$ are constants (i.e., $\sigma'_{\text{ATN},0}$ and $\beta\sigma'_{s,0}$) throughout the uniform filter; $\sigma'_{s,0}$ dominates $\sigma'_{\text{ATN},0}$ since quartz fibers attenuate visible radiation mostly through scattering with little absorption. $I'_-(0)$ and $I'_+(1)$ represent R and T measured by the photodetectors. The boundary conditions require $I'_+(0) = 1$ and $I'_-(1) = 0$, so the analytical solution of Eqs. (1) and (2) that relates R and T to $\sigma'_{\text{ATN},0}$ and $\beta\sigma'_{s,0}$ is

$$R = I'_-(0) = \frac{\beta\sigma'_{s,0}(1 - e^{-2\sigma'_{\text{ATN},0}})}{2\sigma'_{\text{ATN},0}}, \quad (3)$$

$$T = I'_+(1) = e^{-\sigma'_{\text{ATN},0}}. \quad (4)$$

Using Eqs. (3) and (4), $\sigma'_{\text{ATN},0}$ and $\beta\sigma'_{s,0}$ can be determined for blank quartz-fiber filters from measured R and T ; they are found to be 5.40 and 0.21, respectively, for $R = 1.9 \times 10^{-2}$ and $T = 4.5 \times 10^{-3}$. $\beta \sim \beta\sigma'_{s,0}/\sigma'_{\text{ATN},0} = 0.04$ is small, consistent with $< 5\%$ of the scattered radiation is detected by the reflectance photodetector.

A two-layer approach (aerosol layer atop filter layer) is commonly applied to filters that have collected a deposit of ambient particles (Petzold, Kopp, & Niessner, 1997; Lindberg, Douglass, & Garvey, 1999). In this study, effects from the collected particles are treated as perturbations to the attenuation and backscattering coefficients of the blank filter. The dense, optically diffusive properties of the filter medium minimize the change in total scattering cross section caused by embedded particles; light absorption by the particles dominates the perturbation of the attenuation coefficient, $\Delta\sigma'_{\text{ATN}}(z')$. Therefore, for an exposed filter,

$$\sigma'_{\text{ATN}}(z') = \sigma'_{\text{ATN},0} + \Delta\sigma'_{\text{ATN}}(z'); \quad \Delta\sigma'_{\text{ATN}}(z') \propto \Delta\sigma'_a(z'). \quad (5)$$

Limited responses to non-absorbing particles are reported in filter-based measurements of absorption (Petzold et al., 1997; Bond, Anderson, & Campbell, 1999). Kopp, Petzold, and Niessner (1999) and Petzold, Kramer, and Schönlinner (2002) suggested that the filter scattering phase function ($S_n[\theta]$), especially in the backscattering hemisphere, is affected by embedded particles. According to Eq. (3), this may influence R by varying β . The first-order approximation assumes a linear relation between the perturbations of attenuation and backscattering (which both depend on the filter loading); thus,

$$\beta\sigma'_s(z') = \beta\sigma'_{s,0} + \Delta[\beta\sigma'_s(z')] \sim \beta\sigma'_{s,0} + \eta\Delta\sigma'_{\text{ATN}}(z'), \quad (6)$$

where η is referred to as incremental backscattering factor. It is assumed that the particle chemical composition, and therefore its index of refraction is constant.

Integrating both sides of Eq. (5) leads to the total optical depth (τ_{ATN}):

$$\tau_{\text{ATN}} = \tau_{\text{ATN},0} + \tau_{\text{ATN},p}, \quad (7)$$

where $\tau_{\text{ATN},p} = \int_0^1 \Delta\sigma'_{\text{ATN}}(z') dz' \propto \int_0^1 \Delta\sigma'_a(z') dz'$ is the particle-induced optical depth primarily due to absorption. $\Delta\sigma'_{\text{ATN}}(z')$ depends on how particles are distributed within the filter. When air is drawn through a filter during sampling, the penetration of particles into the filter depends on particle size, filter material, and sampling face velocity. If the collection efficiency of particles (particle deposition rate/particle flux ratio) remains constant in the filter, an exponential-decay distribution of particles with distance from the filter's surface is expected:

