Elemental Analysis (EA) of Organic Species with Electron Ionization High-Resolution Mass Spectrometry (EI-HRMS)

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Bulk Organic Aerosol Analysis

• Historically poorly characterized
  – Thousands of species
  – No technique or combination can identify all species present in Organic Aerosol (OA) mass
  – Approaches that characterize bulk organic types

• Elemental Analysis (ex: Atomic O/C)
  – Traditional analysis with offline filters (~ 1 mg sample)
  – Thermal method for Organic O (Pang, Turpin, Gundel 2006 AS&T)
  – FTIR Functional group analysis (S. Gilardoni, L. Russell et al. 2007 JGR)
  – First application with unit mass resolution (UMR) AMS data (Zhang 2005 ACP)

• This work using with high-resolution AMS (HR-ToF-AMS)
  – High time and size resolution
  – No filter sampling artifacts
  – Applicable to many AMS Field Data sets
Elemental Analysis (EA) by EI-HRMS

- EI MS Ion intensities \( \propto \) original mass concentration
- Identify all ions (HRMS)
- Determine Elemental Mass
  - Atomic and Mass Ratios
  - Calibrate method
    - Possible frag. biases

Nonanal spectra (AMS)


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

**HR-ToF-AMS Laboratory Experiments**

- 35 Organic Compounds
- $114 < MM < 426$
- Organic Aerosols (CHNO)
  - POA's (S&P, 1998)
  - Markers: Levoglucosan, Cholesterol
- EA biases specific to this data
  - Compounds
  - Sampling Conditions
Applicability of the Calibrations

- Laboratory standard calibration
- Application to Ambient/Data sampled “in Air”
  - Calibrations in progress
  - Preparing a panel
    - Changes to the fragmentation table
    - Email release
- Will email the group when paper is published
- A whole new “ANIMAL”
  - ANalysis of Ions Measuring Atomic Levels
  - Maybe even APES!
    - Analytical Procedure for Elemental Separation

Mexico City Ground EA (T0, MILAGRO)

AVG’s: O/C = 0.5, H/C = 1.5, N/C = 0.05, OM/OC = 1.84
Fast Measurements from Aircraft over Mexico City

P. DeCarlo et al., C-130, MILAGRO (2006)

Organic Mass (µg/m$^3$)

Time (UTC)

Over Mexico City

Regional Background

Mexico City Outflow

Primary, Secondary, and Ambient OA

Atomic (O/C) Ratio

Mass (OM/OC) Ratio
Conclusions

- EA successful with HR-ToF-AMS
  - High time resolution with very small sample sizes
  - Biases in fragmentation can be calibrated
  - EA can be used to estimate OM/OC

- O/C for aerosol types
  - ~ 30% avg. error (lab standards, potentially better for Ambient)
  - “Aged” SOA/OOA > “Fresh” SOA/OOA ~ Chamber SOA > POA
  - BBOA ~ Fresh OOA

- N/C is low for OA in Mexico City
  - ON ~ 20% of TN
  - Contrast with fog (Q. Zhang, AAAR 2007)

- Need for intercomparisons of emerging methods
- Calibrations for Ambient measurements to come
  - Email release of panel and paper announcement