Equivalence of Elemental Carbon by Thermal/Optical Reflectance and Transmittance with Different Temperature Protocols

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Charring of organic carbon (OC) during thermal/optical analysis is monitored by the change in a laser signal either reflected from or transmitted through a filter punch. Elemental carbon (EC) in suspended particulate matter collected on quartz-fiber filters is defined as the carbon that evolves after the detected optical signal attains the value it had prior to commencement of heating, with the rest of the carbon classified as organic carbon (OC). Heretofore, operational definitions of EC were believed to be caused by different temperature protocols rather than by the method of monitoring charring. This work demonstrates that thermal/optical reflectance (TOR) corrections yield equivalent OC/EC splits for widely divergent temperature protocols. EC results determined by simultaneous thermal/optical transmittance (TOT) corrections are 30% lower than TOR for the same temperature protocol and 70–80% lower than TOR for a protocol with higher heating temperatures and shorter residence times. This is true for 58 urban samples from Fresno, CA, as well as for 30 samples from the nonurban IMPROVE network that are individually dominated by wildfire, vehicle exhaust, secondary organic aerosol, and calcium carbonate contributions. Visual examination of filter darkening at different temperature stages shows that substantial charring takes place within the filter, possibly due to adsorbed organic gases or diffusion of vaporized particles. The filter transmittance is more influenced by the within-filter char, whereas the filter reflectance is dominated by charring of the near-surface deposit that appears to evolve first when oxygen is added to helium in the analysis atmosphere for these samples. The amounts of charred OC (POC) and EC are also estimated from incremental absorbance. Small amounts of POC are found to dominate the incremental absorbance. EC estimated from absorbance are found to agree better with EC from the transmittance charring correction than with EC from the reflectance charring correction.

Introduction

Organic carbon (OC) and elemental carbon (EC) (in some cases also called black carbon; BC) are measured on source and ambient quartz-fiber filter samples by several thermal carbon analysis methods that apply: (i) solvent extraction followed by combustion (1), (ii) continuous temperature ramping (2, 3), (iii) two temperatures in oxidizing and/or non-oxidizing atmospheres (4–16), (iv) thermal/optical reflectance (TOR) (17–20), and (v) thermal/optical transmittance (TOT) (21–29). Thermal methods heat a portion of the sample in a continuous or stepwise manner under different atmospheres, with subsequent detection of the volatileized or oxidized carbon that leaves the sample. With consistent standardization, these methods provide equivalent measures of total carbon (TC, the sum of OC and EC). They define the split between OC and EC based on combinations of combustion temperatures, residence time at each temperature, the composition of the atmosphere surrounding the sample, and light reflected from or transmitted through the filter.

Atmospheric EC, bearing little resemblance to mineral forms such as graphite or diamond, is the dark-colored, low-volatile carbon fraction that does not appreciably evolve without oxidants at temperatures below ~700 °C. However, pyrolyzing and charring of OC on and within the filter as the sample is heated may add to the original EC that was collected from the atmosphere, artificially inflating its concentration. Red light from a laser monitors the darkening of the particle deposit on the filter due to OC charring. When oxygen (O2) is added to the analysis atmosphere (i.e., carrier gas) at a sufficiently high temperature (e.g., > 350 °C) (11), this black char combusts along with the original EC on the filter and the filter becomes whiter. This darkening and lightening is measured by light reflected from the filter surface and transmitted through the entire filter. When the reflected or transmitted light attains its original intensity, the pyrolyzed and charred OC (POC) is considered to have been removed, and all of the remaining carbon is associated with the EC that was originally on the filter. Therefore, a partitioning can be made by assigning carbon evolved before this split point to OC and after this point to EC. Johnson et al. (17) and Yang and Yu (28) pointed out that this partitioning assumes that (i) charred OC evolves before original EC in the thermal analysis and (ii) charred OC and original EC equally attenuate reflectance (R) and transmittance (T).