$$\Delta\sigma'_{\text{ATN}}(z') = Ae^{-z'/d_e}, \quad (8)$$

$$\Delta[\beta\sigma'_s](z') = \eta Ae^{-z'/d_e}, \quad (9)$$

$$A = \frac{\tau_{\text{ATN},p}}{d_e(1 - e^{-1/d_e})}, \quad (10)$$

where d_e is referred to as effective particle penetration depth into the filter, and A is a normalization factor to ensure $\tau_{\text{ATN},p} = \int_0^1 \Delta\sigma'_{\text{ATN}}(z') dz'$. $\tau_{\text{ATN},p}$ can serve as a measure of total light-absorbing aerosol content in the filter. Gas adsorption, if it exists, is expected to have a deeper penetration depth than particle deposition. Fig. 2 illustrates some $\Delta\sigma'_{\text{ATN}}(z')$ based on Eqs. (8) and (10) with the same $\tau_{\text{ATN},p}$ of 1 but various d_e . When $d_e \ll 1$ (e.g., $d_e = 0.01$), particles exist only in a thin layer near the filter surface, and the model is reduced to the common two-layer approach. When d_e is $\gg 1$ (e.g., $d_e = 5$), a substantial fraction of particles penetrates through the filter and the deposition is so uniform throughout the filter that this becomes a single-mixed-layer problem. By specifying d_e , η , and $\tau_{\text{ATN},p}$ in Eqs. (8)–(10) to obtain $\sigma'_{\text{ATN}}(z')$ and $\beta\sigma'_s(z')$ in Eqs. (5) and (6), differential equations (1) and (2) can be solved numerically to determine I'_+ and I'_- as well as R and T [$R = I'_-(0)$ and $T = I'_+(1)$]. Examples of T vs. R for $0 < \tau_{\text{ATN},p} < 5$ are shown in Fig. 3 for several d_e and η . For the same total loading of particles, a more uniform distribution throughout the filter results in less material near the surface and a higher filter reflectance. A larger η increases backscattering, also leading to a higher reflectance. Filter transmittance is nearly independent of d_e and η and thereby is more indicative of the total loading (i.e., $\tau_{\text{ATN},p}$). Increasing d_e or η always leads to a higher R/T ratio. The detection limit of transmittance is $\sim 3.2 \times 10^{-4}$, and this corresponds to $\tau_{\text{ATN},p}$ of ~ 2.5 (reflectance never reaches the detection limit). Fig. 3 implies the possibility of retrieving particle penetration depth and backscattering factor from filter R and T measurements at various loadings.

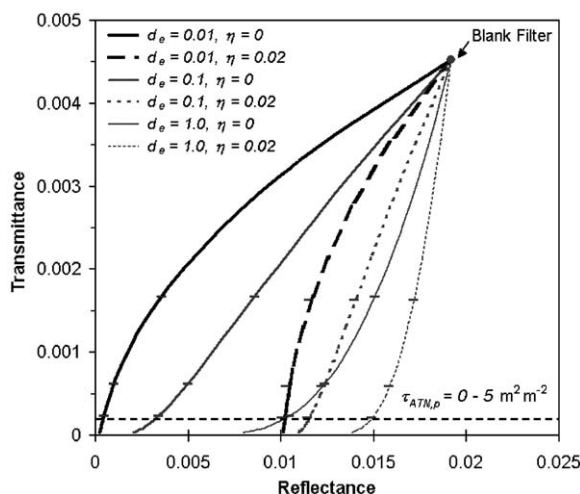


Fig. 3. Modeled transmittance (T) vs. reflectance (R) for filters loaded with light-absorbing particles at different penetration depths (d_e) and backscattering factors (η). An exponential distribution is assumed and particle absorption ($\tau_{\text{ATN},p}$) ranges from 0 to 5 with short bars indicating every step of 1. The horizontal dashed line indicates the detection limit of filter transmittance.

4. Measured and modeled T and R

Fig. 4 shows the T vs. R for a blank filter and four carbon black samples with different loadings. By varying particle penetration depth, d_e , and the incremental backscattering factor, η , in Eqs. (8)–(10), the best-fit $R(\tau_{\text{ATN},p})$ and $T(\tau_{\text{ATN},p})$ are determined from Eqs. (1) and (2) so that the root mean square difference between the measured (R, T) and the fit curve are minimized (Fig. 4). This radiative transfer model best explains observations for carbon black samples with $d_e = 0.014 \pm 0.001$ and $\eta = 0.01 \pm 0.002$. Particle absorption, $\tau_{\text{ATN},p}$, is then estimated from the measured T , ranging from 0 to 2.65 (Table 1). The measured R is highly correlated with R calculated from $\tau_{\text{ATN},p}$, d_e , and η ($r^2 > 0.99$; i.e. the model explains $> 99\%$ of the variation in R). For the most heavily loaded filter, $\tau_{\text{ATN},p}$ reaches a level of $\sim 50\%$ of $\tau_{\text{ATN},0}$ for a blank filter and backscattering $\eta \times \tau_{\text{ATN},p} \sim 12\%$ of $\beta\sigma'_{s,0}$. The change in filter absorption is more pronounced than in filter backscattering.

