Thermal Spectral Analysis

ODELLE HADLEY, Craig Corrigan
Scripps Institution of Oceanography

Thomas W. Kirchstetter
Lawrence Berkeley National Laboratory

Gavin McMeeking
Colorado State University

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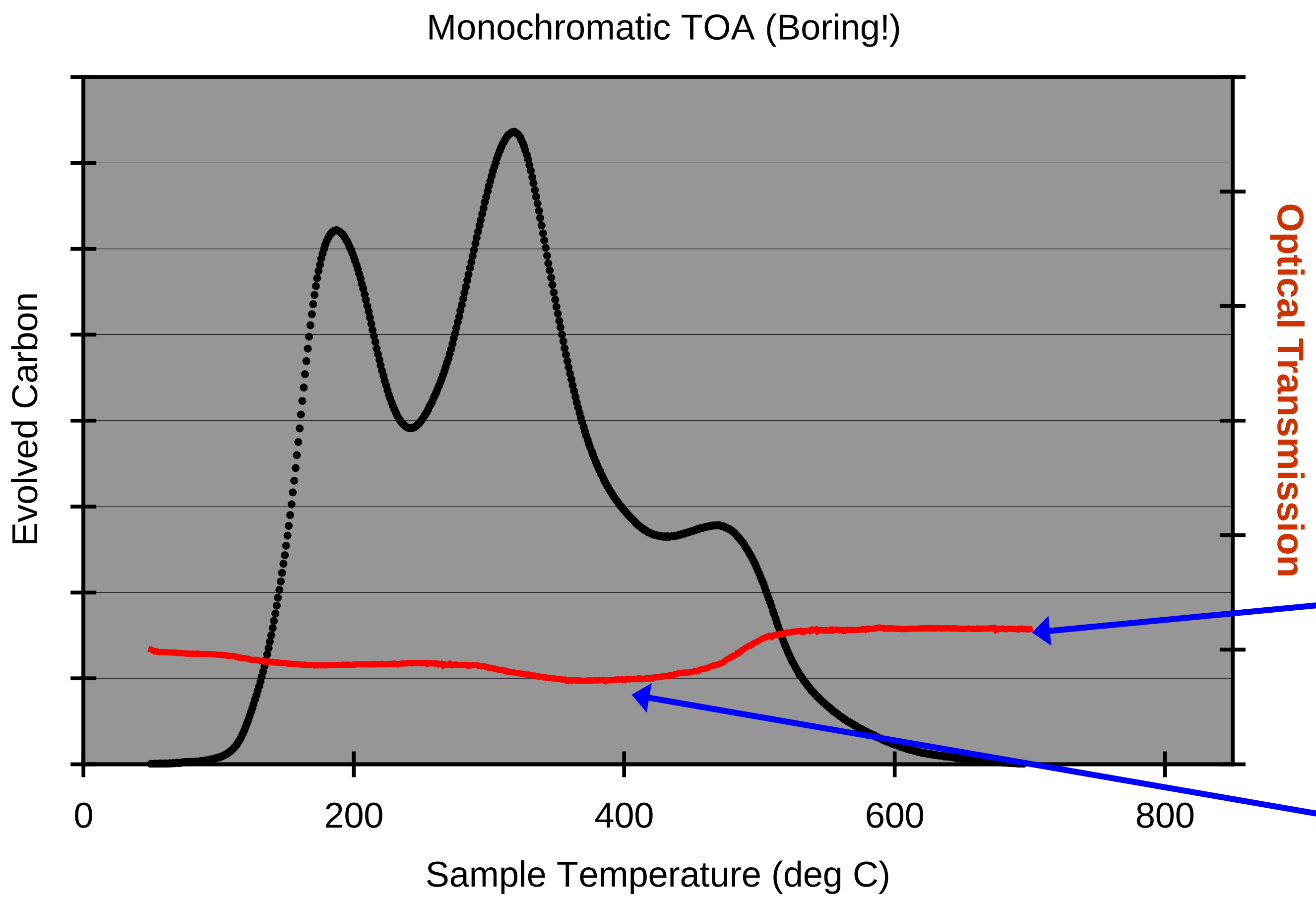
What this Presentation Deals With

- Thermal-optical analysis (TOA) of carbonaceous particles on quartz filters
  - Optical correction for pyrolysis of organic carbon (i.e., charring)

- Aerosol absorption selectivity
  - Variation in light absorption vs. wavelength (λ)
  - Often expressed using power law: Abs = c $\lambda^{-Åexp}$
  - Absorption Ångstrom exponent, $Å_{exp}$:
    - Weak selectivity, $Å_{exp}$~1: black carbon is primary absorber
    - Strong selectivity, $Å_{exp}$~2 to 5: organic carbon (i.e., "brown" carbon) contributes to absorption, especially at short λ

(Monochromatic) Thermal-Optical Analysis ☹

- 1978 – present: TOA methods monitor transmission or reflection of monochromatic light (e.g.,633nm He-Ne laser) from filter sample

