Washington University in St. Louis
James McKelvey School of Engineering
Department of Energy, Environmental & Chemical Engineering

Offline Aerosol Mass Spectrometry (AMS) Technique for Chemical Characterization of Filter Samples

Jhao-Hong Chen, Yuxuan Ren, Brent Williams

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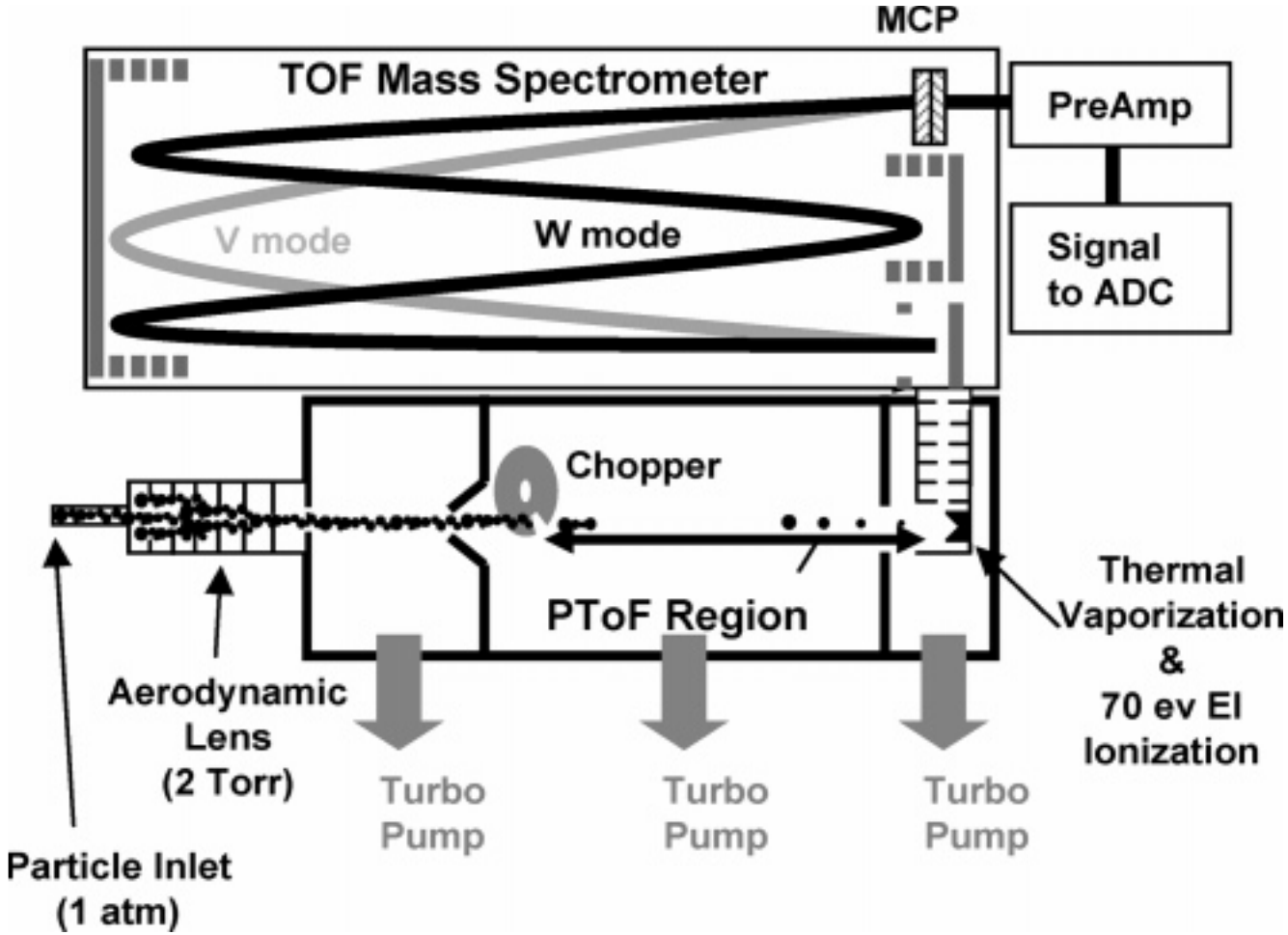
center for aerosol science and engineering

SPARTAN
Global Particulate Matter Network

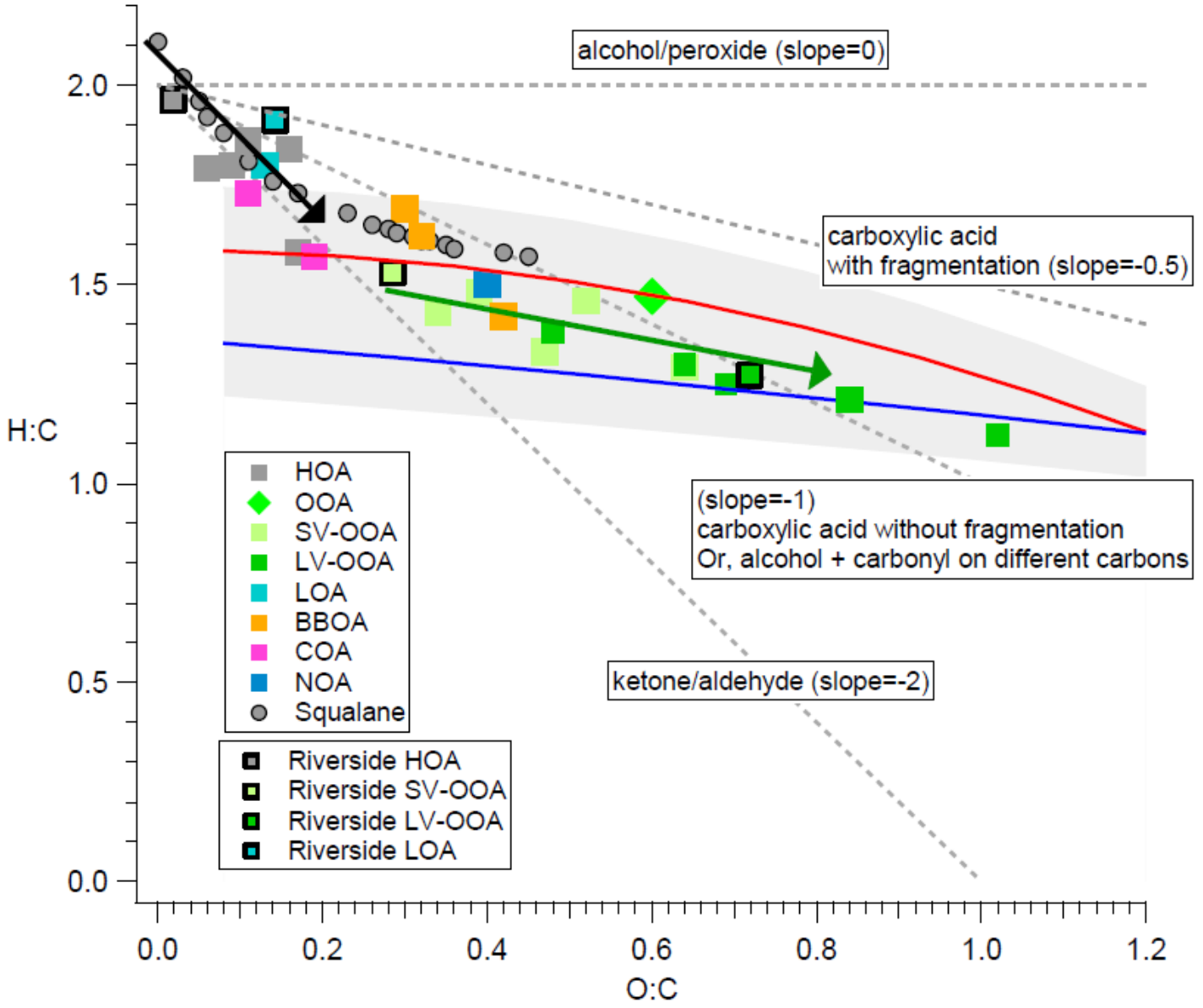
High-Resolution Time-of-Flight AMS (HR-ToF-AMS)

