Basis and limitations of Organic Elemental Analysis with the AMS (HR and UMR)

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Overview
1. Canada is a great country 😊
2. How to calculate O/C etc. from AMS spectra
3. Fragmentation biases
4. Approximation from 44/OA
5. Additional topics
   • N/C, org. nitrates & sulfates
Going from AMS spectra to O/C etc.

- Counter-intuitive, NO ONE seems to understands it by default
- Wrong method occurs to everyone first
  - Many people feel extremely strongly that the wrong method is the correct one!
- After much pain and explanation, semi-foggy understanding sets in
- Happy to discuss offline
- Will post these slides on the web, please refer to them if confused
Converting Ion Signals to Element Mass

- Pika (AMS HR code) generates ion signal (area) for each HR fragment
- Consider the simple mass spectra that was generated in Pika for a SINGLE MOLECULE that contains only two mass fragments, CH$_3^+$ and CO$^+$ (physically unrealistic)
- (Note that RIE doesn’t matter since we start from a single molecule)

Question: the fragments have the same intensity (= number of ions). But CO is bigger, i.e. it has more mass

A. CO signal should count more than CH$_3$
B. CO signal and CH$_3$ signals should be equally weighed

Ionization Efficiency $\alpha$ Electrons

Jimenez et al., JGR, 2003
Bird area represents the mass (cross section) of molecules in the ionizer.

Machine gun represents electrons for ionization.

Pieces on bottom represent ions detected.

3 times more mass means 3 times more ions. It doesn’t matter what the size of the detected ions is.

Adapted from Jimenez et al., JGR, 2003.
AMS Organic Quantification

Same mass in larger molecules (so fewer molecules) will produce the same number of ions

Adapted from Jimenez et al., JGR, 2008

Converting Ion Signals to Element Mass

Question: what is the O/C mass ratio for this species?

A. 0.35  
B. 0.46  
C. 0.5  
D. 0.61  
E. 0.7

• Calculation
  – CO mass fractions
    • C = 12/28 * 20 = 8.6
    • O = 16/28 * 20 = 11.4
  – CH₃ mass fractions
    • C = 12/15 * 20 = 16
    • H = 3/15 * 20 = 4

Elemental Analysis (EA) by EI-HRMS

- EI MS Ion intensities \( \alpha \) original mass concentration
- Identify all ions (HRMS)
- Determine Elemental Mass
  - Atomic and Mass Ratios
  - Calibrate method
  - Possible frag. Biases
- Aside: HOA vs C,H, vs elements in spectra

Potential Positive Ion EI-MS Biases

- Fragmentation with respect to electronegativity
  - Possibility for more electronegative ions to be preferentially lost as neutrals
  - Do the HRMS fragments represent the original composition?
  - Largest issues for Oxygen

- Rearrangements (ex: McLafferty):

- Is quantitative elemental analysis still possible despite these biases?
NIST EI Database Analysis

- National Institute of Standards and Technology (NIST) Database of EI MS
  - Not HRMS, Unit mass resolution (UMR)
  - Limited range of compounds (16 < MM < 90)
- 20 compounds
  - Complete MS used
  - ~ 3 replicates each (from different labs)
- Atomic H/C and O/C determined, some bias but calibration is possible

Calibration of HR-AMS Elemental Analysis

- Nominally much less accurate than thermal CHNO analyzers
  - Precision ~ 3%
  - But real time (10s), 10^7 less sample (0.1 ng vs. 1 mg), mixed with inorganics
OC vs. m/z 44/OA

From Field Data: Ground & Aircraft in Mexico City

\[ f(x) = (0.0382 \pm 0.0005)x + (0.0794 \pm 0.0070) \]

\[ R^2 = 0.84 \text{ (95\% CI)} \]


Extracting the right \( m/z 44 \) (or 60 etc.)
Extracting the right $m/z$ 44 (or 60 etc.) II

- Need to do it with the species in the batch table (e.g., Org44)
  - Also for 60/OA as BB marker, etc.
  - Otherwise concentrations are NO$_3$ equivalent and results are wrong
  - Also subtraction of gas-phase CO$_2$
- RIE and CE should be the same as for organics
- Can define additional species if needed

### O/C vs. 44/OA

Aiken, Ground & Aircraft in Mexico City

- Difference at 10% 44/Org $\sim$ 0.06/0.43 = 14%
- Evaluate it at your $m/z$ 44 level
- Doug doesn’t like right plot, it’ll be revised, but point remains about additional error when using the approx.