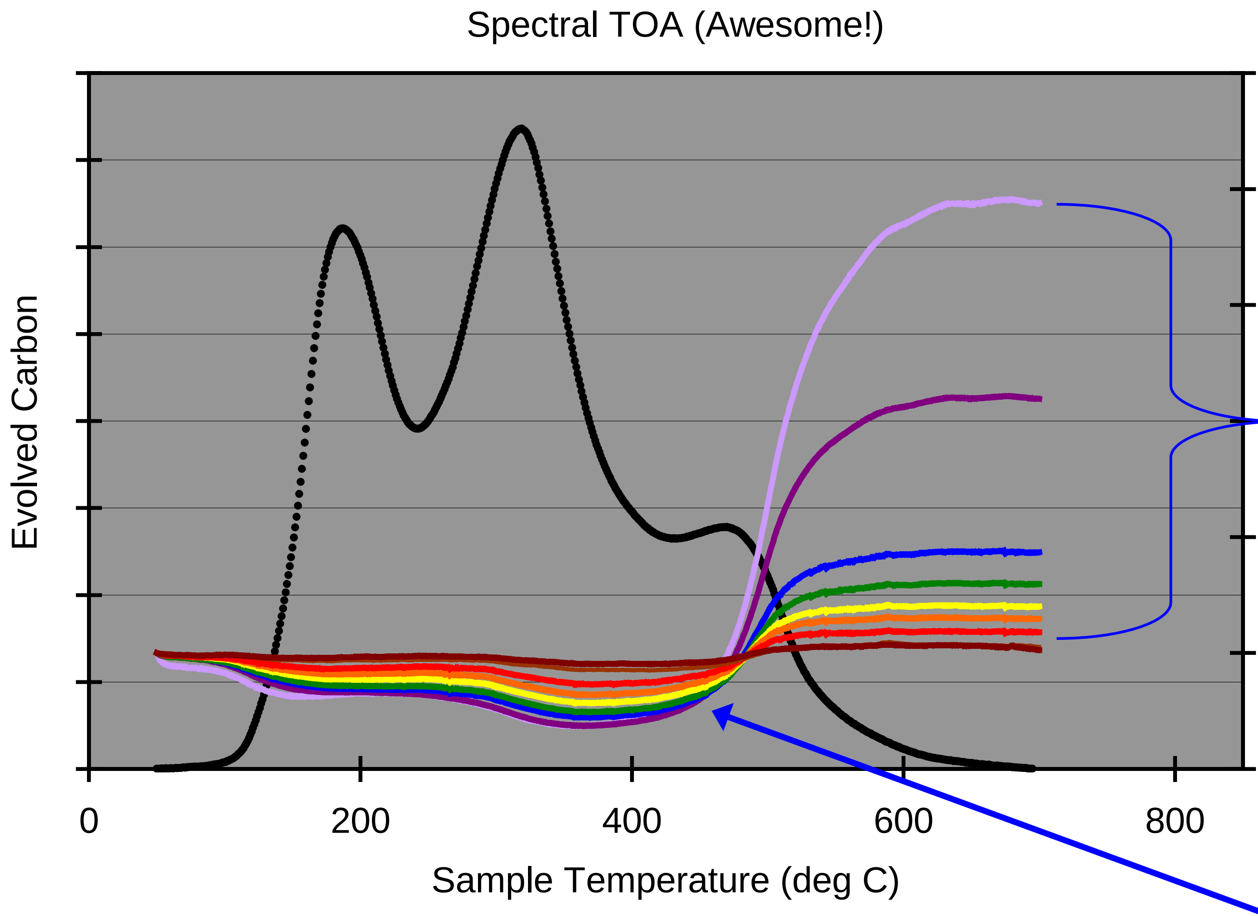


Difference between initial and final intensity yields sample optical attenuation

Decrease in transmission indicates sample charring

Thermal-Spectral Analysis (TSA) ☺

❖ Why not enhance TOA by monitoring sample over broad spectrum?