- **Promising Development**



(DeCarlo et al., 2006)

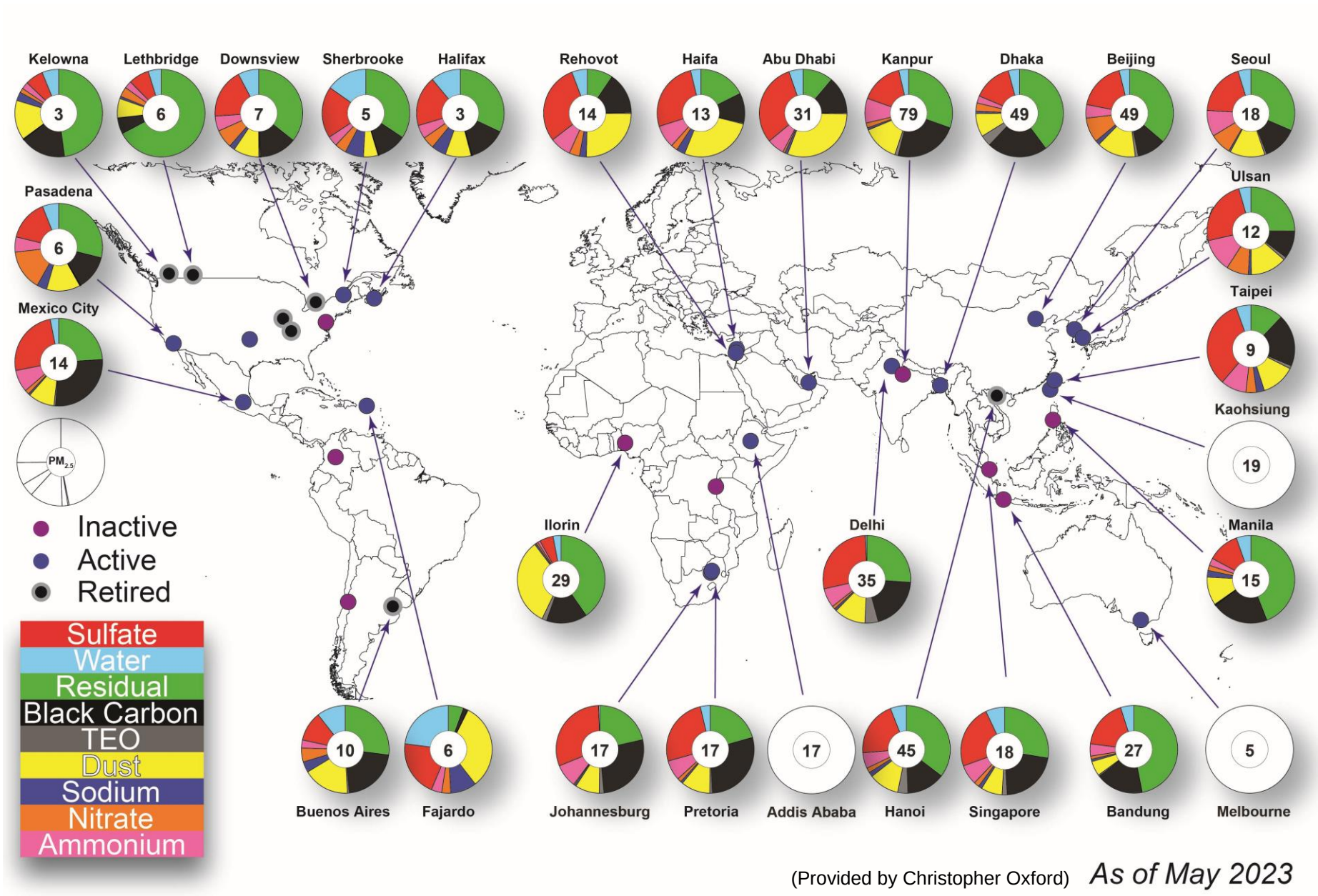
HR-AMS Provides Elemental Composition of Organics



(Ng et al., 2011)

