Integrating the thermal behavior and optical properties of carbonaceous aerosol

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Motivation/Project Philosophy
(repeat from Year 1)

- Need to understand existing & incoming data
  - Like it or not, data are widely used!
  - Approaches developed *must* be applicable on retrospective basis
- “Artifacts” might be interpretation opportunities
  - Take advantage of wealth of data in optical & thermal traces
- No method is “right” or “wrong”
  - Different optical+thermal responses observed
  - Hope: results of any methods can be interpreted on common ground
Outline

1. Reactor Model
2. Light-absorbing carbon optics
3. Pyrolysis/charring
4. Can kinetics help?
5. Back to the model
6. Recommendations

Definitions:
“native LAC” = particles that absorbed light when deposited on filter
“pyrolytic carbon” = PC = material that pyrolyzed during analysis
“organic carbon” = OC = other non-carbonate carbon
Each “artifact” can be summarized thus:

- Analysis does not account for co-evolution of different types of carbon.
  (So let’s account for it!)

- System has two outputs:
  carbon (FID) and absorption (ATN)

- **Required**: only 2 types of carbon evolving simultaneously.
1. Reactor Model

Formal reactor model for TOA

\[ \tilde{y} = \begin{bmatrix} \Delta FID \\ \Delta ATN \end{bmatrix} \]

System state
\[ \tilde{x} = \begin{bmatrix} OCc \\ OCn \\ PC \\ LAC \end{bmatrix} \]

could have 5 (shown later)

Transfer function
\[ \tilde{y} = R \Delta \tilde{x} \]

\[ R = \begin{bmatrix} 1 & 1 & 1 & 1 \\ K_C \sigma_C & K_N \sigma_N & K_P \sigma_P & K_L \sigma_L \end{bmatrix} \]
1. Reactor Model

- Two equations, four unknowns
  - Need more constraints!
- Default approach: assume yields
  - used in present TOA

Carbon Optics

\[
\begin{bmatrix}
\text{FID} \\
\Delta \text{ATN}
\end{bmatrix}
\begin{bmatrix}
1 & 1 & 1 & 1 \\
K_C \sigma_C & K_N \sigma_N & K_P \sigma_P & K_L \sigma_L
\end{bmatrix}
\Delta
\begin{bmatrix}
\text{OCC} \\
\text{OCn} \\
\text{PC} \\
\text{LAC}
\end{bmatrix}
\]
We explore controlled & source samples

N Description
71 Hexane soot (lab generated)
50 Model compounds (some ~water-soluble)
55 Wood combustion (lab generated)
50 Wood combustion (cookstoves)
136 Diesel vehicles (DIESEL project, Bangkok)

1. Reactor Model
2. Optics

\[ \Delta ATN \text{ vs carbon mass} \]

The short story: Differentiate the laser signal.

The long story:

\[ 100 \ln \frac{I}{I + \Delta I} = \sum_{n=1}^{N} K \sigma_{\text{abs,n}} \Delta L_n \]

- Transmittance of clean filter
- Transmittance of loaded filter
- Enhancement by collection on filter
- Loading of species I (\( \mu g/cm^2 \))
- Absorption cross-section of suspended species I (\( m^2/g \))

Examples to follow…
2. Optics

Smoldering woodsmoke “thermabsgram”

**Q12B-1019_reg Oak 311 C for 10 minutes**

- FID*100 (ug/cm2)
- Temp/100
- laser/1000
- absC*100 (ksigma=45)

EC: 0.19  OC: 12.13
Diesel thermabsgram

2. Optics

![Graph showing diesel thermabsgram data with various lines representing different measurements such as FID*100 (ug/cm2), Temp/100, laser/1000, and absC*100 (ksigma=15.64). The graph includes a time axis (0 to 1000 sec) and a y-axis showing measurements (up to 14) with annotations for EC: 7.95 and OC: 0.00.]
Fulvic acid thermabsgram

