

## Optimizing the Measurement of Light-Absorbing (Black) Carbon in Atmospheric Aerosols that Impact Regional Climate

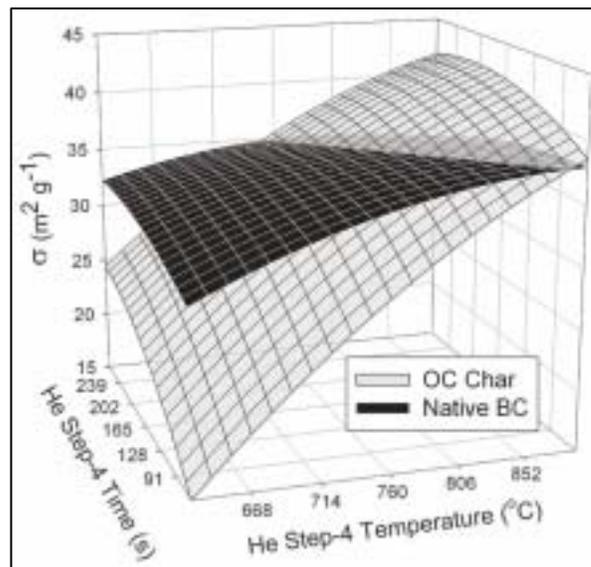
*NIST researcher established a new protocol for thermal optical transmission analysis (TOT) in support of EPA's national air monitoring systems. TOT combines a multi-step thermal protocol for removing carbonaceous material on a particle-laden quartz fiber filter with a system to optically monitor the filter during heating. The mass of carbon removed from the filter is measured by flame ionization detection. To determine BC, particulate organic carbon (OC) must also be quantified. This is accomplished by monitoring the light absorption of OC as it is pyrolyzed. Unfortunately, BC and pyrolyzed OC often evolve concurrently. To accurately distinguish the mass of BC from OC in this approach, two criteria must be met: 1) OC must be sufficiently pyrolyzed to avoid a positive measurement bias from unpyrolyzed OC, and 2) the specific absorption cross sections for BC and pyrolyzed OC must be equivalent.*

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Uncertainty in how atmospheric aerosols absorb and scatter solar and long-wave radiation is a major impediment toward predicting the temperature shift associated with climate change in different regions. As a result, the U.S. Climate Change Science Program has identified the reducing of scientific uncertainties associated with aerosols as the number #1 priority [1]. A critical component in reducing these uncertainties is the measurement of the mass of the light-absorbing component of aerosols, i.e., black carbon (BC), which is associated with combustion emissions. Methods for determining BC based directly on the Beer-Lambert Law are problematic because the attenuation coefficient varies when BC in an aerosol particle is mixed with other species such as sulfate, nitrate, or organic carbon. Thus, the attenuation coefficient varies for different types of aerosols. As an alternative, thermal optical transmission analysis (TOT) measures BC mass based on optical behavior, but does not require an absolute determination of the attenuation coefficient. Thermal-optical analysis is the principal method of the U.S. Environmental Protection Agency's National Air Monitoring System for determining refractory carbon from combustion in particulate matter <2.5  $\mu\text{m}$ .

Response surface models of the specific absorption cross sections ( $\sigma$ ) for BC and pyrolyzed OC (char) were used to determine the optimal TOT thermal protocol for BC measurement. **Figure 1** shows the overlay of  $\sigma_{\text{Char}}$  and  $\sigma_{\text{BC}}$  surfaces determined for aerosol collected in a residential neighborhood of Seattle during winter, which likely contains substantial carbon from residential wood burning. ( $\sigma$  was not corrected for the absorption enhancement effect from multiple scattering that occurs when particles are on a highly reflective substrate such as quartz-fiber filters.) The figure shows how the specific absorption cross sections intersect, and thus exhibit equivalence (2<sup>nd</sup> optimization criterion), at various temperatures and durations for the critical step in the analysis (step 4 in helium). At the highest temperatures and longer step-4 durations,  $\sigma_{\text{Char}}$  is larger than  $\sigma_{\text{BC}}$ , indicating that OC is over charred. The parabolic shape of the  $\sigma_{\text{BC}}$  surface indicates a plateau of  $\sigma_{\text{BC}}$  maxima at higher step-4 temperatures. The lower  $\sigma_{\text{BC}}$  values associated with lower temperatures in Figure 1 are likely due to the influence of inadequately charred OC being measured as native BC. Thus, the  $\sigma_{\text{BC}}$  plateau reveals the conditions where OC pyrolysis is optimized (1<sup>st</sup> optimization criterion).