TOR and TOT methods have been compared with each other and with other OC and EC methods in several published inter-method and inter-laboratory studies (25, 27, 30–35) with inconclusive results. Methodological differences between OC and EC vary depending on the nature of the samples analyzed, the analysis protocols, and the instrumentation applied. Analysis protocols and instrumentation differ with respect to (i) temperature plateaus, (ii) residence time at each plateau, (iii) charring corrections by light reflectance or transmittance, (iv) optical monitoring configuration and wavelength, (v) combustion atmospheres, (vi) temperature ramping rates, (vii) carrier gas flow through or across the sample, (viii) oven flush, (ix) sample aliquot and size, (x) location of the temperature monitor relative to the sample, (xi) oxidation and reduction catalysts, (xii) evolved carbon detection method, and (xiii) calibration standards. Different samples may react differently with various analysis protocols, thereby giving different results. Potential sample biases include (i) nonuniform particle deposits on the filter; (ii) particle deposits that are too light or too dark, making TOR and TOT charring corrections uncertain; (iii) organic vapor filter adsorption and its charring during heating (iv) catalytic
and oxidation interactions between OC, EC, and non-carbonaceous material in the sampled particles; and (v) changes in optical properties of the particles during thermal evolution.

Each of these variables needs to be studied systematically to quantify their contributions to differences among the many thermal methods applied throughout the world. The objective of this work is to evaluate differences in the OC/EC split due to two variables: temperature protocol and detection of charring by R or T. This is done by comparing the EC measured with two temperature protocols that bracket the conditions applied in U.S. PM2.5 (particles with aerodynamic diameters less than 2.5 μm) networks and simultaneously monitoring R and T for different aerosol mixtures. All other variables remain constant by performing these analyses on the same instrument with the same carrier gases. This experimental approach is complemented by a modeling effort that reinforces its findings (35). The experimental approach is described below, followed by the results and a discussion of the observations.

Experimental Approach

Ambient PM2.5 samples on quartz-fiber filters (2500 QAT-UP, Pall Life Sciences, Ann Arbor, MI) from the nonurban IMPROVE (Interagency Monitoring of Protected Visual Environments) visibility network (36) and the urban Fresno, CA, supersite (37) were used for these experiments. IMPROVE samples are acquired on 25 mm diameter filters from which only three 0.506 cm² punches can be taken, one of which is used for carbon analysis (20). Thirty IMPROVE samples were chosen for this study representing a variety of compositions to generalize the findings from the single-site Fresno samples.

To perform several experiments requiring numerous separate punches, large samples were taken on prebaked 406 cm² quartz-fiber filters (tissue quartz, Pall Life Sciences, Ann Arbor, MI) at the Fresno supersite. These filters were mounted in a high-volume (1130 L min⁻¹) sampler with a PM2.5 size-selective inlet (Andersen Instruments, Smyrna, GA). Samples were taken from 0000 to 2400 PST approximately one to two times per week from August 24, 2002, through April 18, 2003. PM2.5 carbon at Fresno includes contributions from vegetative burning, cooking, diesel exhaust, gasoline exhaust, and secondary organic aerosol that vary throughout the year (38–43). The high-volume filters were not preceded by organic vapor denuders because previous comparisons with and without denuders found approximately equivalent positive and negative sampling artifacts for Fresno aerosol (42), and real OC was much larger than artifact OC after dynamic blank subtraction for most 24-h samples. Fifty-eight of these Fresno samples were used in this study.

Figure 1 illustrates the analysis configuration that is capable of implementing a variety of thermal and optical carbon analysis protocols. One low-temperature (LowT) protocol (20) and one high-temperature (HighT) protocol (26) were adopted to represent extremes for the magnitude of temperature plateaus and the residence time at each temperature. As documented in Figure 2a, the LowT protocol achieves plateaus of 120, 250, 450, and 550 °C in an ultrahigh-purity helium (He) atmosphere (He > 99.999%, followed by a moisture/hydrocarbon/O₂ trap), remaining at each plateau until a well-defined carbon peak has evolved. In general, R and T begin to decrease at temperatures > 250 °C, indicating that some of the remaining OC on and within the sample is charring. After 2% O₂ in 98% He is added at 550 °C, additional carbon evolves, most of which consists of EC and POC, as indicated by the rapid increase of both R and T. These optical signals achieve their original values (horizontal dotted lines in Figure 2a) at different times during the analysis, and the difference in the charring correction between the two methods (i.e., TOR or TOT split) is identified in Figure 2a. The LowT protocol continues to increase temperatures from 550 to 700 °C and then to 800 °C, with the residence time defined by the flattening of carbon signals. R usually returns to its initial value before T; therefore, EC determined with the TOR charring correction is usually higher than with the TOT correction.