Fig. 4 also shows T vs. R for the US IMPROVE and Hong Kong samples and their respective best-fit [$R(\tau_{\text{ATN},p})$, $T(\tau_{\text{ATN},p})$]. The blank filters for Hong Kong show mean $\sigma'_{\text{ATN},0}$ and $\beta\sigma'_{s,0}$ of 5.50 and 0.21, respectively, compared to 5.40 and 0.21; respectively, for blanks from the U.S. IMPROVE samples, probably due to their different composition. Unlike uniform carbon black samples, each ambient particle deposit has different chemical compositions. It is assumed that d_e and η are constant for the same substrates and sampling procedures (e.g., flow and sampling duration); R and T depend only on $\tau_{\text{ATN},p}$. The degree of model agreement with measurements provides an evaluation of this assumption.

The best-fit $R(\tau_{\text{ATN},p})$ explains $\sim 98\%$ of the observed variation in R for each case; this supports the assumption that d_e and η do not vary appreciably with filter loading. Excluding samples that exceed the detection limit ($T < 3.2 \times 10^{-4}$) does not change the best fit. Measurement and model results agree best for d_e of 0.25 ± 0.01 and 0.42 ± 0.01 for the IMPROVE and Hong Kong samples,

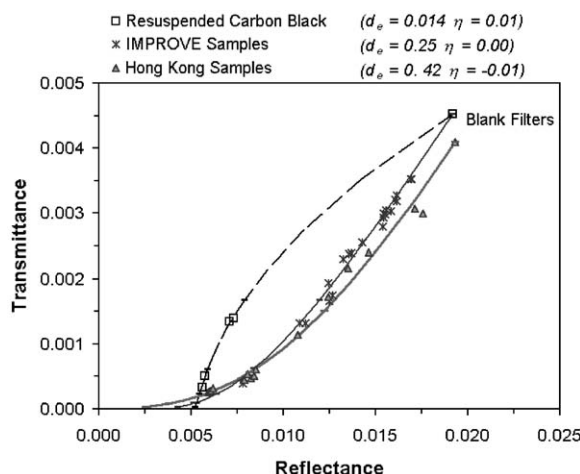


Fig. 4. Measured filter transmittance (T) vs. reflectance (R) for reference carbon black and ambient samples from the non-urban United States (IMPROVE) and urban Hong Kong monitors for several concentration levels. Best-fit curves are calculated using the extended K–M theory radiative transfer model, with best least square fits to d_e and η .

respectively. This is consistent with $> 80\%$ of the particle deposit being located within the top $\frac{1}{3} - \frac{1}{2}$ of the filter, in agreement with microscopic examination (Chow et al., 2004). Ambient sample d_e are larger than that for the resuspended carbon black samples ($d_e \sim 0.014$). In fact, the deposition layer on the carbon black resuspension filters was so thin that it could be peeled from the surface with forceps. The sampling time for the IMPROVE and Hong Kong samples is 24 h. The typical sampling time to collect enough ($> 30 \mu\text{g cm}^{-2}$) geological dust particles ($< 2.5 \mu\text{m}$) using the resuspension chamber is 30–60 min (Chow et al., 1994). For carbon black particles it takes < 3 min, likely due to the dominance of fine particles in the material. The extremely high deposition rate onto the quartz-fiber filter could have clogged filter pores and prevented deeper penetration (e.g., Walsh & Stenhouse, 1996, 1997).

The incremental backscattering factor, η , is 0.01 ± 0.002 and 0 ± 0.002 for the carbon black and IMPROVE samples (quartz-fiber filter), respectively, but is -0.01 ± 0.002 for the Hong Kong samples (quartz/borosilicate glass-fiber filter). Petzold et al. (2002) showed the dependence of filter backscattering phase function on the chemical composition of deposited particles; pure EC and a scattering EC/NaCl mixture could produce opposite effects. η likely depends on the relative backscattering efficiencies of quartz/glass fibers and deposited particles. From T the particle-induced attenuation, $\tau_{\text{ATN},p}$, is estimated to range from 0 to 2.46 for the IMPROVE samples and 0 to 2.78 for the Hong Kong samples (Table 1). (Note that $\tau_{\text{ATN},p} > 2.5$ is beyond the detection limit.) With d_e, η , and $\tau_{\text{ATN},p}$, $\Delta\sigma'_{\text{ATN}}(z')$ for each sample can be uniquely determined (Eqs. (8)–(10)).

