Thermal Spectral Analysis

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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 ($\lambda$)
  - Often expressed using power law: $\text{Abs} = c \lambda^{-\text{Åexp}}$
  - Absorption Ångstrom exponent, $\text{Åexp}$:
    - Weak selectivity, $\text{Åexp} \approx 1$: black carbon is primary absorber
    - Strong selectivity, $\text{Åexp} \approx 2$ to 5: organic carbon (i.e., “brown” carbon) contributes to absorption, especially at short $\lambda$
1978 – present: TOA methods monitor transmission or reflection of monochromatic light (e.g., 633nm He-Ne laser) from filter sample.

**Graph: Monochromatic TOA (Boring!)**

- **Y-axis:** Evolved Carbon
- **X-axis:** Sample Temperature (deg C)
- **Legend:**
  - Optical Transmission
  - Difference between initial and final intensity yields sample optical attenuation

**Graph Notes:**
- Decrease in transmission indicates sample charring.
Thermal-Spectral Analysis (TSA) 😊

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

![Graph showing Spectral TOA](image)

- 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 ($\text{Å}_{\text{exp}}$)
   - Distinguishes between fossil and biomass burning sources
   - Filter analysis is routine - why not also routinely measure $\text{Å}_{\text{exp}}$?
   - 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 $\lambda$ can be corrected
- TSA compares well with stand-alone spectrometer

![Graph: Firewood Smoke and Diesel Exhaust](attachment:graph.png)

- Diesel Trucks
- Spectrometer, Firewood Smoke
- TSA, Firewood Smoke

Normalized Optical Attenuation vs. Wavelength, nm
1) $\bar{\alpha}_{\text{exp}}$ – 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 $\bar{\alpha}_{\text{exp}} < 1$
2) Optical Prop. of Char: $\bar{\alpha}_{\text{exp}}$ Thermogram Smoldering Cellulose Smoke: $O_2$ vs. He

- Char is initially not black:
  - $\bar{\alpha}_{\text{exp}}$ increases markedly as sample begins to char ($T < 300^\circ C$)
- At end of He analysis, the char has blackened
  - $\bar{\alpha}_{\text{exp}}$ 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

- $\hat{A}_{\text{exp}}$ 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
- \( \text{MAE} = \text{mass attenuation efficiency} \)

\[
\text{BC} = \frac{\text{ATN}}{\text{MAE}}
\]
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 m²/g)
  - Char (0.5-7 m²/g)

\[ \frac{ATN_{BC}/MAE_{BC}}{ATN_{char}/MAE_{char}} = \text{Total light absorbing carbon} \]
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 $\Delta_{\text{exp}}$ thermogram tells the “color” of char
  - Improved estimate of BC based on distinct optical properties of BC and char