On “refractory organics” and other assorted issues related to AMS quantification

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Outline

• Motivation
  – Summarizing (my reaction to) feedback from outside the AMS community
  – Non-AMS people often complain to me when any AMS User does something (with AMS data) that they don’t think is correct or justified
Topics

• Reported accuracy and precision
• CE ($E_b$) estimation in the field
• “Refractory organics”
• HOA vs OOA-I vs OOA-II etc.
  • 2-week old review from ES&T: “These loose, unspecific definitions are of almost no practical value, as they do not provide any quantitative measure to the parameters being defined.
  • More tomorrow…

Reporting Accuracy and Precision

• NASA now wants
  – Precision: 20 ng m$^{-3}$ or 10%, whichever is larger
  – Accuracy: 50 ng m$^{-3}$ or 25%, whichever is larger

• Survey of reported uncertainties:
  – Most papers don’t report one
  – Lab: ±5%
  – Field: ±15%, ±20%, ±20%, ±25%, ±30%
  – Need to get more rigorous and do uncertainty propagation (inc. CE, IE, RIE, refractory, etc.)
On CE Estimation in the Field

• \( CE = E_s \times E_b \times E_L \)
  - \( E_s \) is just our size cut ("PM1", "PM0.8"...)
  - \( E_s \) is minor for typical ambient aerosol (should keep doing this)
  - \( E_b \) can vary depending on composition (phase)

• Two schools of thought
  - Dry particles and estimate CE from composition and relationships derived in previous studies
    - CE = 0.5 except in high acidity, high nitrate (size-resolved if needed)
  - Scale CE from specific comparisons to other instruments
    - "Fudge factor"
    - I strongly object to this unless you have a reason to suspect the AMS had a problem (misaligned less, could not calibrate, etc.)
    - CE becomes the wastebasket to all disagreements (often unfairly)
  - Otherwise you transfer the uncertainty and problems of the other instrument to the AMS
    - Other instruments have problems at least as frequently as the AMS, and often they get less attention
    - [Paul Wennberg]: “You can’t separate the instrument from its operator”

Evolution of Asian aerosols during transpacific transport in INTEX-B

E. J. Duree\(^1\), P. F. DeCarlo\(^1\), A. C. Alfar\(^1\), J. R. Kimmel\(^1\), R. E. Porter\(^1\),
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S. G. Howell\(^3\), A. D. Clarke\(^1\), L. P. Emmons\(^3\), E. S. Apte\(^3\), G. D. Pfister\(^1\),
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• Estimating CE as 0.5 with acidity correction

ACPD
8, 15375–15461, 2008

Evolution of asian aerosols during transpacific transport
E. J. Duree et al.
Comparison with Submicron Scattering

- Correlation with scattering is often the best of any instrument we compare with
- Ratio of AMS + BC (+ dust etc.) to scattering is nominal mass scattering efficiency (MSE)
- MSE can be calculated from AMS size distributions using Mie theory
  - Shows good agreement for MILAGRO and INTEX-B datasets from AMS C-130 (Fig 1d)
  - Recommend doing this every time you can

Risk of estimating CE from individual intercomparisons

- Official intercomparison of nominally identical instruments by same group in 2 airplanes
  - AMS is very often intercompared with this instrument
- Scaling to another single instrument can be extremely risky

Fast airborne aerosol size and chemistry measurements above Mexico City and Central Mexico during the MILAGRO campaign

From Gao Chen, NASA
50% of organics are refractory?

MIYAZAKI ET AL: WSOC IN THE ASIAN OUTFLOW

Figure 1. A typical thermogram for OC and EC during the study period, produced by the thermal-optical method. The solid line shows the nondispersive infrared (NDIR) response; the dashed line represents temperature. The gray solid line indicates laser attenuation, where I is the laser intensity and I₀ is the initial laser intensity through the sample. Parameter abbreviations are defined in the text.

Closed vs Diff Signal for PbCl₂

- Low volatility compounds have significant signal in closed spectrum

Mexico City, T0 supersite during MILAGRO
From Salcedo, Onasch, Aiken, Jimenez et al., in preparation, 2008

AMS vs PESA Organics (H)

- Comparison of the organic H mass with AMS organic aerosol measurements indicates that about 75% of the mass of these species evaporated under a vacuum. However, ~25% of the organics does remain under a vacuum, which is only possible with low-vapor-pressure compounds, and which supports the presence of high-molecular-weight or highly oxidized organics consistent with atmospheric aging.

AMS vs PESA Organics (H)

- PESA is ¼ of AMS
- 75% of OA evaporates under PESA vacuum

"Refractory Organics" II

- Recent review from ES&T: The Authors claim that the AMS measures the "non-refractory" aerosol mass that has not evaporated after passing through the TD, but do not describe what they mean by non-refractory. [...] If this non-refractory portion of the aerosol is not 100% of the particle that passes through the AMS, how might changes in the 'fraction that is refractory' influence the results.
- Could the AMS be missing as much of the ambient organic as implied by Miyazaki? (50%)
- Likely much less
  - Single particle evaporation under vacuum
  - So no filter or other particles
  - Less chance of charring
- Can we quantify this in some way?
  - Yes! Look at closed spectra
  - Can and should be done by everyone all the time
  - Also optimize parameters to reduce it

3 Timescales of evaporation in the AMS

- Evaporation time scale to see signal in:
  - PToF mode: ~ 1 ms
  - MS mode (Diff): ~ 1 s
  - MS mode (closed): ~ hours
- This is why we scale PToF to MS
- Consistent with previous discussions from Tim Onasch, Ann Middlebrook
- Consistent with previous work from Frank Drewnick

Diethylhexyl sebacate (DEHS) + methyl oleate (MO);
vaporizer at 107°C; 20s cycles, 2.2 Hz saves

Rate of m/z 185 rise: 0.34 s⁻¹

From Jesse Kroll
ToF-AMS Menu Setting (new “mx” version)

• ~10% Organic signal in closed
• ~20% for sulfate
• Small for nitrate
• More important for chloride
• Jesse: some of it is not “refractory” but bounced particles evaporating slowly elsewhere in the ionizer (250C vs 600C)
MS Diff. vs. Closed during SOAR-1 (Riverside)

- $D_{\text{diff}} \sim 160$
- $D_{\text{closed}} \sim 50$
- 30% more m/z 44 on closed spectrum!
  - Implications for quantification (RIE), uncertainties, O/C etc

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ch3o_Diff
co2_Diff
ch3_Diff
c2h3_Diff
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From Docherty, Huffman, Jimenez et al., in preparation, 2008

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**Slow evaporation: what to do?**

- **Average users**
  - Minimize it by allowing maximum time for vaporization in MS mode
  - Run vaporizer at 600 C, not 550 C
  - Quantify it and report it

- **Core users**
  - Think about impact on our quantification
  - Calibrations and intercomparisons have ignored slow evaporation, so they already include this effect on an average sense
    - If we add this mass, may need to lower RIE, (O/C)$_{\text{cal}}$, etc.

- **Very advanced user (Jesse)**
  - Use evaporation rate as another probe for chemistry ("internal thermal denuder")

- **Is there some organic that doesn’t even show up in closed spectrum?**
  - My take: unlikely, but worth thinking about it…