Formation of Refractory Black Carbon by SP2-induced Charring of Organic Aerosol

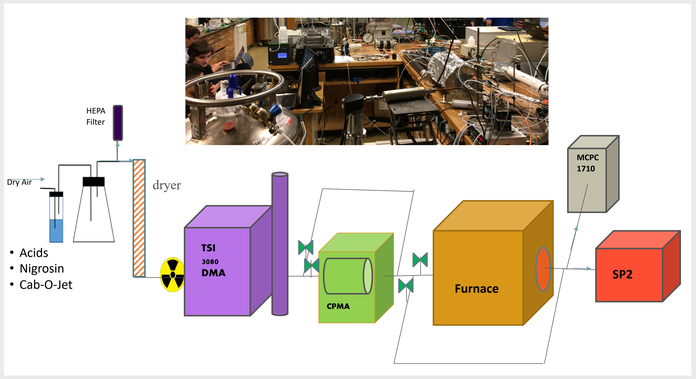
A.J. Sedlacek, III[1], T. B. Onasch[2], L. Nichman[3], E. R. Lewis[1], P. Davidovits[3], A. Freedman[1], and L. Williams[1]

[1]Brookhaven National Laboratory; [2]Aerodyne Research Inc.; [3]Boston College

Abstract

Black carbon (BC) in the atmosphere continues to be a focus of research because its light-absorptive properties put it second only to CO_2 as a warming agent of Earth's climate. Towards this end, the measurement of ambient BC has been aided greatly by the development of the Single Particle Soot Photometer (SP2) – an instrument that detects refractory black carbon (rBC) through laser-induced incandescence. Potential interference from other substances that can incandesce under 1064 nm illumination (e.g., some metals and minerals) is mitigated through the use of spectral bandpass filters (color temperature) to ensure that the SP2 remains highly selective to rBC. Here, we report on the detection of rBC that is produced through SP2 laser-induced charring (i.e., carbonization) of organic aerosol particles during the Boston College 5 (BC5) study. Nigrosin and fulvic and humic acids – non-BC-containing materials – were used as a surrogates for light-absorbing organic aerosols. The color temperature of the detected particles originating from these charred organic aerosols is near that of carbon black, fullerene soot, and ethylene soot, indicating that the incandescent particles are composed of rBC. Tar balls, a type of carbonaceous particle produced in wildfire fires and biofuel combustion/pyrolysis that absorb in the visible and near, may also undergo carbonization in the SP2. Failure to properly account for this heretofore unidentified artifact of the SP2 will lead to an overestimate of rBC loadings, which could, in turn, impact aerosol radiative forcing model predictions.

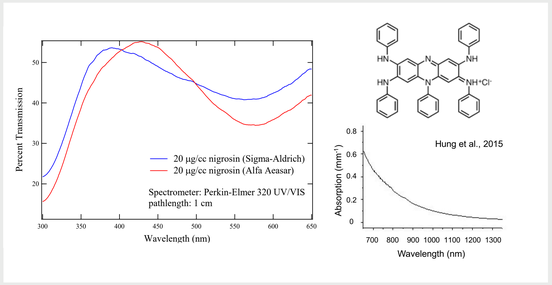
Methods



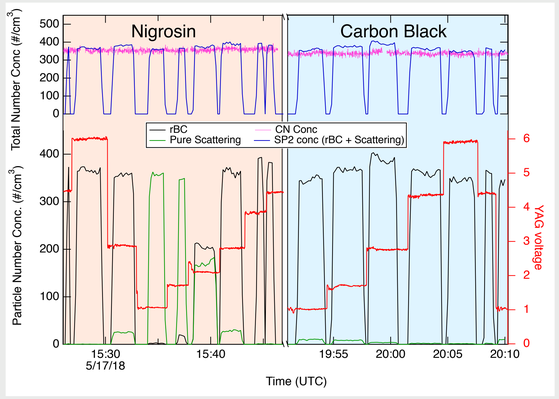
- Aerosols were generated from deionized water-based stock solutions of nigrosin (Aldrich, 198285) and carbon black (CAB-O-JET® 200 pigment), fulvic and humic acid.
- Particles were selected by their mobility diameter (DMA) or the combination of mobility diameter and mass using a Centrifugal Particle Mass Analyzer (CPMA).
- Tube oven (Lindberg/Blue M) was used to heat the fulvic and humic acid particles to induce absorption at 1064 nm.
- Single Particle Soot Photometer (SP2) was used to detect rBC.
- To minimize the effects of particle size on SP2 detection efficiency 400 nm mobility diameter particles were studied exclusively, and the particle number concentrations were kept low (<1000 cm^{-3}) to minimize particle coincidence in the instrument.