For the carbon black samples, the filter R and T did not change until the oxidation of carbon black began in 2% O_2 . The scatter plot of T vs. R for the four samples during thermal analysis is shown in Fig. 5(a), which is consistent with the results of the radiative transfer model in Fig. 4. d_e and η vary little while the carbon black (i.e., $\tau_{\text{ATN},p}$) is depleted. This observation is consistent with a homogeneous removal of the collected particles, likely because carbon black particles reside only in a very thin layer near the surface. At the end of a thermal combustion cycle (i.e., blank filters),

Table 1

Summary of the optical and carbon measurements for four carbon black samples and 38 ambient samples

Type	Sample	$R \times 10^3$	$T \times 10^3$	$\tau_{\text{ATN,p}}$	TC	EC+POC	TOR EC	TOT EC	$\tau_{\text{ATN,p}}/(\text{EC} + \text{POC})$
Carbon black $d_e = 0.014$ $\eta = 0.01$	CB01	7.3	1.39	1.19	0.456	0.411	0.411	0.406	2.9
	CB02	7.1	1.33	1.23	0.433	0.389	0.389	0.379	3.2
	CB03	5.8	0.51	2.17	0.849	0.803	0.803	0.803	2.7
	CB04 ^a	5.6	0.32	2.65	1.137	1.085	1.085	1.085	2.4
US IMPROVE samples $d_e = 0.25$ $\eta = 0.00$	US01	19.2	4.39	0.00	0.024	0.001	0.003	0.000	—
	US02	17.7	3.82	0.16	0.084	0.022	0.011	0.007	7.3
	US03	17.6	3.65	0.20	0.094	0.027	0.013	0.008	7.6
	US04	17.5	3.62	0.21	0.065	0.018	0.007	0.003	11.8
	US05	17.5	3.53	0.23	0.074	0.028	0.010	0.004	8.4
	US06	16.9	3.53	0.24	0.128	0.037	0.017	0.007	6.4
	US07	17.0	3.52	0.24	0.067	0.022	0.010	0.005	10.9
	US08	16.1	3.18	0.34	0.084	0.033	0.017	0.009	10.1
	US09	15.6	3.05	0.38	0.091	0.040	0.020	0.009	9.6
	US10	15.8	3.03	0.39	0.105	0.031	0.016	0.010	12.5
	US11 ^b	15.5	2.93	0.42	0.135	0.064	0.028	0.010	6.6
	US12	15.4	2.79	0.47	0.103	0.048	0.023	0.008	9.8
	US13	14.3	2.55	0.57	0.097	0.041	0.024	0.017	14.0
	US14	13.3	2.30	0.68	0.178	0.074	0.038	0.021	9.2
	US15	12.5	1.93	0.86	0.243	0.096	0.053	0.030	9.0
	US16	12.7	1.74	0.97	0.186	0.084	0.047	0.022	11.4
	US17	12.5	1.66	1.01	0.189	0.079	0.046	0.022	12.8
	US18	11.2	1.32	1.24	0.166	0.077	0.056	0.042	16.1
	US19	10.9	1.31	1.25	0.355	0.135	0.072	0.027	9.3
	US20 ^a	7.8	0.39	2.46	0.651	0.221	0.206	0.095	11.1
Hong Kong samples $d_e = 0.42$ $\eta = -0.01$	HK01	17.1	3.07	0.27	0.052	0.018	0.009	0.007	15.5
	HK02	17.6	3.00	0.30	0.039	0.013	0.008	0.006	23.3
	HK03	14.6	2.40	0.53	0.094	0.041	0.027	0.018	12.9
	HK04	13.5	2.17	0.63	0.092	0.048	0.033	0.021	13.1
	HK05 ^c	12.5	1.72	0.88	0.106	0.054	0.043	0.028	16.4
	HK06	10.8	1.13	1.29	0.186	0.101	0.077	0.040	12.8
	HK07	8.5	0.61	1.89	0.192	0.121	0.114	0.103	15.7
	HK08	8.1	0.53	2.04	0.234	0.156	0.142	0.109	13.1
	HK09	8.4	0.50	2.09	0.271	0.163	0.143	0.103	12.8
	HK10	8.3	0.46	2.17	0.244	0.163	0.149	0.117	13.3
	HK11	7.8	0.45	2.21	0.260	0.170	0.160	0.146	13.0
	HK12	7.9	0.45	2.21	0.319	0.187	0.173	0.107	11.8
	HK13 ^a	6.2	0.32	2.57	0.433	0.325	0.317	0.295	7.9
	HK14 ^a	6.1	0.27	2.71	0.707	0.487	0.483	0.369	5.6
	HK15 ^a	6.1	0.27	2.74	0.589	0.455	0.385	0.382	6.0
	HK16 ^a	6.0	0.27	2.74	0.649	0.482	0.394	0.478	5.7
	HK17 ^a	6.0	0.27	2.74	0.684	0.510	0.431	0.453	5.4
	HK18 ^a	5.9	0.26	2.78	0.761	0.571	0.536	0.466	4.9

The unit for TC, EC + POC, TOR EC, and TOT EC is gC m^{-2} . 1 gC m^{-2} corresponds to an ambient concentration of $87.5 \mu\text{g m}^{-3}$ for IMPROVE samples and $57.5 \mu\text{g m}^{-3}$ for Hong Kong samples. EC + POC consists of all carbon evolved after oxygen introduction; TOR EC and TOT EC refer to carbon evolved after filter reflectance and transmittance return to the initial values, respectively.