The HighT protocol (Figure 2b) implemented here heats the sample to 310, 480, 615, and 900 °C over set periods of 60–90 s in the same pure He atmosphere used for the LowT protocol. The sample is then cooled to 600 °C, at which time the 2% O₂ in 98% He atmosphere is introduced. The final temperature plateaus are 600, 675, 750, 825, and 920 °C for 45–120 s. In Figure 2b, R achieves its original value before the addition of O₂, indicating the removal of EC, POC, or other light-absorbing material in the pure He environment. Chow et al. (25) attributed the early evolution of EC to increased oxidation or catalysis at high temperatures (> 700 °C) by minerals (e.g., MnO₂, Fe₂O₃, SiO₂, Al₂O₃) that coexist with the carbon particles in the atmosphere or are part of the filter. Lin and Friedlander (44) demonstrated how catalysts, such as NaCl, lower the EC decomposition temperature, while Fung (13) quantifies how the reaction kinetics between pure graphite and MnO₂ increase with temperature. Most of the Fresno samples retain a reddish tinge rather than the white
FIGURE 2. Example thermograms for a medium-loaded Fresno sample (TC = 24.5 μg/cm² or 6.9 μg/m²) for (a) the low-temperature (LowT) protocol and (b) the high-temperature (HighT) protocol implemented in the Figure 1 configuration. Reflectance (R) and transmittance (T) are in relative units. The nominal LowT temperature plateaus in pure He are 120 °C (OC1), 250 °C (OC2), 450 °C (OC3), and 550 °C (OC4). Temperatures are increased when the flame ionization detector (FID) response returns to baseline or remains at a constant value. Temperature plateaus in the 2% O₂ in 98% He atmosphere are 550 °C (EC1), 700 °C (EC2), and 800 °C (EC3). Pyrolyzed/charred organic carbon (POC) is defined as the carbon that is measured after the introduction of the He/O₂ atmosphere at 550 °C but before R and T return to their initial values. POC is reported as a negative value when R or T attain their initial values prior to O₂ introduction. OC is defined as OC1 + OC2 + OC3 + OC4 + POC, and EC is defined as EC1 + EC2 + EC3 – POC. The HighT temperature plateaus in He are 310 °C (60 s), 480 °C (60 s), 615 °C (60 s), and 900 °C (90s). Temperature is reduced to ∼600 °C before addition of 2% O₂ in He followed by temperature plateaus at 600, 675, 750, and 825 °C, each for 45 s, and 920 °C for 120 s. POC for both TOR and TOT corrections are reported as positive or negative relative to the time at which O₂ is added. The early dip in reflectance in the HighT analysis (at ∼100 s) likely results from the rapid volatilization of nitrate.
Figure 3 demonstrates that LowT and HighT temperature protocols yield the same TC for the 58 Fresno samples. A similar equivalence was demonstrated for the 30 IMPROVE samples (slope = 0.99 ± 0.005, intercept = 0.1 ± 0.2 μg/cm², R² = 0.999). These TC comparisons indicate that the sample deposit is homogeneous and that the carbon analysis precision is within ±2 μg/cm² or ±5% for the average Fresno carbon concentration of 46 μg/cm². It also shows that the maximum temperature applied in the HighT protocol (120 °C higher than the maximum in the LowT protocol) does not release additional carbon, which might not be the case if some carbonaceous material (possibly carbonates) evolved at temperatures >800 °C (45). The maximum TC for Fresno samples is 145 μg/cm², corresponding to an ambient concentration of 40.9 μg/m³.

