Comparison of Organic Functional Groups from FTIR and Organic Mass Fragments from AMS at Six North American Field Studies

LYNN M. RUSSELL, S. Gilardoni, L. Hawkins, R. Schwartz, S. Takahama, Scripps Institution of Oceanography, UCSD;
T.S. Bates, Pacific Marine Environmental Laboratory, NOAA;
J. D. Allan, H. Coe, University of Manchester;
D. Baumgardner, National Autonomous University of Mexico;
J.L. Jimenez, P. DeCarlo, E. Dunlea, University of Colorado at Boulder;
T.B. Onasch, M. Canagaratna, D.R. Worsnop, Aerodyne Research Inc.

FTIR Organic Bulk Particle Measurements

• Technique:
  – Calibrated FTIR spectroscopy
  – Teflon filter in situ analysis
Calibrated Transmission FTIR of Submicron Aerosol on Teflon Filters

FTIR/EGA Comparisons: Organic Carbon (OC)

- FTIR bond absorption calibrated to OC for each functional group

Maria et al., 2002

Gilardoni et al., 2007

Maria et al., 2003

NEAQS-RHB 2004

ACE-Asia-C130 2001

OC = [carbonyl-C] + [hydroxyl-C] + [alkene-C] + [alkane-C] + [aromatic-C] + [organoN-C] + [organoS-C]

Russell, 2003
FTIR Groups and AMS Fragments

FTIR/AMS Comparisons:
Bonds and Fragments

- FTIR measures bond
- AMS measures mass

FTIR and AMS are laboratory-calibrated (independently) to (different) compounds chosen to model atmospheric components. Goal is to identify correlations based on chemistry rather than sources.

- OM from FTIR
  - Calibrated for individual groups, then summed
- OM from AMS
  - Calibrated by model compounds for sum of fragments
FTIR/AMS Comparison Projects

FTIR/AMS Comparisons:
Organic Mass (OM)

- FTIR bond absorption calibrated to OM for each functional group

\[ OM = [\text{carbonyl-M}] + [\text{hydroxyl-M}] + [\text{alkene-M}] + [\text{alkane-M}] + [\text{aromatic-M}] + [\text{organoN-M}] + [\text{organoS-M}] \]

Gilardoni et al., 2007

Russell, 2003
FTIR/AMS Comparisons:
OM Measurements

• OM from FTIR
  – Calibrated for individual groups, then summed for functional groups
  \[ \text{OM} = [\text{carbonyl-M}] + [\text{hydroxyl-M}] + [\text{alkene-M}] + [\text{alkane-M}] + [\text{aromatic-M}] + [\text{organoN-M}] + [\text{organoS-M}] \]

• Missing groups are omitted
  – OM is biased low when some groups are below detection

• OM from AMS
  – Calibrated by model compounds for sum of fragments
  \[ \text{OM} = \text{[collection efficiency]} \times \text{[scaled m/z peaks]} \]
  \[ = 2 \times [k_{43}m_{43} + k_{44}m_{44} + k_{55}m_{55} + k_{57}m_{57} + ...] \]
  – Missing peaks are accounted for by collection efficiency
  – Missing 800+ nm?
  – Corrected to total OM by calibration (e.g. EGA)

FTIR/AMS Comparisons:
OM < 10 $\mu$g m$^{-3}$

• FTIR and AMS OM are correlated for all projects
  – FTIR < AMS (consistent with expected bias)
  – Scatter is substantial (consistent with ±20%)

![Graph showing FTIR and AMS OM comparison for different projects](image)
FTIR/AMS Comparisons: Oxidized Fraction

- **FTIR** measures absorption by bonds
  - **Max Acid Mass Fraction**
    - Maximum possible acid is minimum number of carbonyl or hydroxyl groups
    \[ \text{Max Acid} = \text{MINIMUM}(\text{[carbonyl]-M}, \text{[hydroxyl]-M})/\text{OM} \]
  - **Oxygen/Carbon Ratio**
    - Adds carbonyl and hydroxyl groups together for total oxidized fraction
    \[ \text{O/C} = (\text{[carbonyl]-O} + \text{[hydroxyl]-O})/\text{OC} \]