Chemical Composition of SPARTAN Network Filter Samples

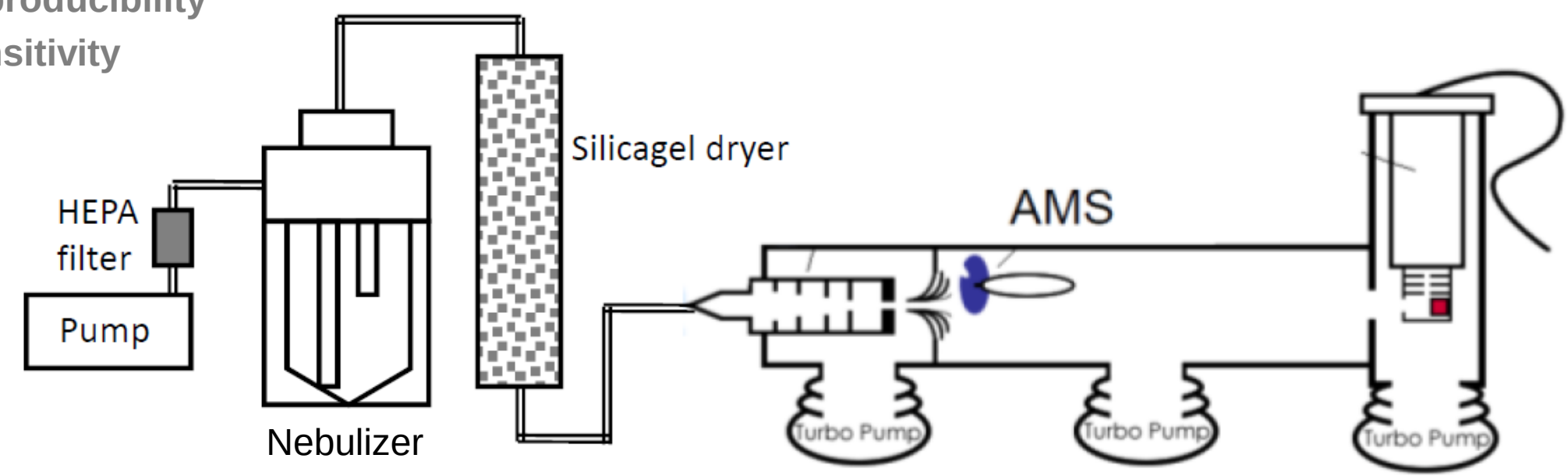
- **Residuals**



(Provided by Christopher Oxford) *As of May 2023*

Offline AMS Technique for Chemical Analysis

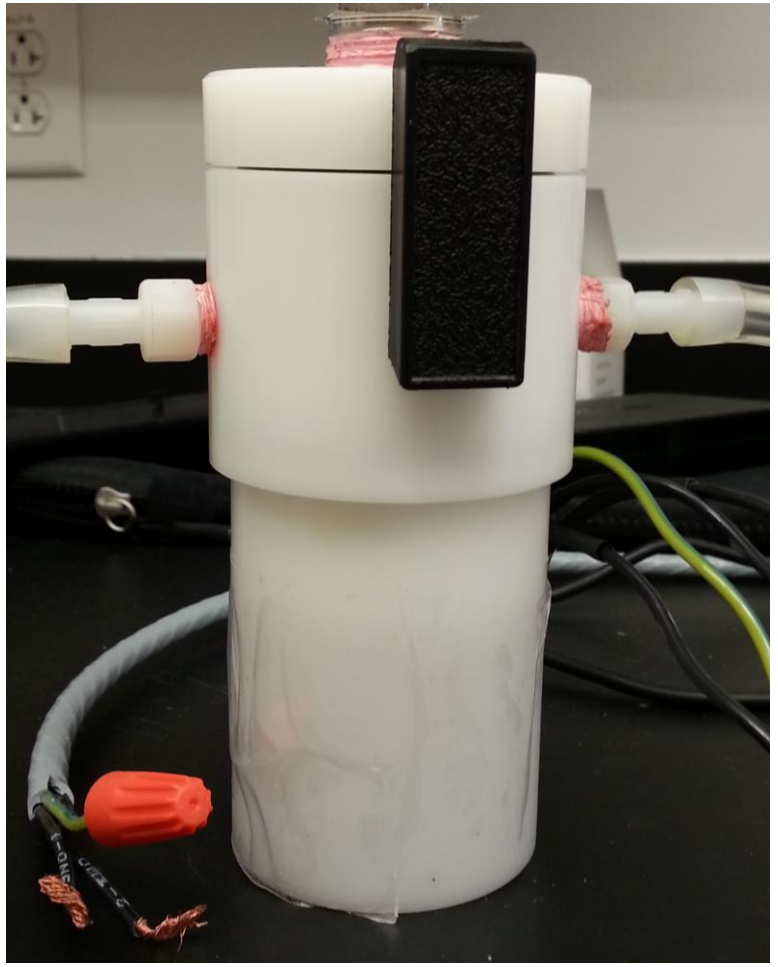
- **Literature:**
  - Sun et al. 2010 and Sun et al. 2011 first used this technique
  - Daellenbach et al. 2016 first used the term “offline AMS” in the title of research
  - O’Brien et al. 2019 analyzed samples at mg level
- **Challenges:**
  - Inconsistent sample extraction procedures
  - Qualitative analysis
  - Reproducibility
  - Sensitivity



(El Haddad et al., 2012)

Method Development: Nebulizer Tests

- **Ultrasonic nebulizer**
  - Analysis at mg level
  - Hard to clean
  - Difficult to setup
  - Time resolution
  - Reproducibility
- **Collison nebulizer**
  - Easy to clean
  - Simple setup
  - Higher time resolution (~15 min)
  - Reproducibility
- **Internal Standard**
  - Quantitative Analysis
  - Calibration for HR analysis
  - Compatible with SPARTAN

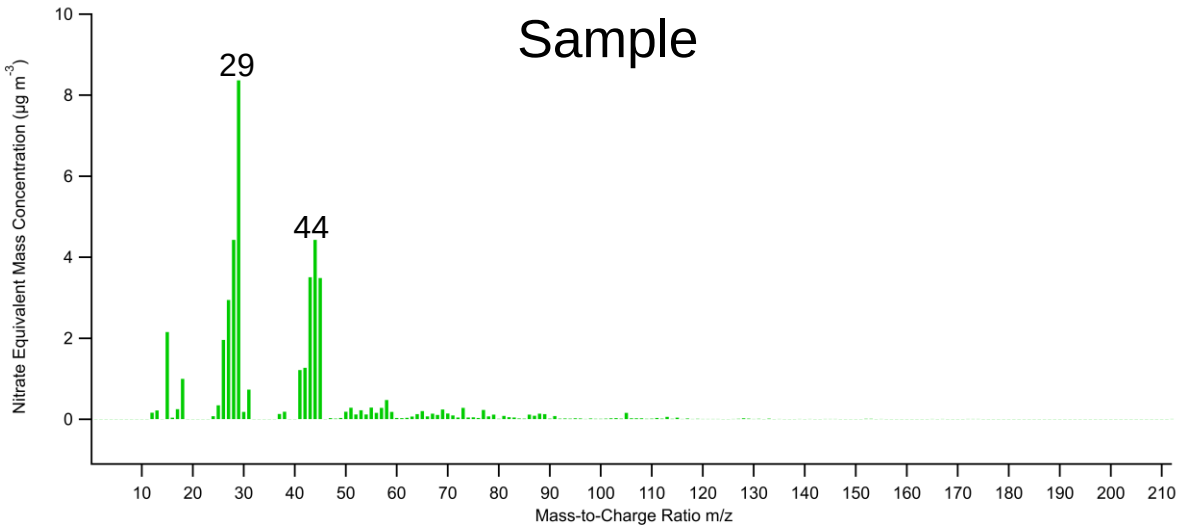


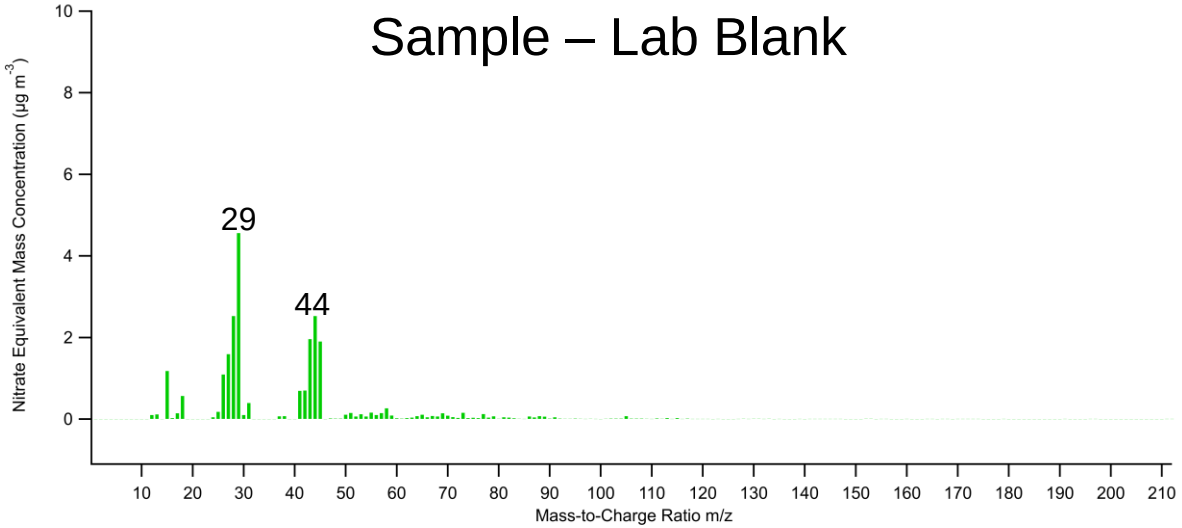
Ultrasonic nebulizer (O'Brien et al., 2019)