^a T and $\tau_{\text{ATN,p}}$ are beyond the instrumental detection limit ($T < 3.2 \times 10^{-4}$).

^bSample HECA-1 from Hells Canyon, OR, United States.

^cSample HT-1 from Hok Tsui, Hong Kong, China.

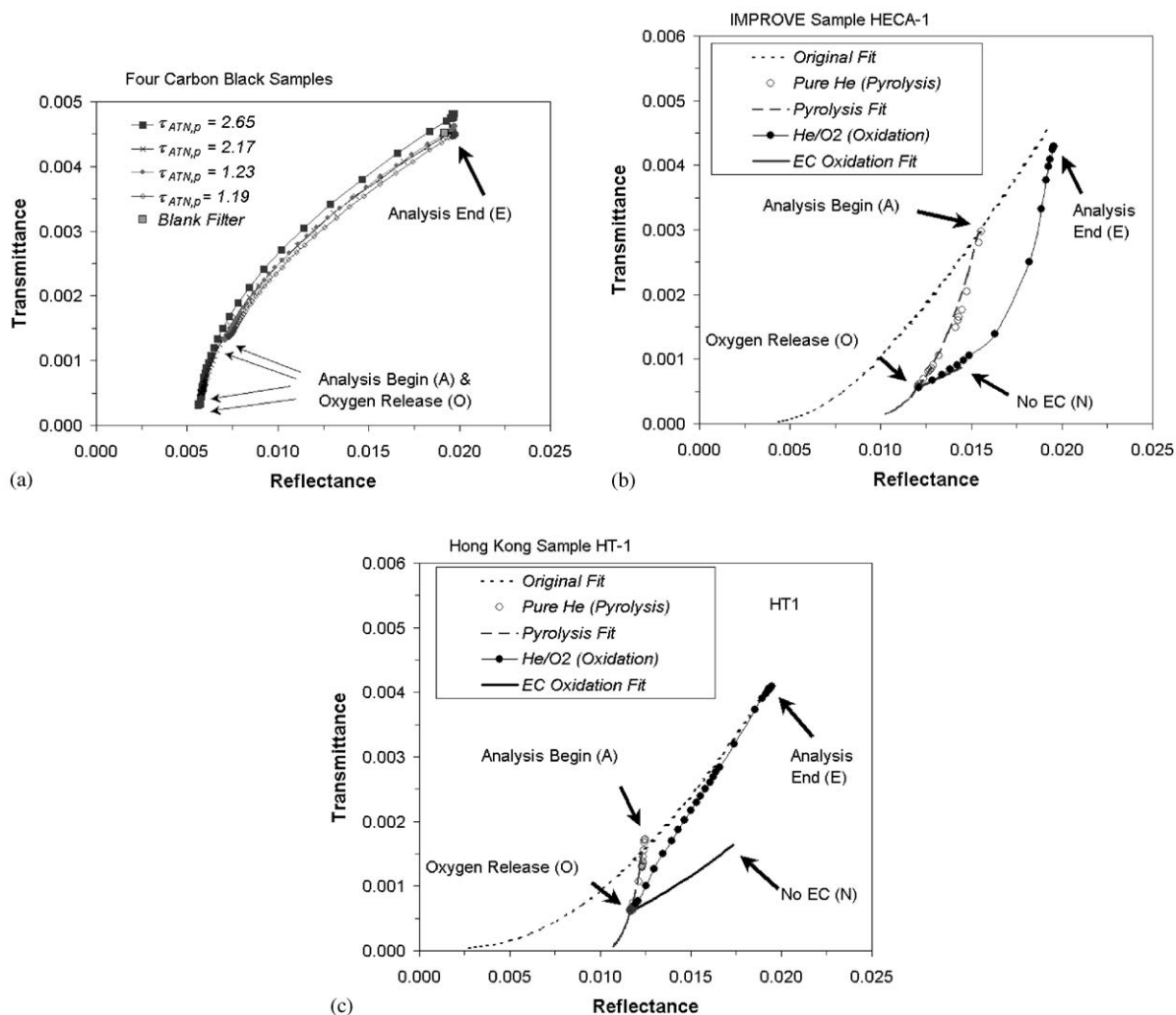


Fig. 5. Variations of measured filter transmittance (T) vs. reflectance (R) for: (a) reference carbon black; (b) IMPROVE sample (HECA-1) from Hells Canyon, OR, United States (1/12/2003); (c) Hong Kong sample (HT-1) from Hok Tsui, Hong Kong, China (5/5/2001) during thermal/optical analysis. Points A and E represent the beginning and ending of each analysis, respectively. Dots indicate every (a) 1 s (b) 30 s (c) 20 s step. The point O indicates the addition of O₂ during the thermal analysis. Point N shows that EC is reduced to zero by assuming stable POC. The “original fit” is the same as that of Fig. 4.