**Figure 1.** Overlay of  $\sigma_{\text{Char}}$  and  $\sigma_{\text{BC}}$  response surfaces for Seattle (low-carbon limit).



**Figure 2** shows the intersection of the  $\sigma_{BC}$  surface with the upper and lower 95 % confidence intervals for the  $\sigma_{Char}$  surface in Figure 1. For  $\sigma_{BC}$  and  $\sigma_{Char}$  equivalence (2<sup>nd</sup> criteria) the BC surface must lie between the upper and lower  $2\sigma$  surfaces for char which corresponds to conditions associated with the back right portion of the BC surface i.e. higher temperatures and longer times. Particularly useful are the 2-D projections of the intersections of the  $\sigma_{BC}$  surface and the confidence interval surfaces for  $\sigma_{Char}$ . **Figure 3** shows these 2-D projections for models of aerosol samples collected during summer in Atlanta and during autumn in Los Angeles, in addition to the wintertime samples from Seattle. A comparison of response surface models for samples from all three sites revealed a single optimized TOT thermal protocol for different aerosol types. The temperature and duration of the critical heating step that best satisfies all cases is marked with the star in Figure 2 and corresponds to 785 °C for 150 s.

This work was funded by the EPA through Interagency Agreement DW 13939973.

The EPA currently employs a TOT thermal protocol for its air monitoring system that is substantially different from the optimized thermal protocol determined here. It is expected that the EPA will revise its thermal protocol to agree with this work.

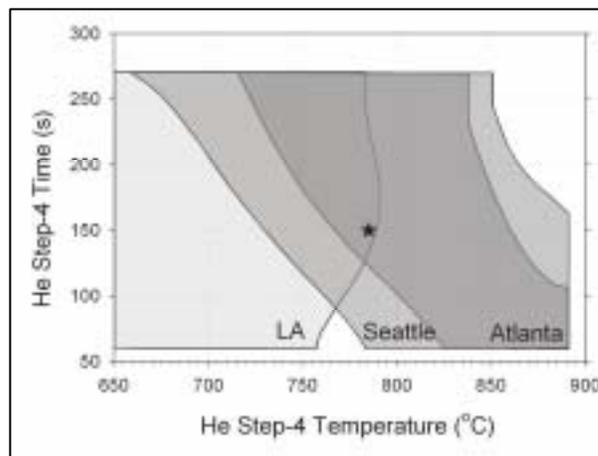
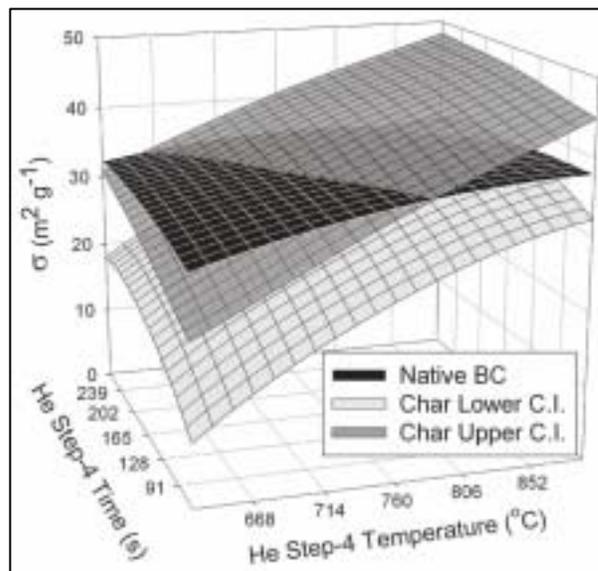
**Report:**

J.M. Conny, *The Optimization of Thermal-Optical Analysis for the Measurement of Black Carbon in Regional PM2.5: A Chemometric Approach (Final Report to the U.S. EPA)*, 2006.

**Publication:**

J.M. Conny and R.A. Cary, “*Optical Corrections and the Apparent Specific Absorption Cross Section in Thermal-Optical Transmission Analysis for Atmospheric Black Carbon*,” *Aerosol Sci. Technol.*, 2006.

**Figure 2. Intersection of the  $\sigma_{BC}$  surface in Fig. 1 and the 95 % confidence intervals (C.I.) for the  $\sigma_{Char}$  surface in Figure 1.**



**Figure 3. 2-D projections of intersections of  $\sigma_{BC}$  and  $\sigma_{Char}$  confidence intervals (viz. Figure 2) for three sample types and showing region of agreement on step-4 conditions and the optimal point (star).**

[1] *Our Changing Planet: The U.S. Climate Change Science Program for FY2006*, report by the Climate Change Science Program and the Subcommittee on Global Change Research, Washington, DC, 2006.