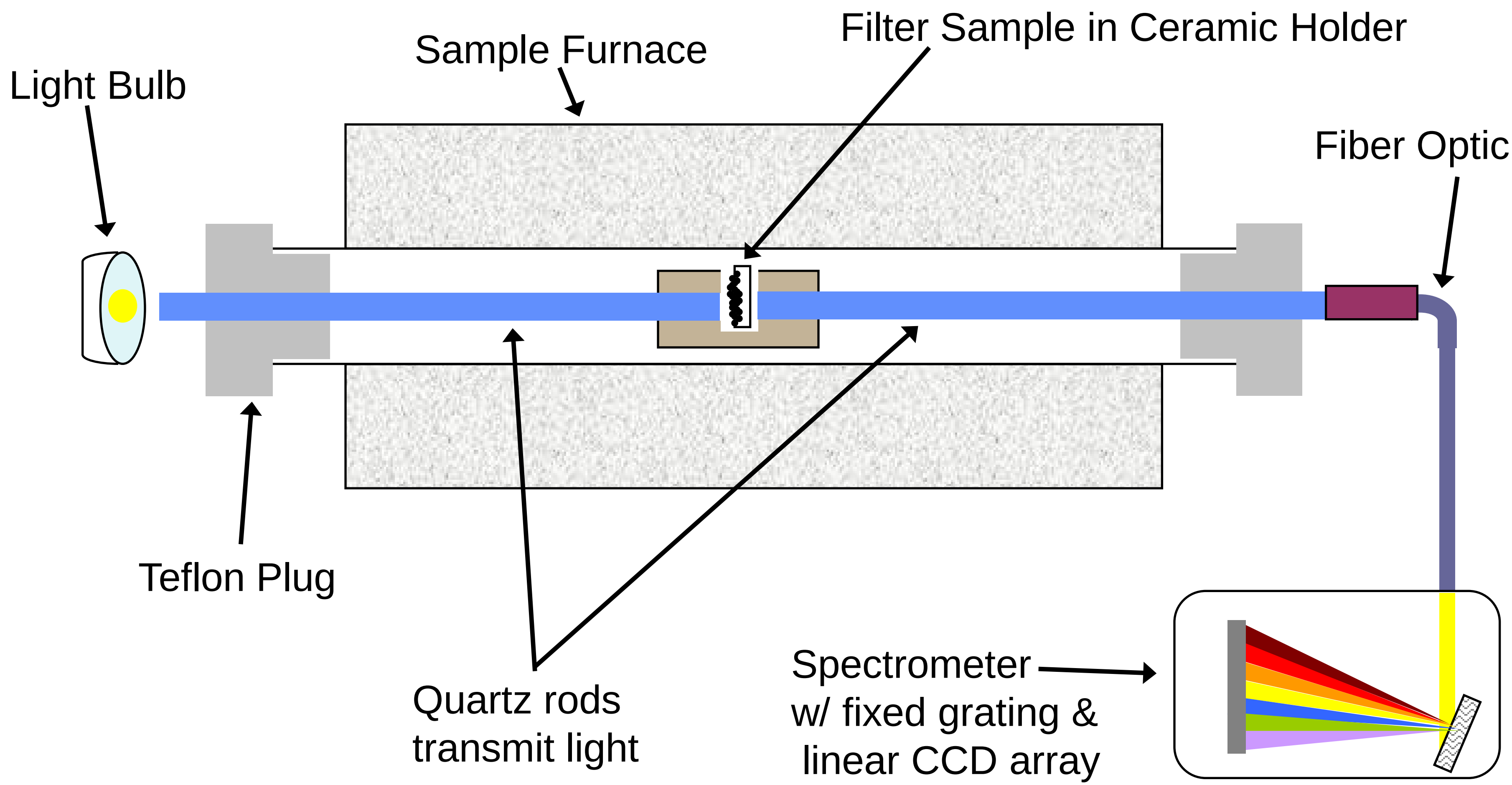


Spacing between wavelengths yields the sample Absorption Ångstrom Exponent

Spacing between wavelengths yields the “color” of char

Setup of Thermal Spectral Analyzer

- Pairs a broadly emitting, stable lamp with a fast spectrometer
- Transmits light to and from filter sample with quartz guides



What can TSA give us that TOA cannot?

1) Absorption Ångstrom exponent ($Å_{exp}$)

- Distinguishes between fossil and biomass burning sources
- Filter analysis is routine - why not also routinely measure $Å_{exp}$?
- Archived filters can be analyzed for retrospective analysis

2) Optical properties of char formed during thermal analysis

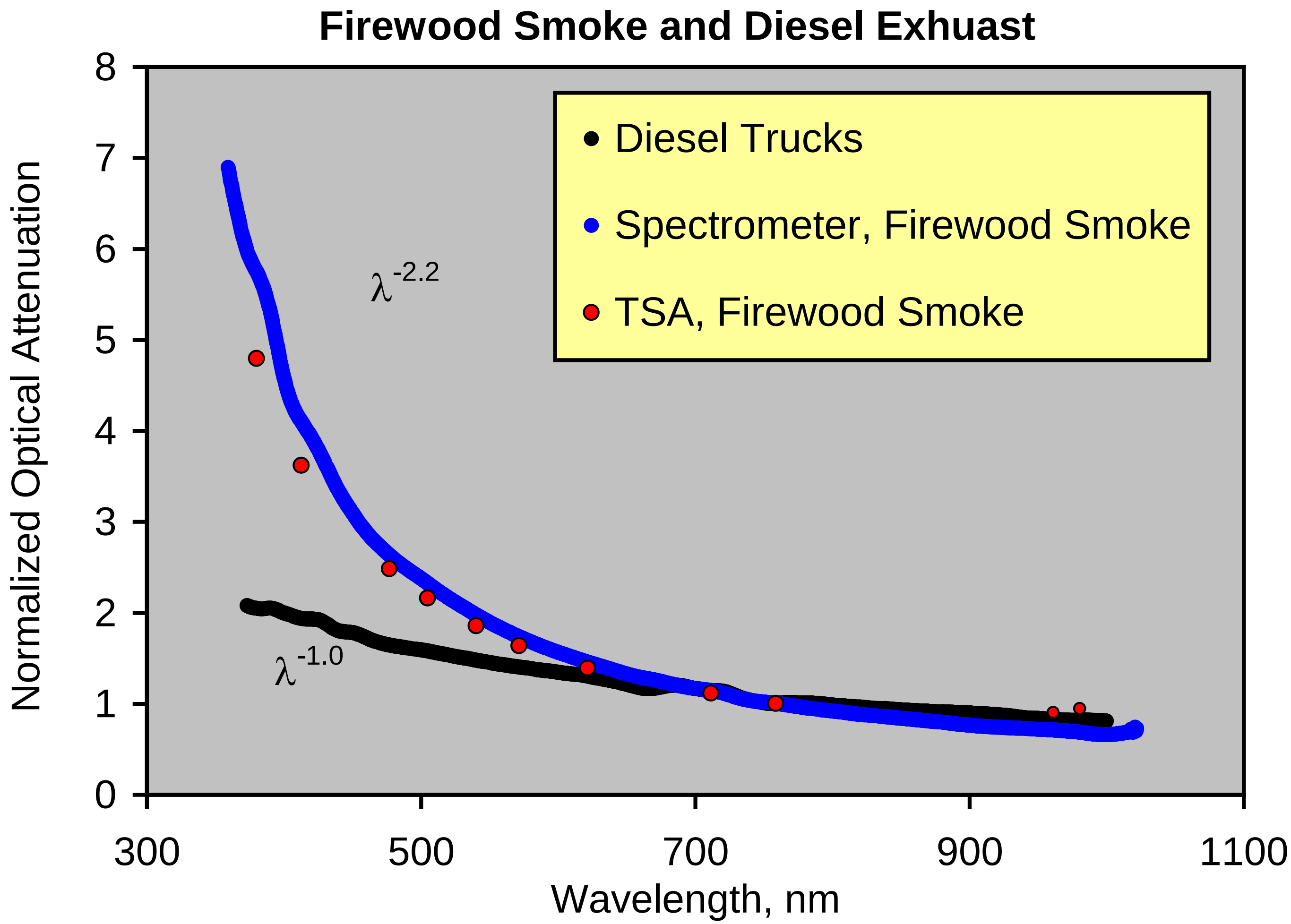
- What is the "color" of char and how does it compare to BC?
- How much does analysis atmosphere matter: He vs. O_2?