On average, TOT resulted in ~30% lower EC than TOR for the LowT protocol and ~70% lower EC for the HighT protocol, as shown in Figure 4. Figure 5a shows that EC with the TOR correction is the same regardless of the temperature protocol for the Fresno samples. On the other hand, LowT_TOT EC is about twice the HighT_TOT EC (Figure 5b). Therefore, LowT_TOR EC and HighT_TOT EC differ the most, with a slope of 0.29 ± 0.03 (Figure 5c), very similar to that of HighT_TOR and HighT_TOT in Figure 4 (0.29 ± 0.02). Figure 6 also shows the discrepancy between TOR and TOT corrections for the IMPROVE samples. A good agreement between TOR EC from the two temperature protocols for the IMPROVE samples (Figure 6) demonstrates that the Results 5 results are not caused by some peculiarity of the Fresno aerosol.

In summary, within a given temperature protocol, TOR and TOT corrections give different EC results, with their differences amplified in the HighT protocol as the initial and maximum temperatures in a non-oxidizing atmosphere increase and residence times at each plateau decrease. Regardless of the operational definitions for EC, the results for these samples show that the TOR charring correction gives equivalent EC estimates for large differences in thermal evolution temperatures. This finding is consistent across a range of sample locations and source contributions.

Discussion

Potential Causes of TOR and TOT Differences. To elucidate how optical monitoring affects the charring correction, multiple punches from the same filter were analyzed by both the LowT and HighT temperature protocols for several Fresno samples. The analyses were stopped at different temperatures, the samples were cooled rapidly to a temperature of ~40 °C in the most recent analysis atmosphere (pure He or 2% O₂ in 98% He), and the punches were removed for immediate visual examination. Photographs were taken of the front and back of the retrieved punches. They were then cut in half, sandwiched between two microscope slides, and photographed through an optical microscope to evaluate the visual appearance of the filter cross-section. Results for one of the samples are shown in Figure 7 to illustrate what was found for all of the tested samples. Darkening of both sides of the filter, as previously reported by Huntzicker et al. (18), Chow et al. (20), and Yang and Yu (28), is evident in Figure 7. The cross-sections show continued darkening throughout the filter as temperatures increase in the He environment, even though most of initial light absorbing material, representing the ambient PM₂.₅ deposit, appears to be near the surface. This is consistent with POC forming within and throughout the filter thickness.

Figure 7a shows an example of a heavily loaded Fresno sample during the LowT protocol while Figure 7b shows a punch from the same sample during the HighT protocol.
and T signals (quantified indicated by the reflection and transmission photodetectors, respectively) are also presented to allow a more quantitative estimate of the filter darkening.

The initial T signal (mV) is low for this sample due to a high EC deposit (LowT/HighT TOR EC < 25 µg cm⁻²), which appears to reside at or near the surface of the filter according to the cross-section picture. This agrees with the calculations by Chen et al. (35) that show > 80% of the aerosol deposition is located on the top one-third to one-half of this type of quartz-fiber ambient filter sample. Darkening occurs throughout the filter as heating continues in the pure He environment. T reduces to zero as the filter becomes opaque due to blackening, but changes in R are still detectable. The R signal reaches a minimum of 516 mV at 549 °C for the LowT protocol and 365 mV at 897 °C for the HighT protocol in the He atmosphere, consistent with more charring during the HighT protocol. As shown in Figure 7, the backside and cross-section appear to be darker for the HighT protocol compared to the LowT protocol at the respective minimum R.

The additional charring occurring at higher temperature steps (> 550 °C) in He suggests that certain organic compounds have not completely pyrolyzed below 550 °C in the HighT protocol. This charring could be reduced if a longer residence time were implemented at lower temperature steps to allow more of these compounds to leave the filter prior to the onset of charring. Kirchstetter et al. (45) showed that much of the adsorbed organic gases on backup filters evolve at < 250 °C within a sufficient time. The LowT protocol includes a longer residence time (~10 min) at lower initial temperatures (120 and 250 °C) than the HighT protocol. However, since the LowT protocol never reaches temperatures higher than 550 °C in He, the question of whether this longer residence time produces significantly less charring warrants further investigation. At 677 °C (He/O₂) during the HighT protocol (Figure 7b), the filter transmittance nearly attains its initial values, but the reflectance at this moment is substantially higher than its initial value. This is consistent with the observation that POC within the filter remains when a large fraction of the surface deposit has been removed.