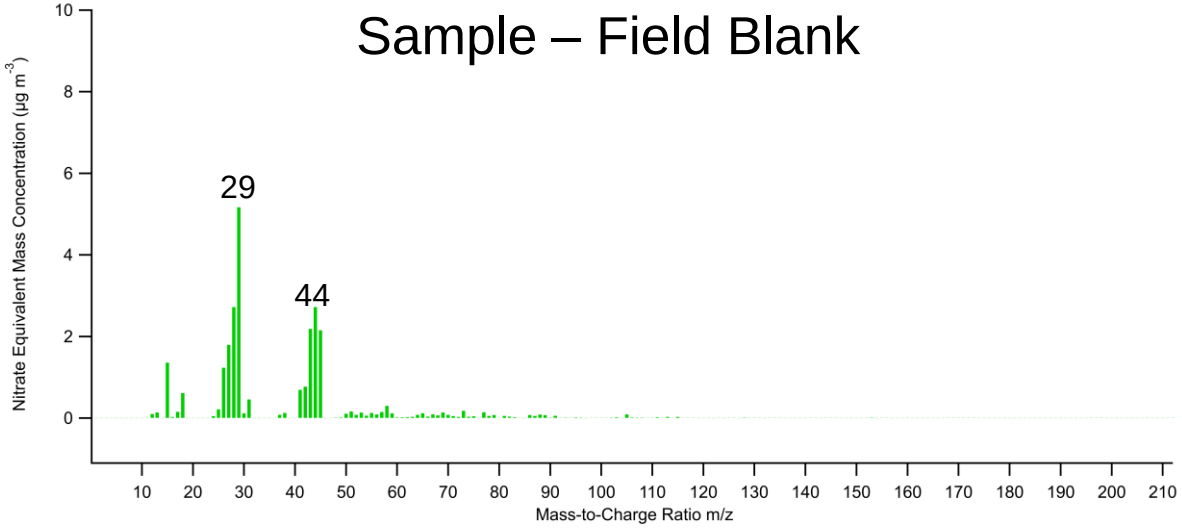
Collison nebulizer

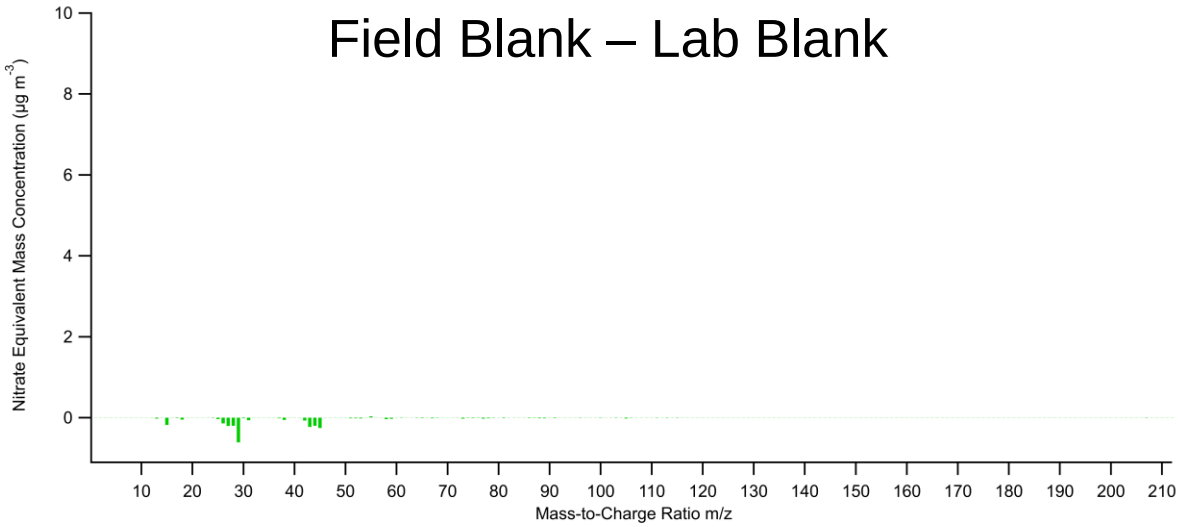
Organic Signals from Sherbrooke, Canada

- **Signal fluctuation influences quantitative analysis**





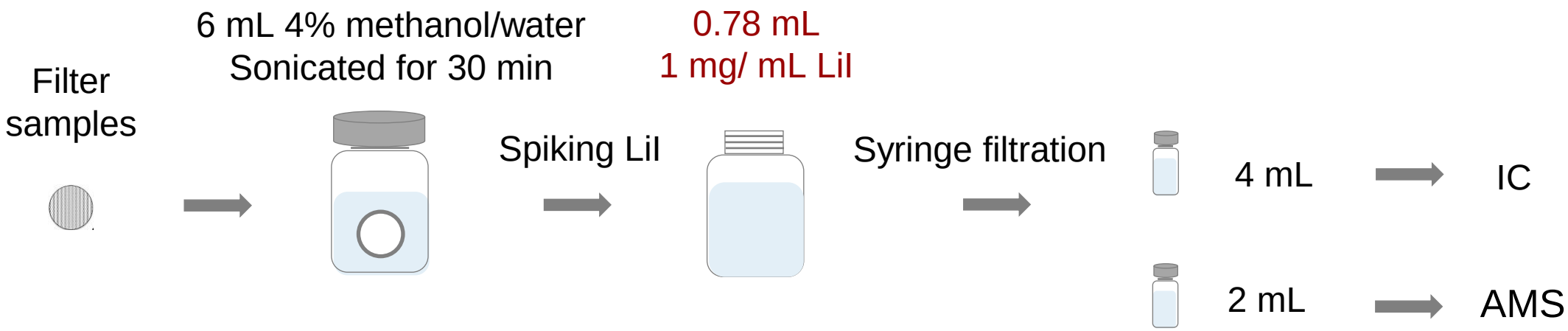




Internal Standard: Lithium Iodide (LiI)

- **Trials:**
  - Isotopically labeled ammonium nitrate ($NH_4{}^{15}NO_3$)
  - Ammonium iodide (NH_4I)
  - Lithium iodide (LiI)