Detection of rBC from nigrosin using the SP2

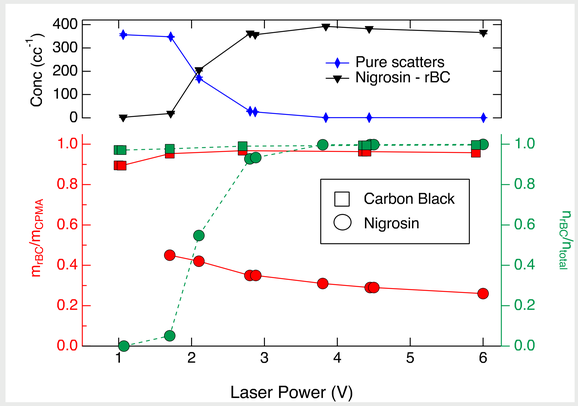
Nigrosin, a water-soluble, polyaniline-based black dye is often used in studies of atmospheric aerosol absorption as it possesses a broad, featureless absorption spectrum in the visible. Nigrosin does not contain any refractory black carbon (rBC).



Nigrosin and carbon black (Cab-o-Jet) were sampled by the SP2.



Production of rBC particles and the loss of pure scattering particles is directly related to SP2 laser power. Increased laser power causes particle heating enhancing reactions that bring about charring and subsequent detection of rBC.

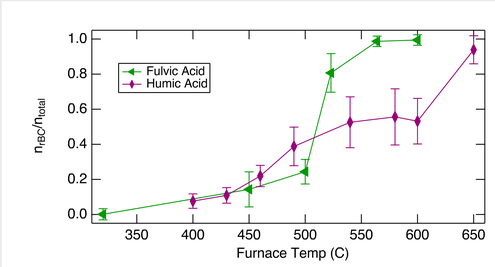


Upper panel: the number of detected rBC (downward triangles) and pure scattering (diamonds) particles as a function of SP2 laser power for nigrosin.

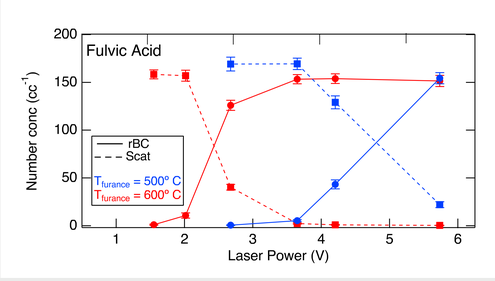
Lower panel, left axis: ratio of SP2-derived rBC particle mass to original particle mass selected by the CPMA as a function of laser power for nigrosin (red circles) and carbon black (red squares); right axis: number fraction of BC particles to total number of particles detected by the SP2 for nigrosin (green circles) and carbon black (green squares) as a function of laser power.

Detection of rBC in HULIS

Heating the humic and fulvic acid – surrogates for HULIS – particles causes them to become more absorbing, and then the SP2 causes them to heat up and char.



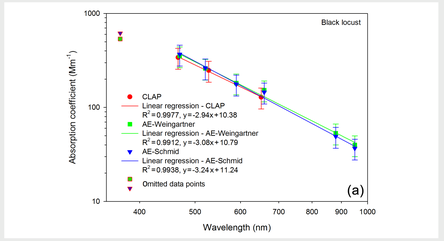
Number fraction ratio of rBC particles to total number of particles for fulvic and humic acids as a function of tube furnace temperature at a constant SP2 laser power of 4.3V.