Two processes might contribute to a uniform distribution of POC in the filter: (i) charring of volatile or semi-volatile organic compounds that adsorb onto quartz fibers during
sampling or (ii) diffusion of vaporized organic matter from
the filter surface downward as the sample is heated. Organic
vapor adsorption is a well-known artifact in ambient car-
bonaceous aerosol sampling (45–47), and charring of these
adsorbed organic materials may account for a substantial
fraction of POC. Similar charring is seen on IMPROVE backup
filter punches (not shown here) with no particle deposition,
but for these backup filters the TOR and TOT corrections are
equivalent and yield negligible EC.

These results are consistent with an extended Kubelka–
Munk radiative transfer model that relates $R$ and $T$ for
different distributions within a filter of materials having
different light absorption and scattering properties (35). This
model is consistent with the convergence of TOR and TOT
corrections in the case of only a shallow surface deposit of
EC or only a uniformly distributed POC through the filter.
It suggests divergence between TOR and TOT corrections
when EC and POC exist concurrently at the surface and are

<table>
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<th>Temperature ($^\circ$C) &amp; Atmosphere</th>
<th>50 (He)</th>
<th>250 (He)</th>
<th>549 (He)</th>
<th>550 (He/He)</th>
<th>551 (He/He)</th>
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<td>Reflectance ($R$)</td>
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<td>516</td>
<td>575</td>
<td>1314</td>
<td>1561</td>
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<tr>
<td>Transmittance ($T$)</td>
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<td>4</td>
<td>0</td>
<td>0</td>
<td>268</td>
<td>538</td>
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**FIGURE 7.** Visual and microscopic investigations of the sample (TC = 122 $\mu g/cm^2$ or 34.4 $\mu g/m^3$) at different temperature stages during (a) LowT and (b) HighT protocols. Reflectance ($R$) and transmittance ($T$) are in relative units of mV. He and He/He are the combustion atmospheres when the sample was retrieved from the analyzer. The fourth column from the left in each sequence shows the temperature and reflectance or transmittance at the point of maximum darkening of the filter. The HighT reflectance (365 mV at 897 $^\circ$C) is much lower than the LowT reflectance (516 mV at 549 $^\circ$C), indicating a larger amount of charring for the higher HighT temperatures. (The punch size is 0.506 cm$^2$, the filter thickness is 0.43 mm, and the areal density is ~5.8 mg/cm$^2$.)
distributed throughout the filter, respectively, especially when the surface EC evolves prior to the POC. Therefore, the difference between TOR and TOT partly depends on the POC/EC ratio in the sample. This theory explains why samples dominated by diesel exhaust and graphite powder with a dark surface deposit often yield the same EC values for TOR and TOT corrections, while complex ambient mixtures yield different EC values (35). It can also explain why backup filters used to evaluate organic vapor adsorption, which have no surface deposit and experience uniform charring throughout their cross-sections, show similar TOR and TOT corrections.

**EC and POC Apportionment.** For quantifying EC, an alternative to the thermal/optical analysis with TOR or TOT charring correction is the estimation of light absorption of an aerosol deposit compared to that of a blank filter. While the absorption of EC within quartz-fiber filters is difficult to measure absolutely, reflectance and transmittance of light have long been used to estimate relative EC on filters (51–54). For example, incremental light attenuation of a filter due to deposited aerosol is widely used in the aethalometer (51, 52) and particle soot absorption photometer (PSAP) (53) to estimate EC concentrations based on a linear relationship between incremental light attenuation and EC mass. Lindberg et al. (54) reevaluated this empirical relationship and confirmed its validity for common atmospheric particulate samples. Incremental light attenuation primarily due to EC absorption (\( \tau_{\text{ATN,EC}} \)) is quantified by

\[
\tau_{\text{ATN,EC}} = -\ln\left(\frac{T_i}{T_f}\right)
\]

where \( T_i \) and \( T_f \) are the filter transmittance at the beginning and end (i.e., blank) of thermal analysis, respectively. The EC mass absorption efficiency within the filter (\( E_{\text{EC}} \)) is defined as