- **Sample extract with internal standard:**

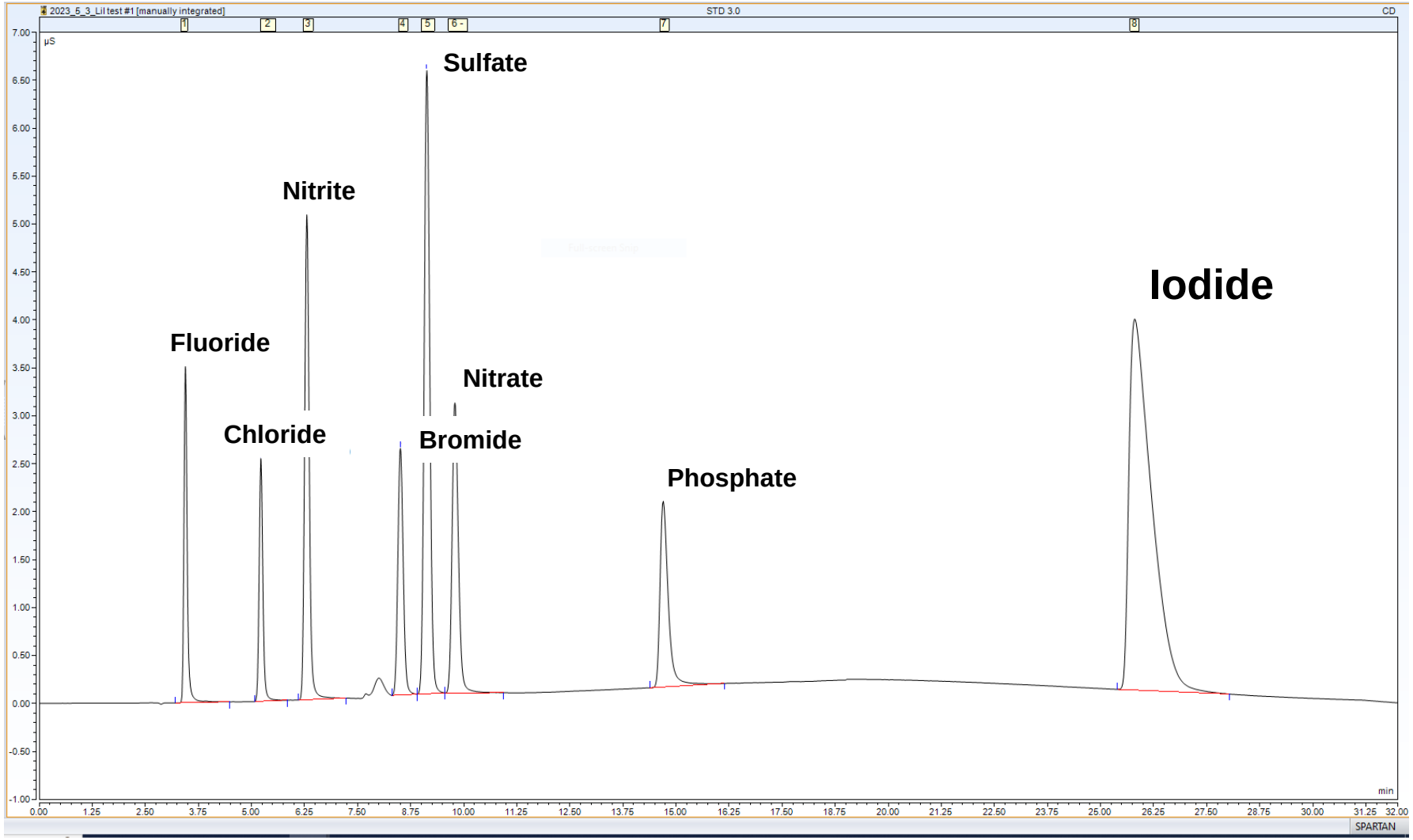


- **Enables quantitative analysis**
- **Provides high m/z for HR analysis calibration**
- **Compatible with Ion Chromatography (IC) method**

Modified from Surratt (UNC) and Kroll (MIT)

Internal Standard: Lithium Iodide (LiI)

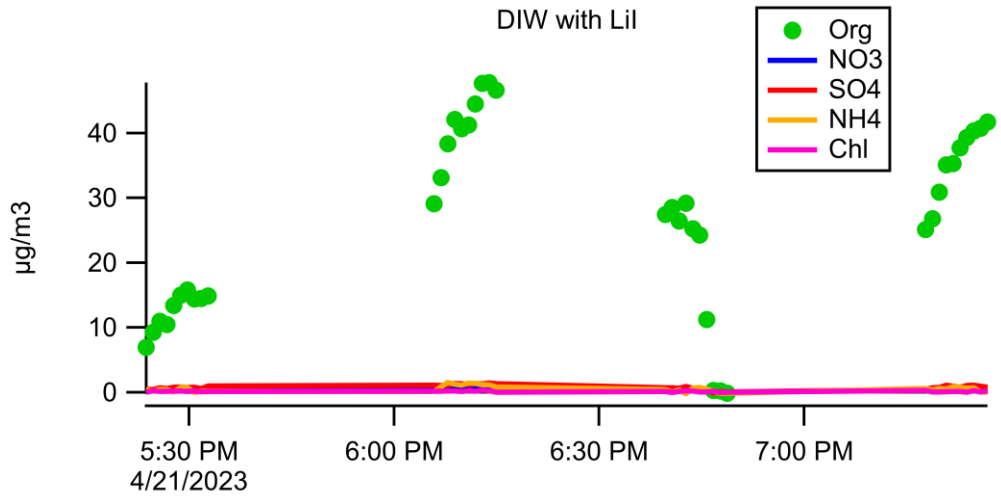
- Separable from other water-soluble ions
- Reasonable retention time (< 30 min)

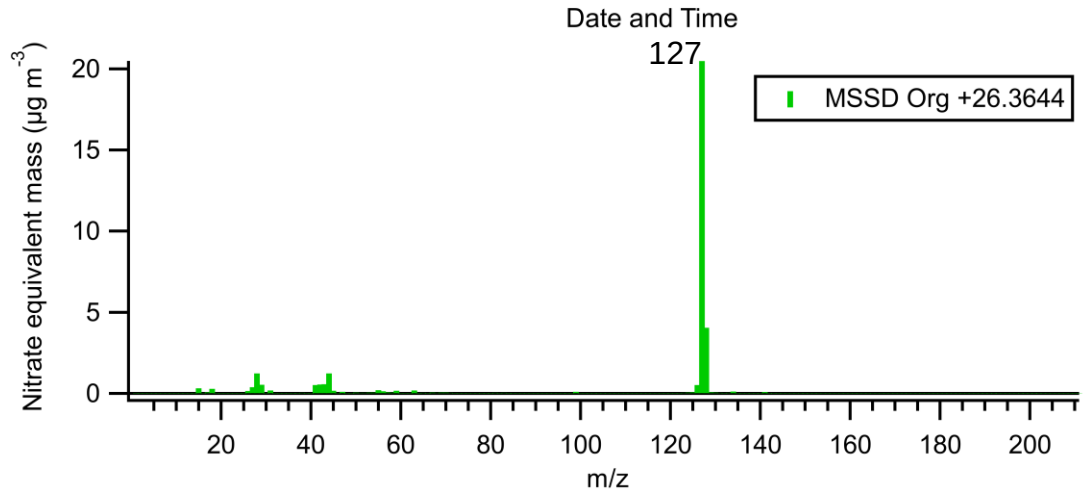


Internal Standard: Lithium Iodide (LiI)