3) Improved accuracy in measurement of BC

- Differentiate BC from OC and char based on spectral selectivity

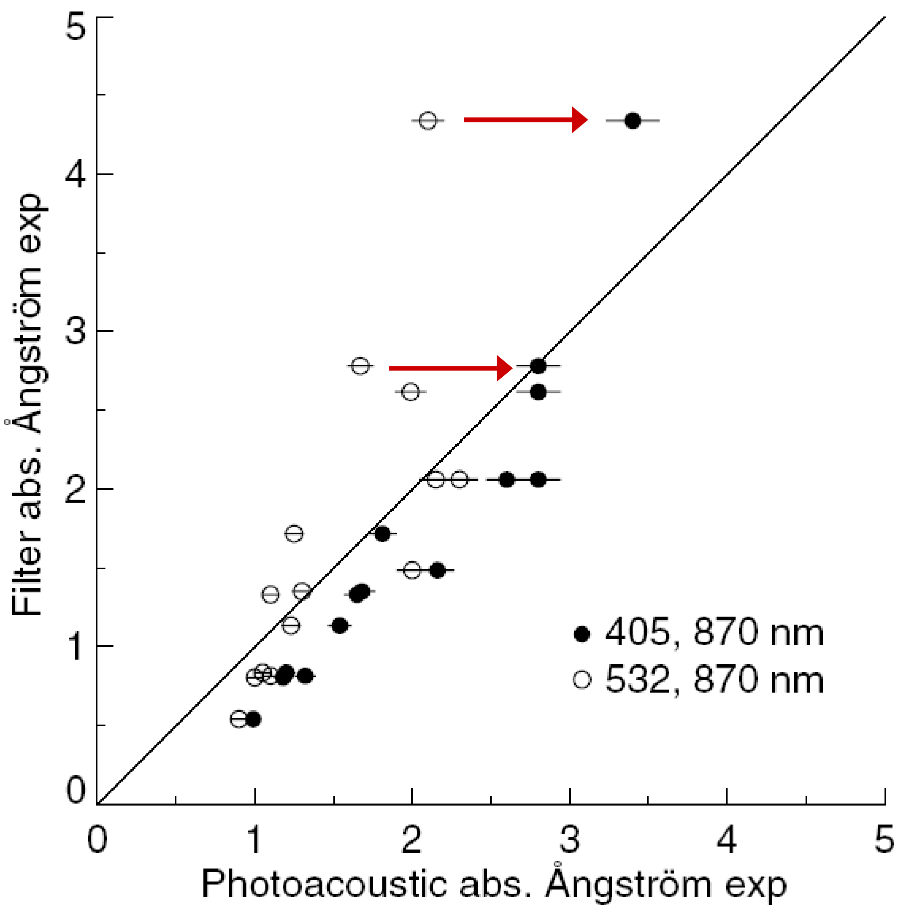
1) Åexp – TSA vs. Stand-Alone Spectrometer

- Radiation interference from furnace at longer λ can be corrected
- TSA compares well with stand-alone spectrometer



1) $Å_{exp}$ – Filter versus In-situ (Photoacoustic)

- Biomass burning at Fire Sciences Laboratory, Missoula, Montana
- Photoacoustic data from Pat Arnott and Kristin Lewis