\[
E_{\text{EC}} = \frac{\tau_{\text{ATN,EC}}}{[\text{EC}]}
\]

where \([\text{EC}]\) indicates the EC areal mass concentration (\( \mu g/cm^2 \)) on the filter. \( E_{\text{EC}} \) (usually in \( m^2/g \)) may be higher than its actual value in the atmosphere due to multiple scattering effects from the filter medium. The incremental light attenuation due to POC (\( \tau_{\text{ATN,POC}} \)) can be defined in analogy to eq 1

\[
\tau_{\text{ATN,POC}} = -\ln\left(\frac{T_i}{T_f}\right)
\]

where \( T_i(t) \) is defined as the transmittance at any instant before EC and POC evolve (i.e., before \( R \) and \( T \) start to increase) during thermal analysis. The POC mass absorption efficiency (\( E_{\text{POC}} \)) becomes

\[
E_{\text{POC}} = \frac{\tau_{\text{ATN,POC}}}{[\text{POC}]}
\]

where \([\text{POC}]\) is the areal mass concentration (\( \mu g/cm^2 \)) of POC. \( \tau_{\text{ATN,EC}} \) is assumed to be constant before oxidation occurs. \( E_{\text{EC}} \), \( E_{\text{POC}} \), \([\text{EC}]\), and \([\text{POC}]\) are unknown for each sample. Parameters being measured every second include \( R \), \( T \), and evolved carbon mass (see Figure 2a); \( \tau_{\text{ATN,EC}} \) and \( \tau_{\text{ATN,POC}} \) before \( O_2 \) introduction can therefore be determined. The 1-s areal carbon concentration determined from the flame ionization detector (FID) does not have a one-to-one correspondence to the optical measurements owing to peak broadening and a tailing effect caused by transit through the \( C \to CO_2 \) and \( CO_2 \to CH_4 \) conversion ovens. Comparison of optical and carbon measurements at the end of temperature plateau, however, is meaningful for the LowT protocol in which the FID signal levels off before the temperature advances to next plateau. Through the LowT protocol, carbon evolved at each temperature plateau is completely measured (see Figure 2a). It is further assumed that carbon left on the filter at the end of the 550 °C plateau before the addition of \( O_2 \) contains only EC and fully formed POC. R and T nearly always attain their minima for the entire analysis at 550 °C in He during the LowT protocol, consistent with no EC or POC being burned. The following analysis will not apply to the HighT protocol because the carbon peaks are not completely associated with specific temperature plateaus owing to the short and fixed residence time at each plateaux.

With these relationships and assumptions, \( T(t) \) in eq 3 is chosen at the end of the 550 °C plateau before the addition of \( O_2 \) to calculate \( \tau_{\text{ATN,POC}} \). The following relationship applies for each sample:

\[
[c\text{arbon}]_{\text{after \( O_2 \)}} = [\text{EC}] + [\text{POC}] = \frac{\tau_{\text{ATN,EC}}}{E_{\text{EC}}} + \frac{\tau_{\text{ATN,POC}}}{E_{\text{POC}}}
\]