- **AMS** measures mass of fragments
  - m/z 44: CO₂
  - m/z 43: C₂H₃O + C₃H₇

FTIR/AMS Comparisons: Acid Mass Fraction and m/z 44

- **General trends for each project** for acids and m/z 44
FTIR/AMS Comparisons:
Acid Mass Fraction and m/z 44

- Acid ~ m/z 44
  - For high m/z 43:
    \( C_2H_3O >> C_3H_7 \)
    Carbonyl>Hydroxyl

FTIR/AMS Comparisons:
O/C Ratio and m/z 44

- O/C ~ m/z 44
  - Only at high m/z 43:
    \( C_2H_3O >> C_3H_7 \)
    Carbonyl>Hydroxyl
FTIR/AMS Comparisons: Bonds and Fragments

- FTIR measures bond absorption, e.g.
  - Carbonyl C=O
  - Hydroxyl C-OH

- AMS measures mass fragments, e.g.
  - m/z 44: CO$_2$
  - m/z 43: C$_2$H$_3$O + C$_3$H$_7$

FTIR and AMS Comparison: Carbonyl, Hydroxyl and m/z 44

- Weak increases in both Carbonyl and Hydroxyl with m/z 43 and 44
FTIR and AMS Comparison: Carbonyl/Hydroxyl and m/z 43/44

- Range of ratios varies by project
  - NEAQS
    - High m/z 43/44
    - High Carbonyl/Hydroxyl
  - Chebogue
    - Varied m/z 43/44
    - Low Carbonyl/Hydroxyl
  - Veracruz, Seattle, Houston
    - Low m/z 43/44
    - Varied Carbonyl/Hydroxyl

FTIR/AMS Comparisons: Summary

- FTIR groups account for up to 60-90% of AMS OM
  - FTIR OM < AMS OM with low bias from missing groups
  - Scatter (±20%) reflects differences in mixtures

- FTIR oxygenated groups correspond to AMS m/z 44
  - FTIR O/C ~ AMS m/z 44 for high m/z 43
  - FTIR Max Acid ~ AMS m/z 44 for high m/z 43

- FTIR bonds and AMS fragments lack 1:1 correlation
  - Overlap in m/z 43, 44 fragmentation of carbonyl, hydroxyl

- FTIR/AMS comparisons suggest correlations in chemistry rather than sources
FTIR/AMS Comparisons: NH$_4^+$ < 4 μg m$^{-3}$

- No evidence for positive NH$_4^+$ artifacts
  - FTIR NH$_4^+$ detection is by difference
  - Correlation comparable to OM
  - FTIR < AMS

FTIR and AMS Comparison: Oxygen/Carbon Ratio

- O/C correlates with m/z 43/44 for two projects
  - Altzomoni
  - NEAQS
FTIR and AMS Comparison:
AMS m/z 44 vs 43

[Graph showing a scatter plot with data points and color gradient indicating differences between AMS m/z 44 and 43.]

Veracruz HR Peak

[C2H3O or m/z 44

C3H7]
FTIR and AMS Comparison:
AMS m/z 44 vs FTIR O/C

FTIR and AMS Comparison:
AMS m/z 44 vs FTIR Acid
FTIR and AMS Comparison:
Carbonyl vs. Hydroxyl

AMS m/z 43+44 vs FTIR O/C
FTIR/AMS Comparisons:
OM in MILAGRO, Houston 2006

- Altzomoni
- Veracruz-C130
- Houston-RHB

FTIR/AMS Comparisons:
OM < 4μg m⁻³

- Bias is less at low OM
  - FTIR ~ AMS
Organic Functional Groups by FTIR

$\nu \text{C} - \text{H}$ Alkane, primary combustion emissions.

$\nu \text{C} = \text{O}$ Carbonyl, indicative of oxidation.