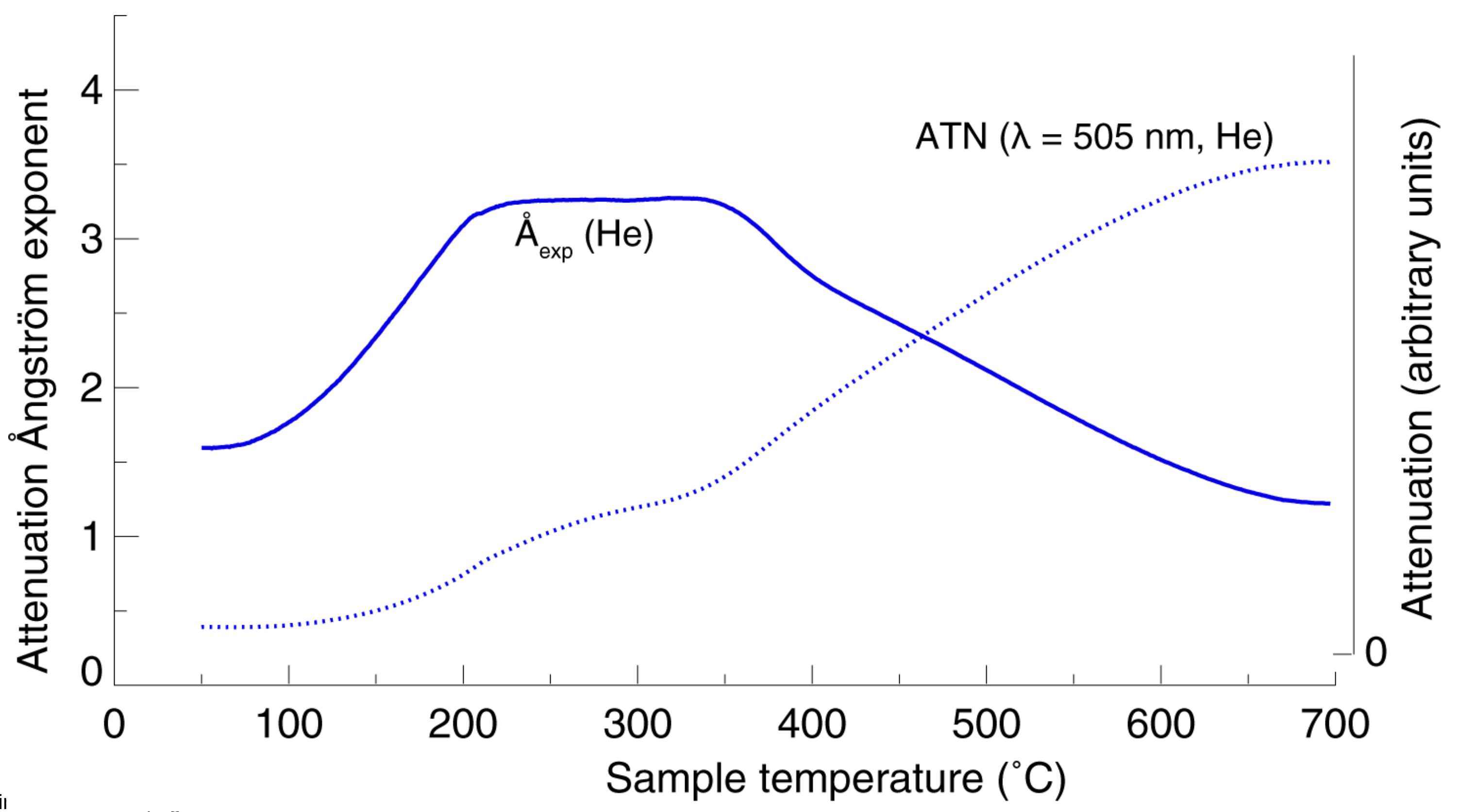


- Two photoacoustic analyzers
  - 405, 870 nm
  - 532, 870 nm
- Filter-based spectrometer
  - 370 to 1000 nm continuous

- Agreement is better with photoacoustic spanning wider spectral range
- Filter-based yields $Å_{exp} < 1$

2) Optical Prop. of Char: Å$_{exp}$ Thermogram Smoldering Cellulose Smoke: O_2 vs. He

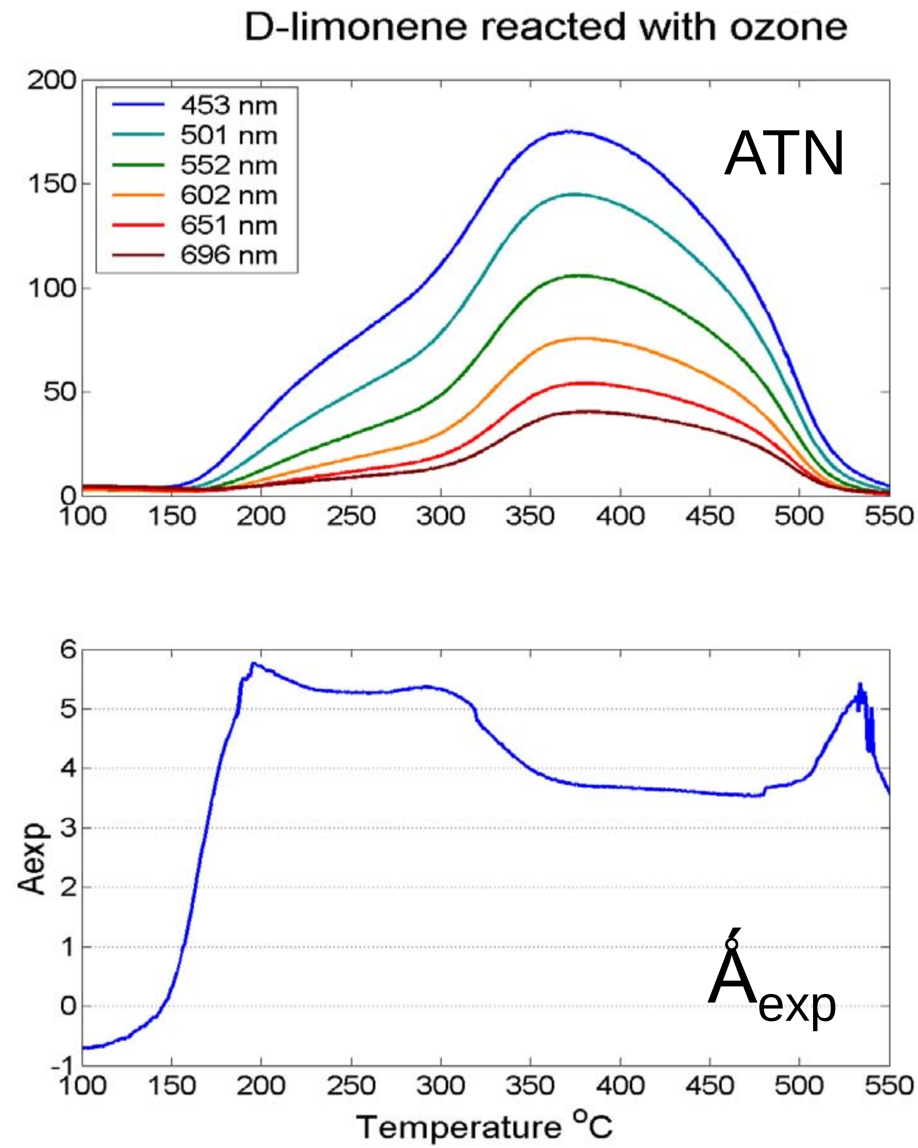
- Char is initially not black:
  - Å$_{exp}$ increases markedly as sample begins to char (T<300^{o}C)
- At end of He analysis, the char has blackened
  - Å$_{exp}$ decreased to ~1 and ATN increased markedly
  - Is standard TOA assumption that char = BC correct?