Shilling et al., $\alpha$-pinene + O$_3$

O/C vs 44/OA – AMAZE (Brazil Rainforest)

O/C can be a noisy measurement, especially at low Org concentrations.

In Mexico City we don’t calculate it below 2 \( \mu \text{g sm}^{-3} \)

In the Amazon \(~1 \mu \text{g m}^{-3}\)

Courtesy of Qi Chen, Harvard
From Chen, Martin, Farmer, Kimmel et al., in preparation
Summary of Uncertainties in O/C quantification and estimation

- Nominal calibration uncertainty from HR
  - From comparison to standards
  - Accuracy: 31% of O/C
    - Probably too pessimistic because of mixture
  - Precision: 3% of O/C (repeating stds)
    - Can be much worse if short time averages and/or low concentrations (precision degrades)
- Additional uncertainty from m/z 44 approximation
  - As a first guess evaluate with difference of Shilling vs Aiken
  - New approximations coming (people welcome to try)
  - E.g. 14% for 44/Org = 10%
  - Combined uncertainty = sqrt(0.31^2 + 0.14^2) = 0.34 = 34%
- Need for additional intercomparisons with other methods
  - Actually quite tricky, will be happy to discuss

Additional topics I

- Higher m/z
  - Aiken et al. paper included all important peaks beyond m/z 100
  - Although lack of PIKA defaults, we recommend that people do that
  - If not, you introduce an error that depends on how much signal is beyond 100 and how different the O/C is for those fragments
- H/C
  - Similar uncertainties, it has gotten a lot less attention
  - Again further calibrations and comparisons with other methods would be useful
- N/C
  - Extremely tricky at typical low concentrations
    - You’ll notice that we have reported a lot less
    - It requires extensive quality assurance of PIKA work
  - Need to have m/z calibration to 0.001 amu
  - Accuracy at m/z 50 = 0.001/50= 20 ppm
    - See your ppm graph in the calibrations
    - Much of the time, accuracy is WORSE unless a lot of care
  - Be REALLY careful, potential to cause major confusion
    - “this AMS group says N/C is huge, that AMS group says that N/C is tiny, on the same study. Thus the AMS is a piece of work.”
Example of typical N-containing peaks

- N-containing peaks are very often on tails of larger peaks
- Small errors in m/z calibration, peak shape on tails etc. can lead to HUGE errors in estimated N/C
- Extreme care and quality control in your PIKA work, for EVERY ion that contributes significant N is CRITICAL if you want to report N/C

Accuracy Graphs (Example from Donna’s Tutorial)
Additional Topics II

• Types of species we haven’t fully characterized for fragmentation biases

• Organonitrates
  – high in models
  – Scattered experimental results for ambient importance
  – Perception: “AMS is blind to organonitrates”, N/C too low (?)
  – Strong evidence that most NO⁺ & NO₂⁺ in most datasets is inorganic
  – Evidence from 3 sets of experiments: most N as NO⁺ and NO₂⁺
    • So indeed the N/C is too low if NO⁺ & NO₂⁺ are not included AND organonitrates are important
    • Need to evaluate NO⁺/NO₂⁺, NH₄⁺ balance etc.
    • Expect a lot of progress by this time next year

• Organosulfates
  – Papers from Claeys, Surratt et al.: ~10% of S
  – C-S bond not as weak as C-O-N for organonitrates
    • If C-S doesn’t break then they are quite small for many ambient datasets
    • If C-S does break then our typical analysis underestimates them
  – Our group is looking at this in collaboration with Caltech
  – Don’t recommend reporting S/C of organics until calibration experiments are completed

The AMS Family thanks you for your attention!