Extractive Electrospray Ionization Mass Spectrometry (EESI-MS) and AMS Measurements of Biomass Burning Organic Aerosol

AMS Users’ Meeting
January 20th, 2021 — Online


- Introduce EESI-MS
- Airborne Deployment FIREX-AQ
- Complementary to AMS
Extractive Electrospray Ionization Time-of-Flight Mass Spectrometry

- Quantitative 1 Hz measurements of individual components of organic aerosol
- 1 Hz detection limits of ng sm\(^{-3}\)
- Highly complementary to AMS

sm\(^{-3}\) = standard conditions: 273.15 K; 1013 mbar
Extractive Electrospary Time-of-Flight Mass Spectrometry

- Strip out VOCs to prevent SESI
- Flow particles through the electrospray
- ESI drops evaporate, ionize, then enter API-ToF
Extractive Electro-spray Time-of-Flight Mass Spectrometry

- Optimization of electro-spray working solution
- Precise control of electro-spray position
- Pressure control within ±1 mbar
- Flight-day and in-flight calibrations with AMS
- Pagonis et al. AMT 2021, In press
FIREX-AQ

- Summer 2019
- 21 research flights
- Deployed EESI-MS and HR-AMS

Western wildfires

Eastern agricultural fires

NASA DC-8

EESI-MS
HR-AMS
Targeted analysis at FIREX-AQ

**EESI(+)**

- $C_6H_{10}O_5Na^+$ calibrated as levoglucosan
- Primary emission from cellulose pyrolysis
- LC-MS confirmation of peak assignments

**EESI(-)**

- $C_6H_4NO_4^-$ calibrated as 4-nitrocatechol

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Finewax et al., *ES&T* 2018
CHARON–EESI–AMS Intercomparison

- Flew EESI(+) alongside CHARON for one flight
- Compared levoglucosan measured by EESI, CHARON, and AMS
- AMS equivalent levoglucosan calculated from $f_{C2H4O2+}$ calibrated with levoglucosan standards
Bulk OA Sensitivity

- Total EESI-MS signal correlates well with AMS OA
- Normalize to levoglucosan sensitivity to compare across campaigns

- Bulk EESI-MS sensitivity varies with OA composition
- Published studies are blind to HOA, highly sensitive to BBOA
- Future work planned using different EESI solvents

Stefenelli et al. ACP 2019
Qi et al. ACP 2019
Brown et al. Indoor Air 2020
Organosulfur emissions at FIREX-AQ

- Discrepancy between AMS sulfate and sulfate on SAGA filters
- AMS SO$_4$ > SAGA SO$_4$
- Evidence pointing towards organosulfur
Support from filter samples and EESI-MS

- Collected filter samples throughout FIREX-AQ
- Collaboration with Alex Laskin at Purdue, HPLC-ESI-OrbitrapMS
- Identify abundant sulfonates (RSO₃)
EESI-MS PMF Analysis

- Balance between SOA formation and POA loss in EESI-MS PMF
Connecting EESI-MS Tracers to AMS Factors

- Unique cross-plume gradients match EESI-MS nitrocatechol to an AMS factor
- Can quantify the contribution of this chemical process (oxidation of phenols) to SOA production
- EESI-MS gives a level of chemical specificity that is not accessible by AMS alone
FIREX-AQ Deployment

Intercomparison of EESI-MS, AMS, CHARON PTR-MS

Chemical Specificity in PMF Analysis

Molecular composition