R and T are not always constant. The optical properties of a quartz-fiber filter may change slightly after heating at high temperature, causing minor biases in the $\sigma'_{ATN,0}$ and $\beta\sigma'_{s,0}$ values.

For ambient samples, R and T typically start to decrease at $\sim 300^\circ\text{C}$, indicating the formation of POC, and they seldom increase before the introduction of O₂ at 550°C . Scatter plots of T vs. R for two ambient samples during thermal analysis are shown in Fig. 5(b) and (c). The first sample (HECA-1) was acquired from Hells Canyon, a remote IMPROVE site at the border of Oregon and

Idaho. The other (HT-1) was from a regional/transport Hok Tsui site on the south coast of Hong Kong. Both filters are medium loaded and considered representative in their respective batches of samples (Table 1).

The points A, O, and E in Fig. 5(b) and (c) indicate the beginning, O₂ introduction, and end of each analysis, respectively. The particle-induced attenuation, $\tau_{\text{ATN,p}}$, is 0.42 for HECA-1 and 0.88 for HT-1. Between A and O, OC is either combusted to CO₂ or pyrolyzed to black carbon; the decrease of R and T can be well modeled ($r^2 \sim 0.98$) by assuming that POC is forming but EC remains stable. $\Delta\sigma'_{\text{ATN}}(z')$ in Eq. (8) becomes the superposition of two exponential distributions, $\Delta\sigma'_{\text{ATN}}(z')_{\text{EC}}$ and $\Delta\sigma'_{\text{ATN}}(z')_{\text{POC}}$. $\Delta\sigma'_{\text{ATN}}(z')_{\text{EC}}$ uses d_e , η , and $\tau_{\text{ATN,p}}$ already determined for each sample. The pyrolysis fits are $\Delta\sigma'_{\text{ATN}}(z')_{\text{POC}}$ that best explain measured $R(\tau_{\text{ATN,op}})$ and $T(\tau_{\text{ATN,op}})$ during pyrolysis. Penetration depths (d_e) of $\Delta\sigma'_{\text{ATN}}(z')_{\text{POC}}$ are 6.0 ± 1.0 for HECA-1 and 2.0 ± 0.2 for HT-1. Incremental backscattering factors (η) of are 0 ± 0.002 for HECA-1 and 0.02 ± 0.004 for HT-1 (Fig. 5(b) and (c)). These depths imply that POC is spread uniformly throughout the filter. Two processes could contribute to a uniform within-filter-charring: (1) pyrolysis of organic gas, liquid, or very fine particles that penetrate quartz fibers during sampling and (2) diffusion of vaporized organic matter from filter surfaces deeper into the filter as the sample is heated. Charring was also observed on backup filters (the second filter in a sequential filter design) that contain little particles. Organic gas adsorption is a well-known artifact in ambient carbonaceous aerosol sampling (Turpin, Huntzicker, & Hering, 1994; Mader & Pankow, 2001), and charred organic gas may account for a substantial fraction of POC. R and T reach their minima at point O just before the O₂ introduction. The POC-induced absorption, $\tau_{\text{ATN,op}}$, is higher for HECA-1 ($\tau_{\text{ATN,op}} = 1.65$) than for HT-1 ($\tau_{\text{ATN,op}} = 0.91$).

After point O (Fig. 5(b) and (c)), POC and EC start to evolve from the filter through oxidation. If POC is removed first, as hypothesized by Yang and Yu (2002), the change of R and T should follow the pyrolysis path to return to point A before moving from A to the complete combustion point E, and by which R and T return to their initial values at the same time. This does not happen for most of the samples. R always returns to its initial value before T , meaning that TOR EC (carbon evolved after R returns) is always greater than TOT EC (carbon evolved after T returns). On the other hand, due to its deposit close to the filter surface and better exposure to O₂ in the analysis atmosphere, EC may be removed prior to POC. To simulate this, the R and T are re-calculated by assuming constant POC (i.e., $\tau_{\text{ATN,op}}$) while gradually decreasing EC (i.e., $\tau_{\text{ATN,p}}$) to zero from point O. This calculation demonstrates a lower T/R slope gradually moving from O to N where EC is depleted (Fig. 5(b) and (c)). The path O–N in Fig. 5(b) agrees with the HECA-1 experiment, at least during the early stage of oxidation, implying that EC is mostly depleted when reflectance returns to its initial value. For this type of sample, the EC determined by TOR or TOT (especially TOT) appears to contain a significant fraction of POC. For HT-1, R and T do not move from O to N, returning to the original fit before reaching E (Fig. 5(c)). POC is depleted first in this case, and TOR or TOT provide equivalent EC estimates.