Replicate analysis has indicated the precision of \( \tau_{\text{ATN,EC}} \) and \( \tau_{\text{ATN,POC}} \), generally within 10%. If \( E_{\text{EC}} \) and \( E_{\text{POC}} \) are reasonably constant from sample to sample, a linear least squares optimization (linear regression) of the measured \([\text{carbon}]_{\text{after \( O_2 \)}}\) on \( \tau_{\text{ATN,EC}} \) and \( \tau_{\text{ATN,POC}} \) yields estimates of the inverse absorption efficiencies for EC and POC. Estimates for EC and POC can then be made for each sample via eqs 2 and 4. Additional conditions are that the minimum \( T_i \) at maximum charring must be detectable, and there are no early OC/EC splits. These conditions were met for 31 of the 58 Fresno samples. For these samples, the zero-intercept correlation (R²) between \([\text{carbon}]_{\text{after \( O_2 \)}}\) and \( \tau_{\text{ATN,EC}} \) is 0.78. R² between \([\text{carbon}]_{\text{after \( O_2 \)}}\) and \( \tau_{\text{ATN,POC}} \) is only 0.37. R² improves to 0.89 for the multiple linear regression model of eq 5. The inverse of the regression coefficients \( E_{\text{EC}} \) and \( E_{\text{POC}} \) are 21.6 ± 1.9 and 52.8 ± 10.6 m²/g of C, respectively. \( E_{\text{EC}} \) of ~20 m²/g of C is at the upper limit of reported values for the EC absorption efficiency (e.g., refs 55 and 56) of atmospheric aerosols, but it is typical of transmission measurements on quartz-fiber filters (57). \( E_{\text{POC}} \) is ~2.5 times higher than \( E_{\text{EC}} \), implying that POC for the same amount as EC causes a stronger attenuation than the atmospheric EC for the Fresno samples. Conny et al. (58) observed very different characteristics between EC and POC in terms of their surface-to-volume ratio with a scanning electron microscope. Multiple scattering within such optically dense quartz-fiber filters could enhance the absorption of EC and POC by different degrees.

The partitioning of EC and POC in \([\text{carbon}]_{\text{after \( O_2 \)}}\) can also be calculated from eq 5 using a \( E_{\text{POC}}/E_{\text{EC}} \) ratio of 2.5 (i.e., ~52.8/21.6). Figure 8 shows the partitioning for the Fresno samples and compares them with the OC/EC splits determined by TOR and TOT with the LowT protocol. TOR EC agrees better with the linear regression EC. For most of the lightly loaded samples, the difference is within ±10%. TOT EC, however, is generally 30–40% less than the calculated EC from regression and TOR EC.

The regression model was also applied to 68 randomly selected samples from the IMPROVE network with carbon concentration ranges (TC): 16–107 \( \mu g/cm^2 \) similar to those of the Fresno samples. Results were similar (R² = 0.85; \( E_{\text{EC}} = 18.5 ± 2.3 \) m²/g of C, \( E_{\text{POC}} = 48.5 ± 3.9 \) m²/g of C). Figure 9 compares the maximum attenuation (\( \tau_{\text{ATN,EC}} + \tau_{\text{ATN,POC}} \)) with \([\text{carbon}]_{\text{after \( O_2 \)}}\) for the Fresno and IMPROVE samples (see eq 5 for their relationship). Generally, the absorption efficiency of each EC and POC mixture falls within the \( E_{\text{EC}} \) and \( E_{\text{POC}} \) estimates. These analyses suggest the utility of
reporting initial, minimum, and final values of \( R \) and \( T \) from temperature profiles that provide well-defined carbon fractions along with the TOR and TOT corrections. Similar estimates of EC and POC partitioning could be made for large numbers of samples as part of the routine measurements in PM\(_{2.5}\) networks.

**FIGURE 8.** Partitions of original EC and POC in carbon evolved after 2\% \( O_2 \) is added to the He atmosphere for the LowT protocol. The partitioning is based on incremental absorbance regression method for 31 Fresno samples with a detectable minimum transmittance. EC determined from reflectance correction (TOR EC) and transmittance correction (TOT EC) is also shown. The error bars indicate the precision of the TOR and TOT EC measurements.

**FIGURE 9.** Comparison of carbon measured after the addition of \( O_2 \), \([\text{carbon}]_{\text{after } O_2}\), with the maximum absorbance during the LowT protocol analysis. The 68 IMPROVE samples were selected from 25 IMPROVE network sites (DENA1, WHPA1, CRLA1, CAB11, SACR1, GRBA1, SAPE1, SAWT1, GRSA1, BOWA1, MEVE1, BRMA1, BOAP1, GRBA1, ZION1, BRE1, COH1, COR1, DOM1, NOCA1, CAB11, LLYB1, CACO1, SIKE1, and SAMA1) during 2001 to represent different types of carbon contributions. These samples were selected at random from the IMPROVE archive and do not overlap with those presented in Figure 6. The absorption efficiency of EC and POC is estimated from multiple linear regression, as explained in the text.

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**Literature Cited**