2) Optical Properties of Char: SOA

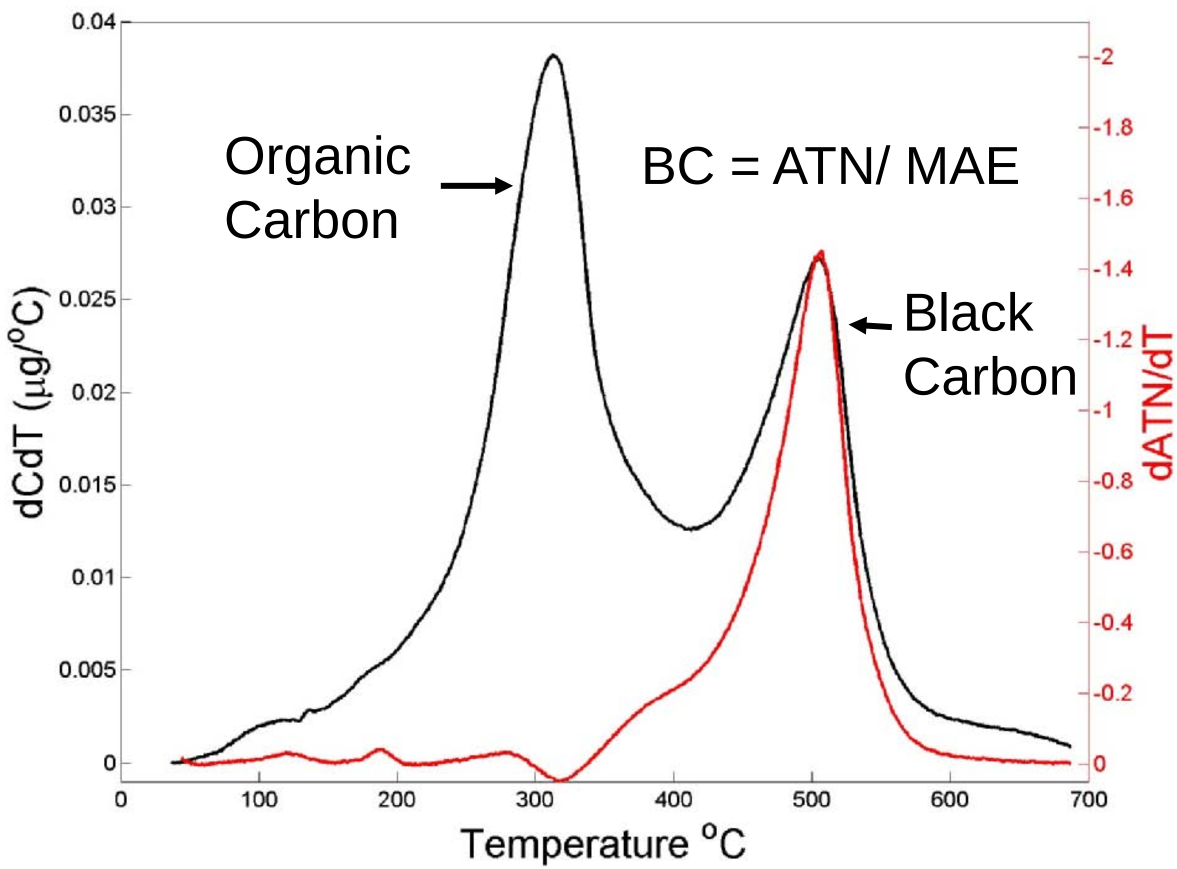
- Initial ATN = 0,
  - No absorption
  - ATN is due only to char formed after heating commences