The difference between Fig. 5(b) and (c) could result from different EC and POC abundances in samples HECA-1 and HT-1. However, the two distinct patterns of R vs. T appear repeatedly for the IMPROVE and Hong Kong samples regardless of the loading. The nature of EC can be another factor. Most of the IMPROVE sites are remote, and vegetative burning (e.g., wild forest fires and camp fires) is often a contributor to black carbon. In Hong Kong, mobile sources (> 60% diesel) dominate the EC emissions. Watson, Chow, Lowenthal, Pritchett, and Frazier (1994) provide

evidence that EC in diesel soot has a higher oxidation temperature than EC in gasoline exhaust. Whether this explains why some EC in the Hong Kong samples appears to evolve later than POC warrants further investigation. This study shows that EC and POC can evolve at the same time. For EC measurement, correcting for charring using either laser reflectance or transmittance cannot be completely unbiased due to: (1) unknown and changing (during analysis) absorption efficiencies of EC and POC mixed with other materials, and (2) the different sensitivities of reflectance or transmittance to POC and EC that have different filter penetration depths. The uncertainty is more pronounced when the POC/EC ratio is large. The reflectance correction is less influenced by POC within the filter than is the transmittance correction.

5. EC absorption efficiency estimate

The simultaneous measurement of filter absorption and carbon mass provides an estimate for the mass absorption efficiency of EC. Particle attenuation, $\tau_{\text{ATN},p}$, indicates EC light absorption in a filter. In this case, it is similar to light attenuation (ATN) calculated from $\text{ATN} = -\ln(T_{\text{sample}}/T_{\text{blank}})$ (Rosen & Novakov, 1983; Hansen, Rosen, & Novakov, 1984). Since R and T reach their minima and the carbon evolution rate is nearly zero just before the introduction of oxygen, it is reasonable to assume that carbon left on the filter after this point contains only EC and POC (i.e., non-absorbing OC is depleted). Table 1 summarizes the initial R , initial T , initial $\tau_{\text{ATN},p}$, and TC of the 42 samples. Carbon evolved after adding oxygen (i.e., EC + POC), TOR EC, and TOT EC are also included for comparison. The $\tau_{\text{ATN},p}/(\text{EC} + \text{POC})$ ratio approximates the lower bound of EC mass absorption efficiency in the filter (i.e., $\tau_{\text{ATN},p}/\text{EC}$). Samples less influenced by charring show higher $\tau_{\text{ATN},p}/(\text{EC} + \text{POC})$ ratios that are closer to $\tau_{\text{ATN},p}/\text{EC}$. The EC absorption efficiency measured on a quartz-fiber filter could be higher than its actual value in the atmosphere due to multiple scattering caused by the filter.

Fig. 6 shows $\tau_{\text{ATN},p}$ vs. EC + POC for the carbon black, IMPROVE, and Hong Kong samples. Since $T < 3.2 \times 10^{-4}$ is not detectable, heavily loaded samples ($\tau_{\text{ATN},p} \geq 2.5$) are excluded. The least square fit for carbon black samples that contain no POC yields a mass absorption efficiency of $2.7 \pm 0.2 \text{ m}^2 (\text{gC})^{-1}$ (632 nm). This is lower than the theoretical value, $\sim 3.3 \text{ m}^2 (\text{gC})^{-1}$, calculated with Mie theory, assuming a pure spherical particle with a diameter of 56 nm, a refractive index of $1.84 - 0.85i$, and a density of 2.4 g m^{-3} obtained from the manufacturer. It is also less than reported soot absorption efficiencies of $4\text{--}8 \text{ m}^2 (\text{gC})^{-1}$ (550 nm, $0.06 \mu\text{m}$ particle diameter) (Petzold & Niessner, 1996; Martins et al., 1998; Fuller, Malm, & Kreidenweis, 1999). The absorption efficiency at 632 nm is expected to be $\sim 15\%$ lower than at 550 nm (e.g., Moosmüller et al., 1998). Moreover, agglomeration of carbon black particles could increase their effective sizes and reduce the absorption efficiency.