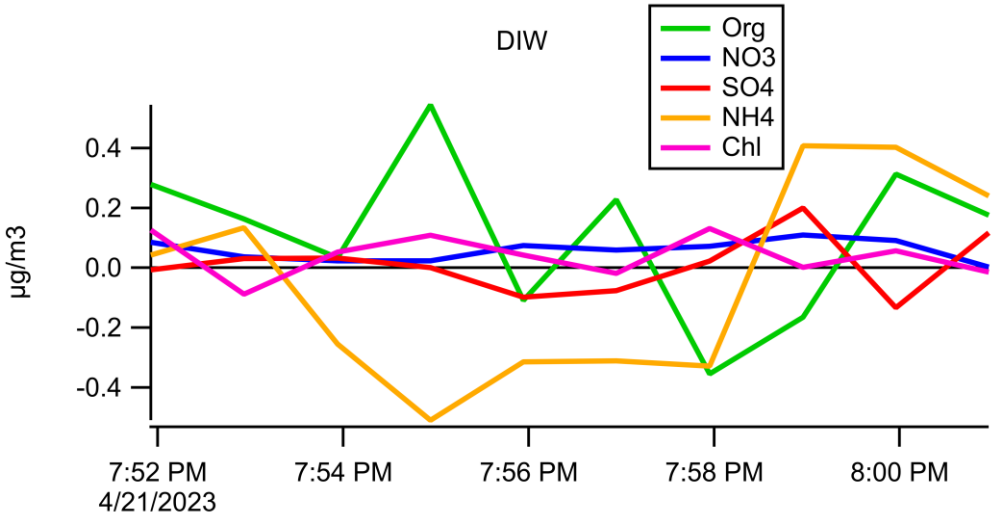
- **Signal fluctuation necessitates the internal standard**