- Å$_{exp}$ averages 4.5 ± 1 for this sample



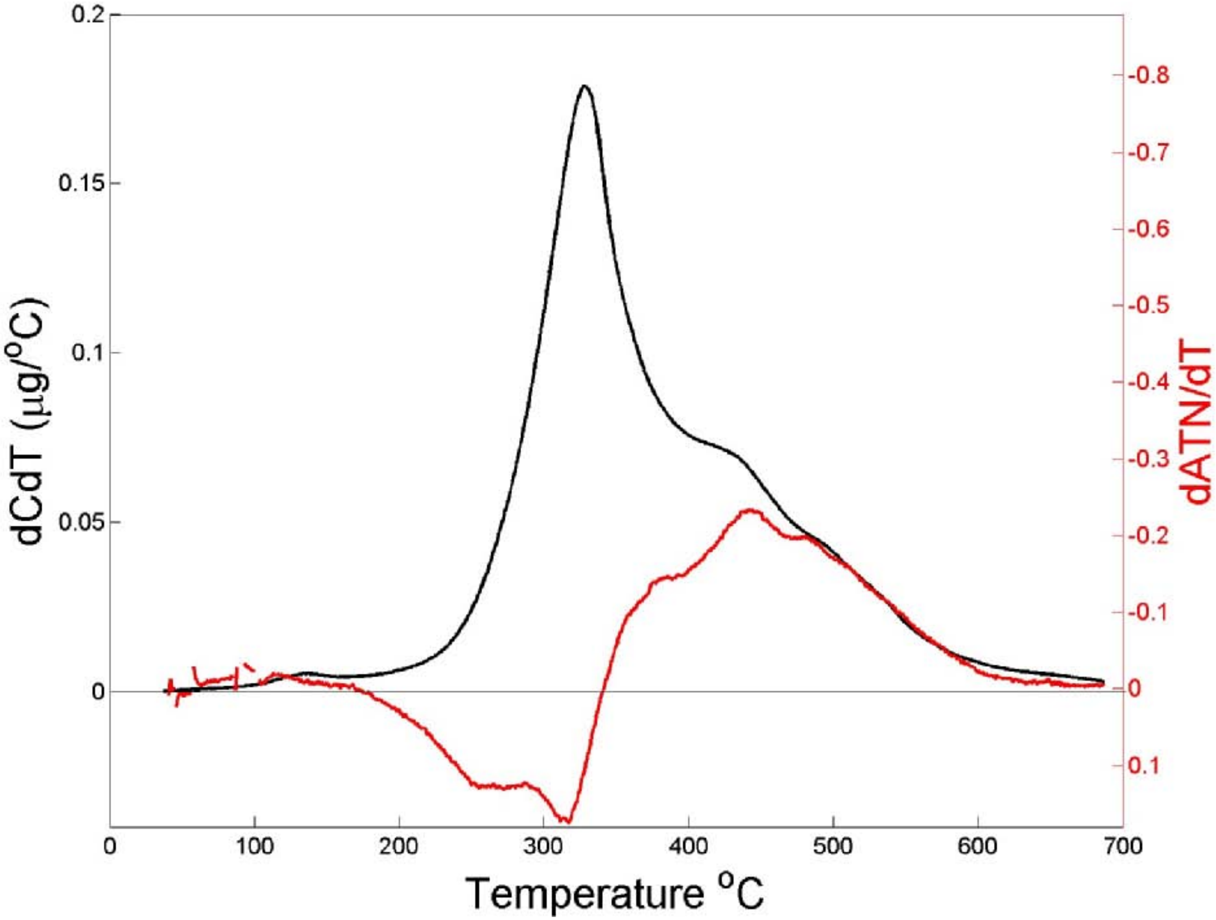
3) Differentiating BC from Char

- When char is negligible, scaling the attenuation to the evolved carbon mass yields BC mass
  - MAE = mass attenuation efficiency