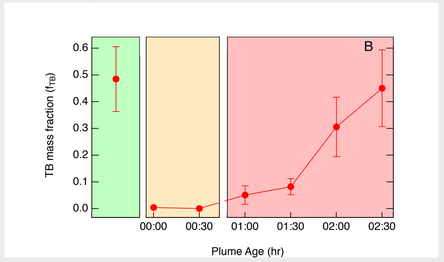
Number concentration of rBC and scattering fulvic acid particles at oven temperatures of 500 and 600 °C as a function of laser power. Higher furnace temperatures cause more chemical changes that subsequently require lower laser power to cause charring.

Atmospheric relevance of SP2-induced charring

One class of atmospherically-relevant BrC particles that absorb at longer wavelengths are tar balls (TBs) - a carbonaceous particle that appears to be the near exclusive byproduct of some types of biofuel combustion/pyrolysis and wildfires.



Hoffer et al., (2016) reported that tar balls absorb into the near-IR

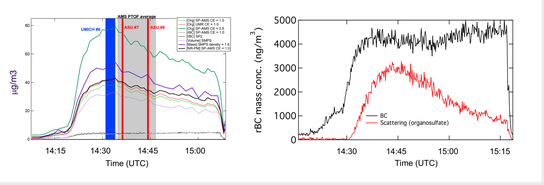


Sedlacek et al., (2018) reported that tar balls can account for 30-40% of aerosol mass in some biomass burn plumes

Laboratory-Generated Tar Balls (TBs)

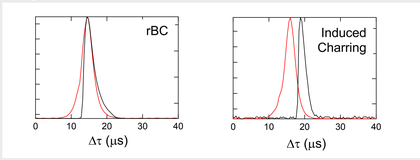
Pyrolysis of pine twigs

TBs slow to evaporate under TEM electron beam, similar to ambient TBs

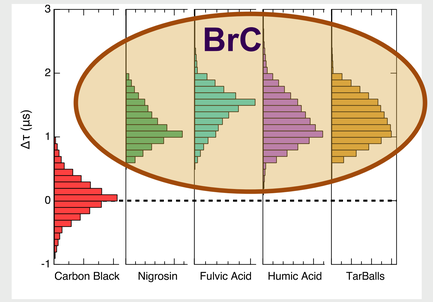


Incandescence Onset Time – $\Delta\tau$:

The time between the peak in incandescence signal and the peak of the scattering signal, $\Delta\tau$, can be used as a proxy for OA particle charring followed by SP2 detection via incandescence



Histograms of the incandescence onset times for carbon black (red), nigrosin (green), fulvic acid (aqua), humic acid (purple), and tar balls (beige). Note: Detection of rBC from BrC!



Incandescence onset times exhibited by laboratory-generated TBs are consistent with that observed for particles known to undergo SP2-induced charring.

Conclusion:

- We have demonstrated that production of rBC can occur by charring of light-absorbing organic particles that did not originally contain rBC.
- Production of rBC requires light absorption at the SP2 laser wavelength as a fundamental property of the substance (nigrosin)
- Substances can be induced to absorb at the SP2 laser wavelength through thermally-catalyzed chemical reactions such as may occur in a thermal denuder (fulvic acid and humic acid).
- rBC detection in laboratory-generated tar balls.
- This behavior could result in an overestimate of rBC, and thus misapportionment of BC and BrC, with implications for models attempting to simulate radiative forcing from biomass burning.

Acknowledgements: authors gratefully acknowledge the microscopy analysis on laboratory-generated tar balls samples by K. Adachi (Met. Research Institute) and P. Buseck (Arizona State U.) and the laboratory assistance of Injae Jung (Boston College) and Brian Heffernan (Boston College). This research was performed under sponsorship of the U.S. DOE under contracts DE-SC0012704, DE-SC0014287 and DE-SC0011935. Researchers thank the DOE Atmospheric Radiation Measurement (ARM) Climate Research Facility

References:

Hoffer et al., (2017) AMT 10, 2353
Hung et al., (2015) EOE 6, 443
Onasch et al., (2017) DOE-ARM Campaign Report SC-ARM-17-007
Sedlacek et al., (2018) AST 10.1080/02786826.2018.1531107
Sedlacek et al., (2018) ACP 18, 11289