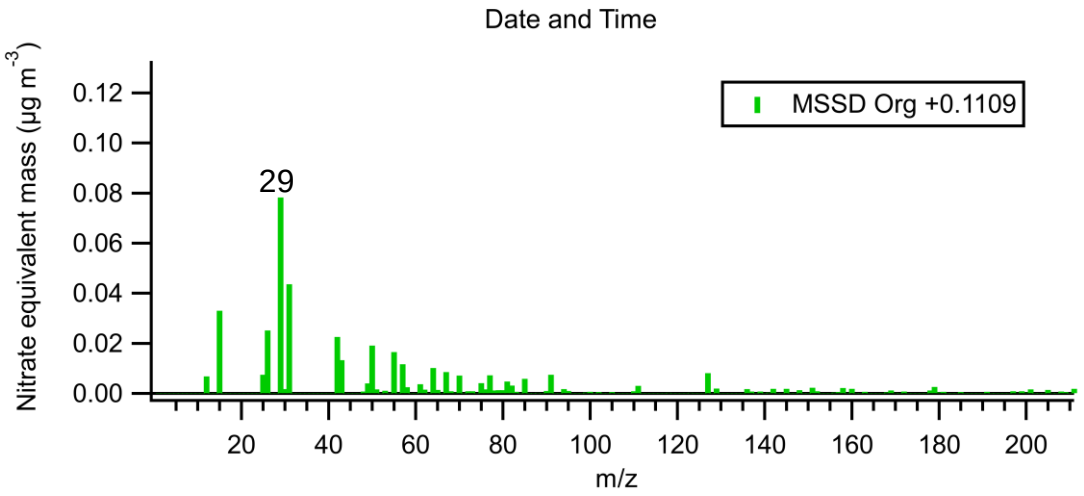
Deionized Water (DIW) spiked with LiI





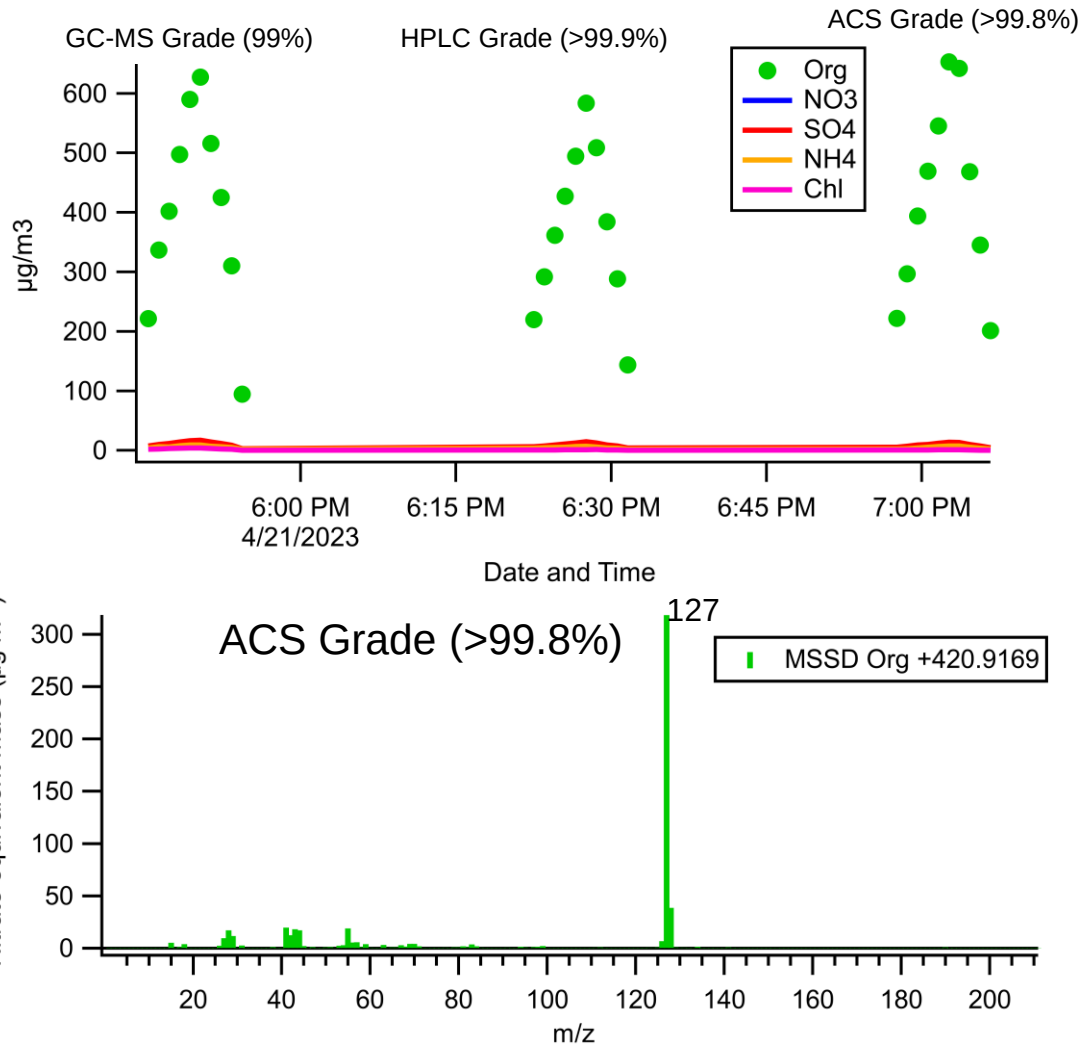
Deionized Water (DIW) without spiking

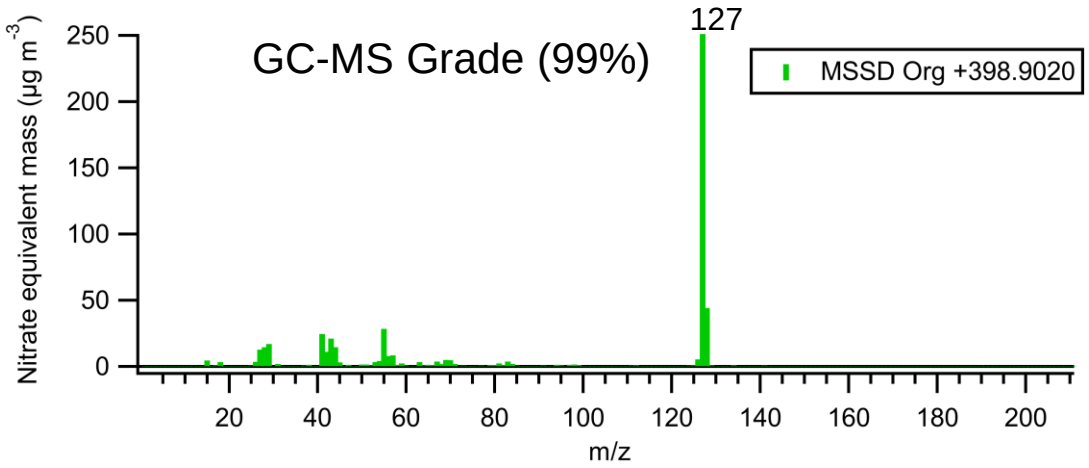


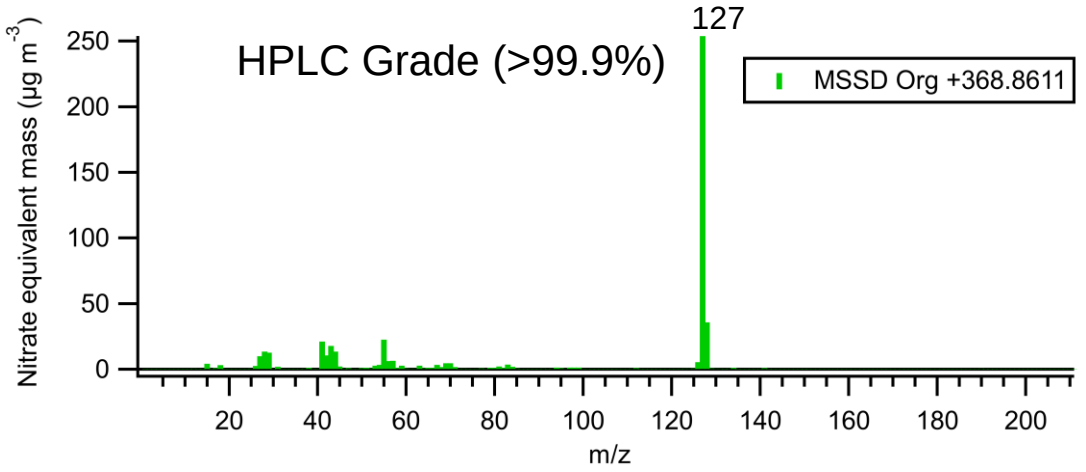


Background Signal: Methanol Comparison

- **Background signal comparable among different grades**
- **Determination of blank signal required**

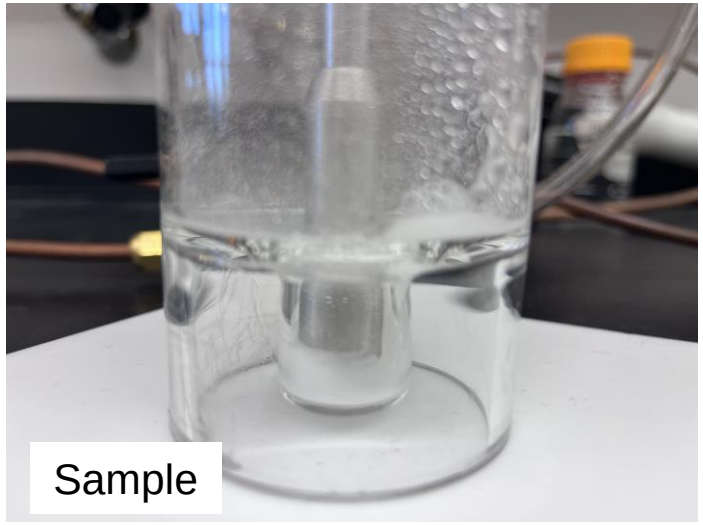


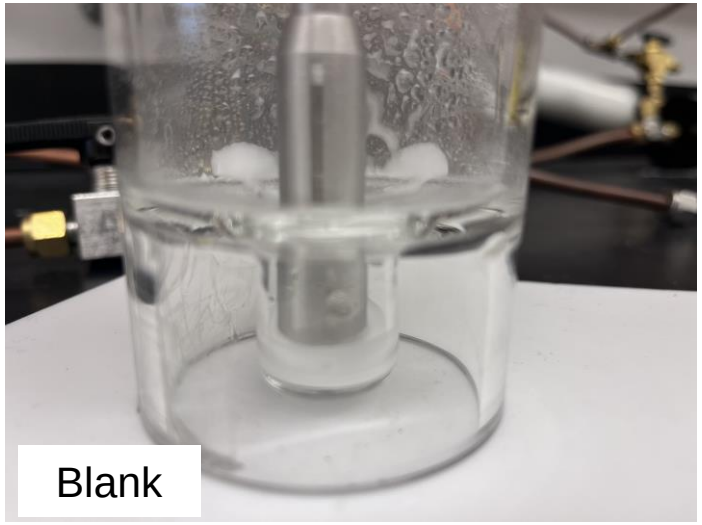


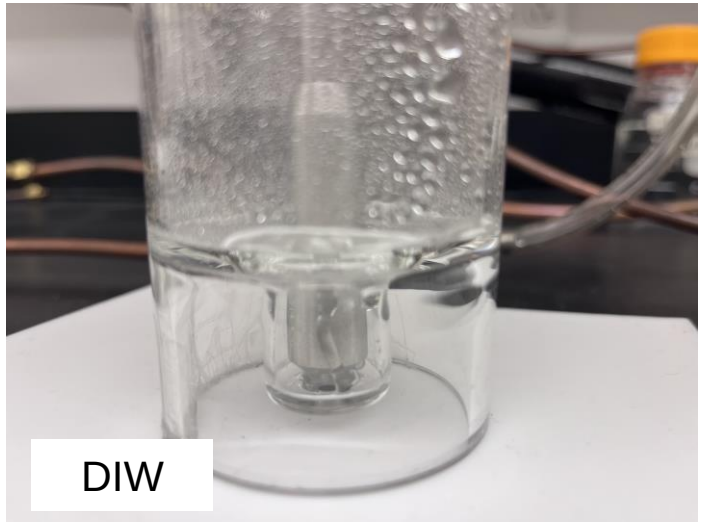


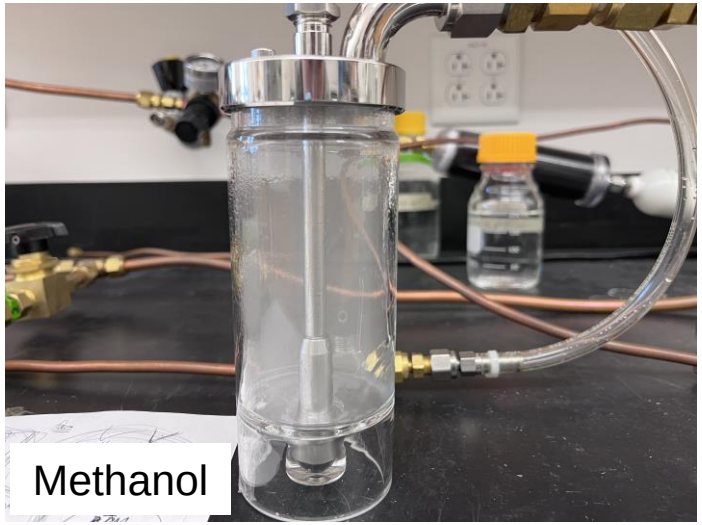
Foaming in the Nebulizer

- **Observed in sample and blanks**
- **Not observed in DIW or methanol**
- **Extent of foaming is related to the relative amount of methanol in DIW**
- **Effect of foaming on the quantitative analysis unknown**