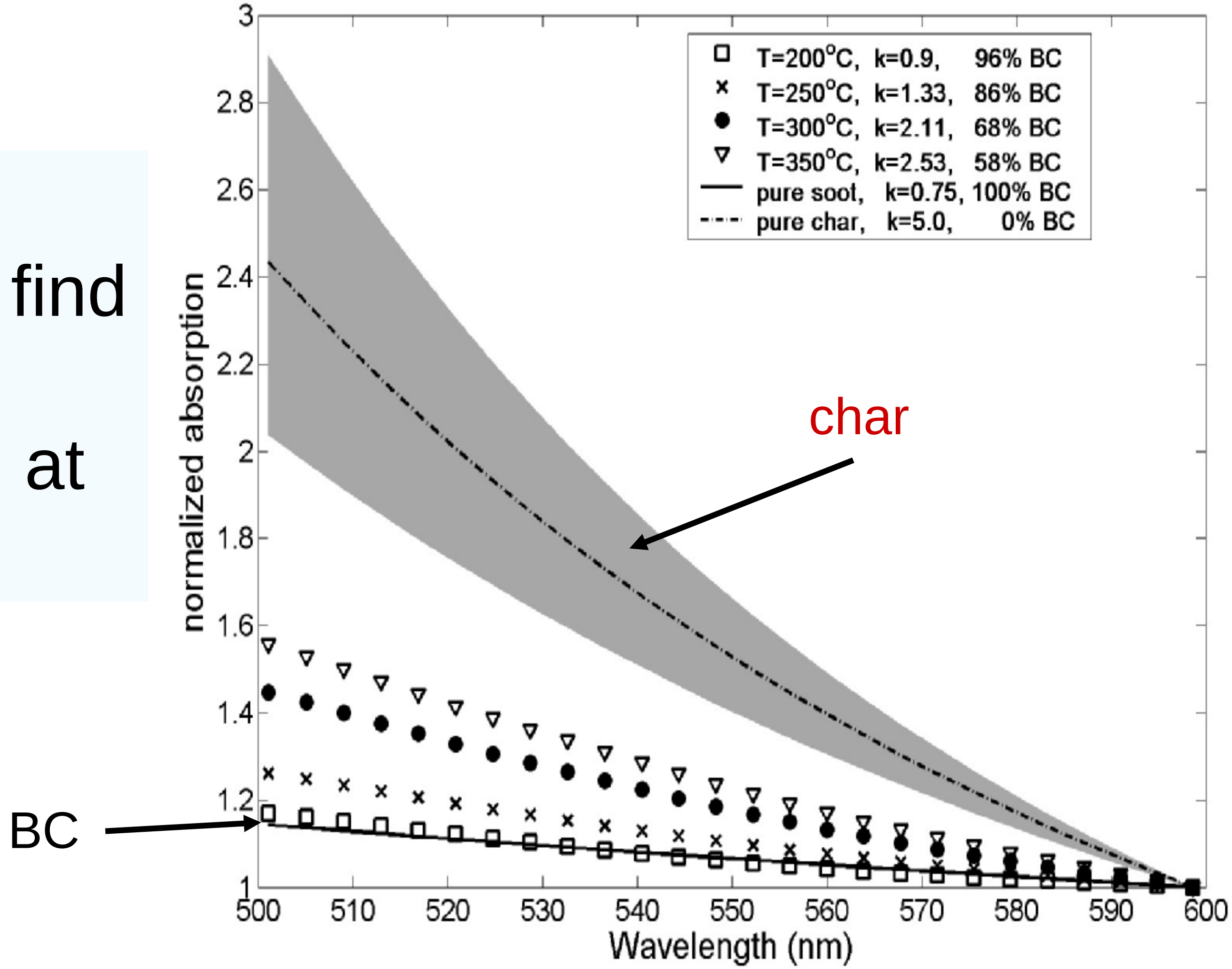
3) Differentiating BC from Char

- If char is significant, can a single MAE value be used to scale both char and BC to carbon mass?



3) Differentiating BC from Char

❖ Use spectral information to find fraction of BC (BC/BC+char) at each temp



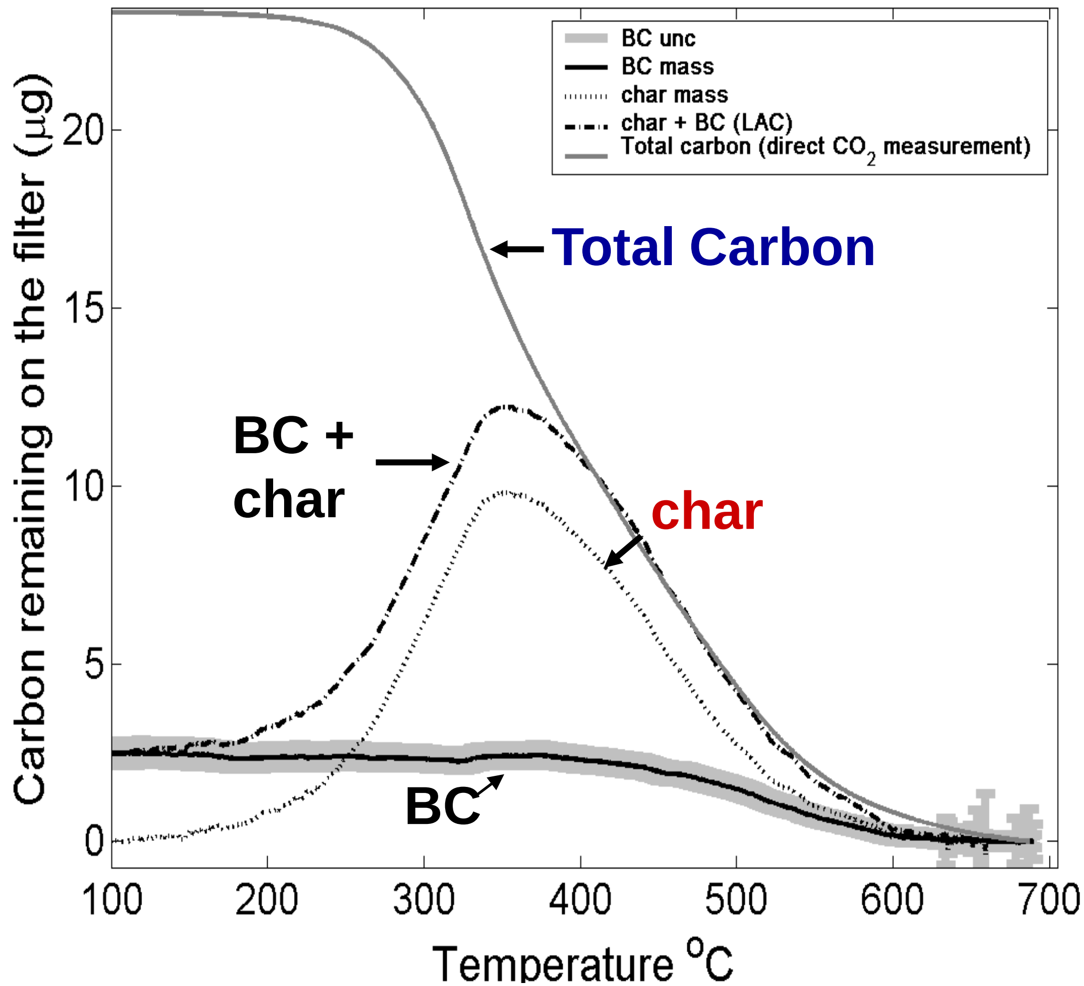
3) Differentiating BC from char

Determine best fit MAE values of BC and char

- Best fit with carbon mass between 480°C and 600°C
- Constrain MAE values
  - BC (10-20 m^2/g)
  - Char (0.5-7 m^2/g)

$ATN_{BC}/MAE_{BC} + ATN_{char}/MAE_{char}$

=Total light absorbing carbon



Summary: Thermal Spectral Analysis (TSA)

- TSA contributes more information than traditional TOA
  - Spectral absorption: yields clues to the dominant aerosol source
  - Aerosol forcing depends on spectral not monochromatic absorption
  - A new dimension: the $Å_{exp}$ thermogram tells the "color" of char
  - Improved estimate of BC based on distinct optical properties of BC and char