2. Optics
All black carbon is not created equal (despite Bond & Bergstrom, 2006)

\[
\frac{d \ln I}{dL} = K \sigma_{\text{abs},n}
\]

K (enhancement) varies with:
- source type
- filter
- transmittance
- mood

\[ p < 0.0001 \text{ (hexane-diesel-wood)} \]
K-\(\sigma\) differs between native LAC & pyrolytic carbon

We knew that. (Chow et al. 2004; Subramanian et al. 2006)

2. Optics
Charrable carbon is liquid on filters

Shapes are consistent with droplet-on-fiber theory

Implies that most OC is present as fiber coatings
Optics summary

- ATN-to-carbon ratio depends on carbon type and filter loading (transmittance)
- PC-ATN and LAC-ATN differ & can be used to distinguish the two
- Repeatability of individual results is limited
What does charring indicate?

- Water-soluble extracts char (Yang and Yu, 2002)
- Methanol removes most of charring (but not all) (Subramanian et al, 2007)
- Biologically-derived and complex molecules char (Cadle et al, 1980)
Most model compounds don’t char

...not even water-soluble compounds!

3. Charring
Complex compounds do char

3. Charring

"Early charring"
Where does “early charring” come from?

3. Charring

[Graph showing average step-wise ATN over different months from July 01 to July 02.]

Figure courtesy R. Subramanian & Allan Robinson, Pittsburgh Supersite
3. Charring

**Review of pyrolysis mechanisms says:**
polymerized material + catalysis
→ further polymerization = charring

...Not from sources!
Two equations, three unknowns…

4. Kinetics?

Released in He-4:  
PC, LAC  
(if oxygen present)  
OC

Released in  
“early” HeOx:  
OC, PC, LAC
Oh, that heavy OC…

4. Kinetics?

- Simple view: 2 mechanisms
  - Decomposition/volatilization
  - Slow volatilization

Plateau = slow volatilization
Idea: Infer heavy OC from traces

**Method 1 (Projection)**

Humic Acid Thermogram showing PC Volatilization

![Humic Acid Thermogram](image)

- FID*100 (ug/cm²)
- Temp/100
- laser/1000
- dATN/Ksigma-abs(LAC)
- dATN/Ksigma-abs(PC)

**Method 2 (Kinetic)**

- He-4 (870 C) $R^2 = 0.4639$
- He-3 (615 C) $R^2 = 0.0431$

4. Kinetics?
Kinetics summary

- Tried *many* approaches using kinetics to draw inferences.
- While punches from identical sample are reproducible, even “similar” samples aren’t.
- Statistical approach (as for optics) seems to be the only possibility.
5. Back to the reactor

(Today’s) Reactor model

Start:
Blank filter

Check
ΣPC

Done?

10-sec step
back (invert matrix)

Done?

zero

yes

non-zero

Change LAC K-sigma

Run 3 times with central, high, low

Get 10-sec FID, ATN, & filter transmission

Apply assumptions
Reactor model results (I)

5. Back to the reactor
Reactor model results (II)

5. Back to the reactor

Mixed wood smoke

Loading (μg/cm²)

-1 -0.5 0 0.5 1 1.5 2

He He/Ox

Release

Formation

OCC OCn PC LAC

current work
Current work: Explicit representation of assumptions

**Safe assumptions**

- No charring in oxygen mode

**Constrainable assumptions**

- PC and LAC lost in He-4 only
- Yield of OC minimal ↔ currently working on representation
- Approach: Central-min-max for each questionable assumption

5. Back to the reactor
Recommendations

1. Fix the laser (and give benchmarks)!
   - There’s good information, but the laser is not stable enough.

2. Minimize co-evolution (650-700C)
   - Sorry, 550 is not enough, & we can’t correct

3. Transmittance *and* reflectance
   - Transmittance sensitive to charring– may be *good*
   - Reflectance relatively insensitive to charring– may be *good*