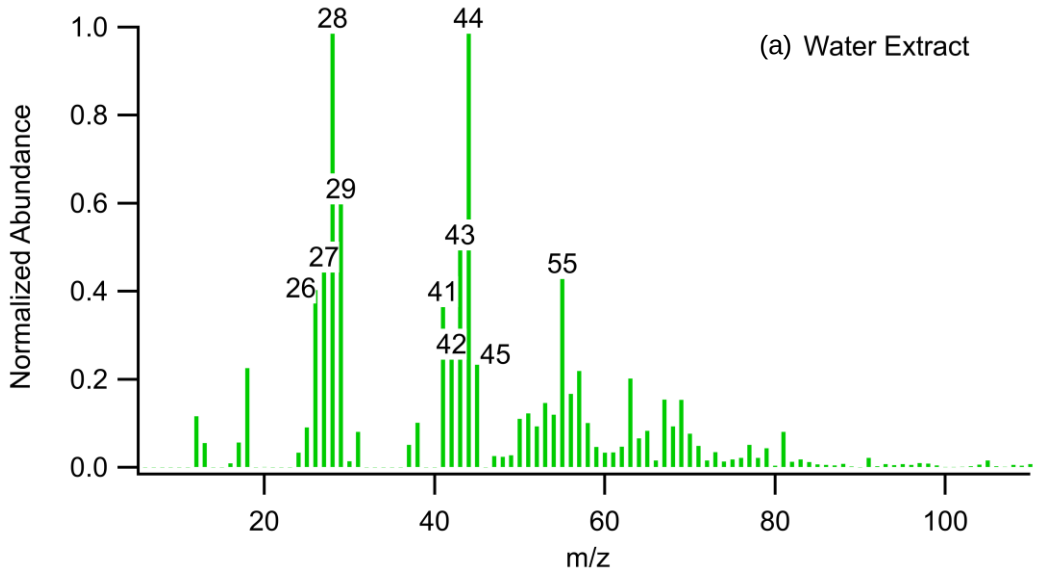


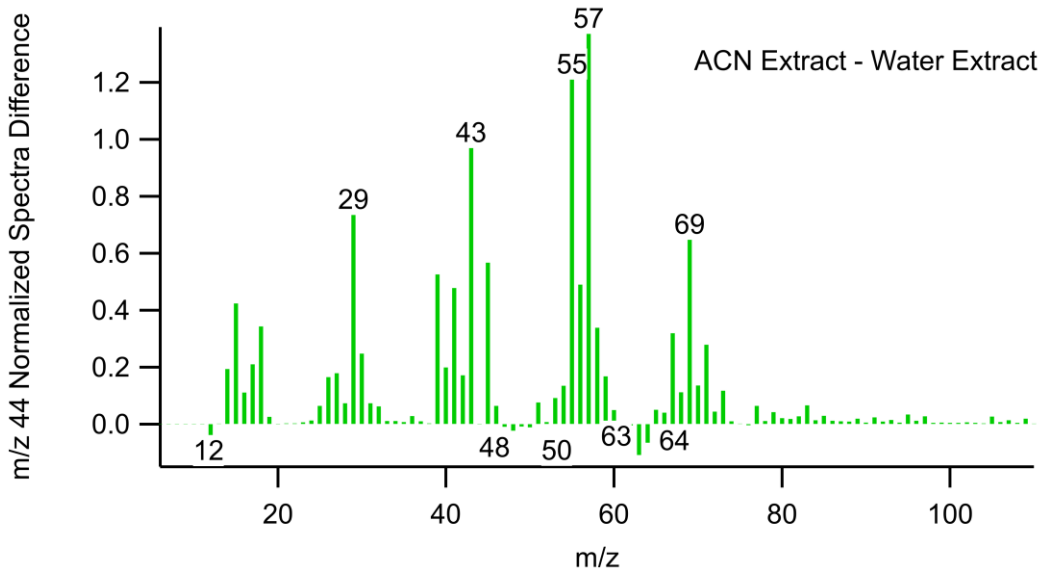


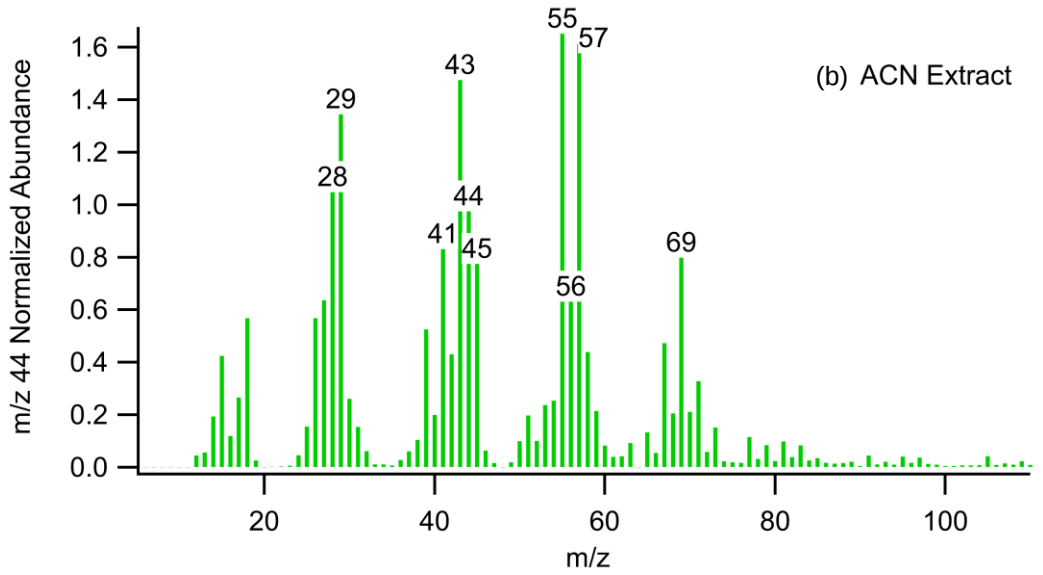


Solvent Comparison (m/z 44 Normalized): Samples from India

- **Water Extract:**
  - High abundance of m/z 28 and 44
  - Indicating oxygenated organic aerosol (OOA)
- **Acetonitrile (ACN) Extract:**
  - Extracting Hydrocarbon-like organic aerosol (HOA) (m/z 29, 43, and 57) in addition to OOA
- **ACN Extract – Water Extract:**
  - The difference looks like HOA







Summary and Future Directions

- Collison nebulizer selected for aerosol generation
- Lithium iodide (LiI) chosen as internal standard
- Internal standard: Compatibility and Quantification

- System cleaning check to determine background signal
- Effect of syringe filter during extraction
- Reproducibility test
- Analyze SPARTAN samples with organic solvent

Thank you!

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