The mass absorption efficiency of ambient carbon is much higher than that of resuspended carbon black. Generally, the Hong Kong samples exhibit higher $\tau_{\text{ATN},p}/(\text{EC} + \text{POC})$ ratios than the IMPROVE samples (Table 1); this might be attributed to a higher EC abundance relative to POC in the Hong Kong samples. The actual EC absorption efficiency in the filter ($\tau_{\text{ATN},p}/\text{EC}$), assessed from the highest $\tau_{\text{ATN},p}/(\text{EC} + \text{POC})$ values in Table 1, does not differ appreciably between the IMPROVE and Hong Kong samples. Nine points in Fig. 6 are chosen to represent the upper boundary of the range of values. The slope from the 9-point linear least square fit, indicative of the lower-bound

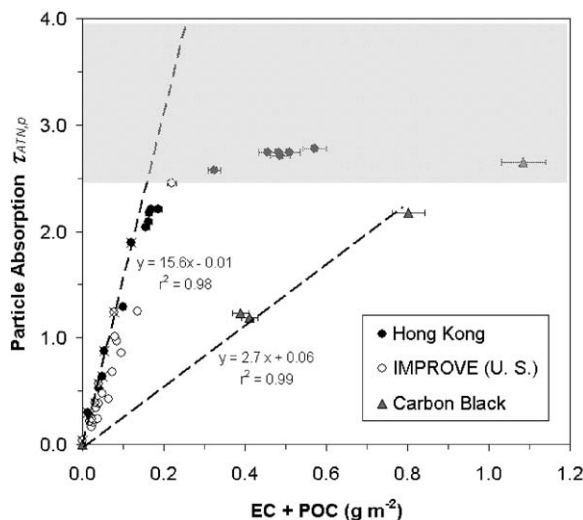


Fig. 6. A comparison of particle absorption ($\tau_{\text{ATN},p}$) in quartz-fiber filters with the sum of EC and POC determined from thermal/optical analysis (carbon evolved after introducing O_2). The shaded area is beyond the instrumental detection limit. The two dashed lines are linear least square fits for reference carbon black and nine ‘boundary’ ambient samples (marked by cross), respectively.

EC absorption efficiency, is $15.6 \pm 0.8 \text{ m}^2 (\text{gC})^{-1}$. This agrees with the efficiency used to convert filter transmittance to black carbon concentrations for the aethalometer ($16.8 \text{ m}^2 (\text{gC})^{-1}$ at 660 nm) (Hansen, 2003). This is also similar to the theoretical specific absorption of soot encapsulated by sulfate (i.e., $13\text{--}20 \text{ m}^2 (\text{gC})^{-1}$ at 550 nm for composite particle radii $> 0.2 \mu\text{m}$; Fuller et al., 1999).

6. Conclusions

Thermal/optical methods have been widely applied to determine particulate EC and OC in particles collected on filters, but the OC/EC split is method dependent. Of particular interest are differences due to either reflectance or transmittance being used to correct for charring of the OC during analysis. A radiative transfer model explains the reflectance and transmittance of EC-loaded quartz-fiber filter samples prior to and during thermal/optical analysis using three parameters, total absorption optical depth ($\tau_{\text{ATN},p}$), particle penetration depth (d_e), and incremental backscattering factor (η).

When this model is compared with experimental measurements of T and R on carbon black and ambient samples from different environments, it is found that particles in ambient samples penetrate deeper into filters than those in resuspended samples, likely due to different sampling configurations. Homogeneous oxidation and removal of carbon black occurs at $> 700^\circ\text{C}$. POC is formed in ambient samples uniformly throughout the filter. Most of the EC in US non-urban samples evolves earlier than POC after oxygen introduction at 550°C . The opposite sequence occurs for Hong Kong urban/suburban samples, consistent with different EC/POC abundances and a different form of the EC. The EC mass absorption efficiency in quartz-fiber filters can be estimated from a plot of

$\tau_{\text{ATN},p}$ vs. the sum of EC and POC; it is found to be $\sim 2.7 \pm 0.2 \text{ m}^2 (\text{gC})^{-1}$ for reference carbon black and $> 15 \text{ m}^2 (\text{gC})^{-1}$ for ambient EC that could be internally mixed.

Whether the within-filter charring is due to adsorbed organic gases, diffusion of vaporized particles during analysis, or liquid organic particles warrants further investigation. Correcting for charred OC using laser reflectance or transmittance is uncertain due to unknown absorption efficiencies and different spatial distributions of POC and EC within quartz-fiber filters. The reflectance correction is less biased by POC within the filter than is the transmittance correction. The simultaneous monitoring of reflectance and transmittance, when coupled with the extended K–M radiative transfer theory, provides additional information on the charring/combustion process within a quartz-fiber filter. This extended K–M theory will also be useful when considering multiple-wavelength reflectance and transmittance measurements that may better differentiate EC and POC.

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