

# **Amines as a Source of Secondary Organic Aerosol**

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**Chemistry and Biochemistry**

**Utah State University**

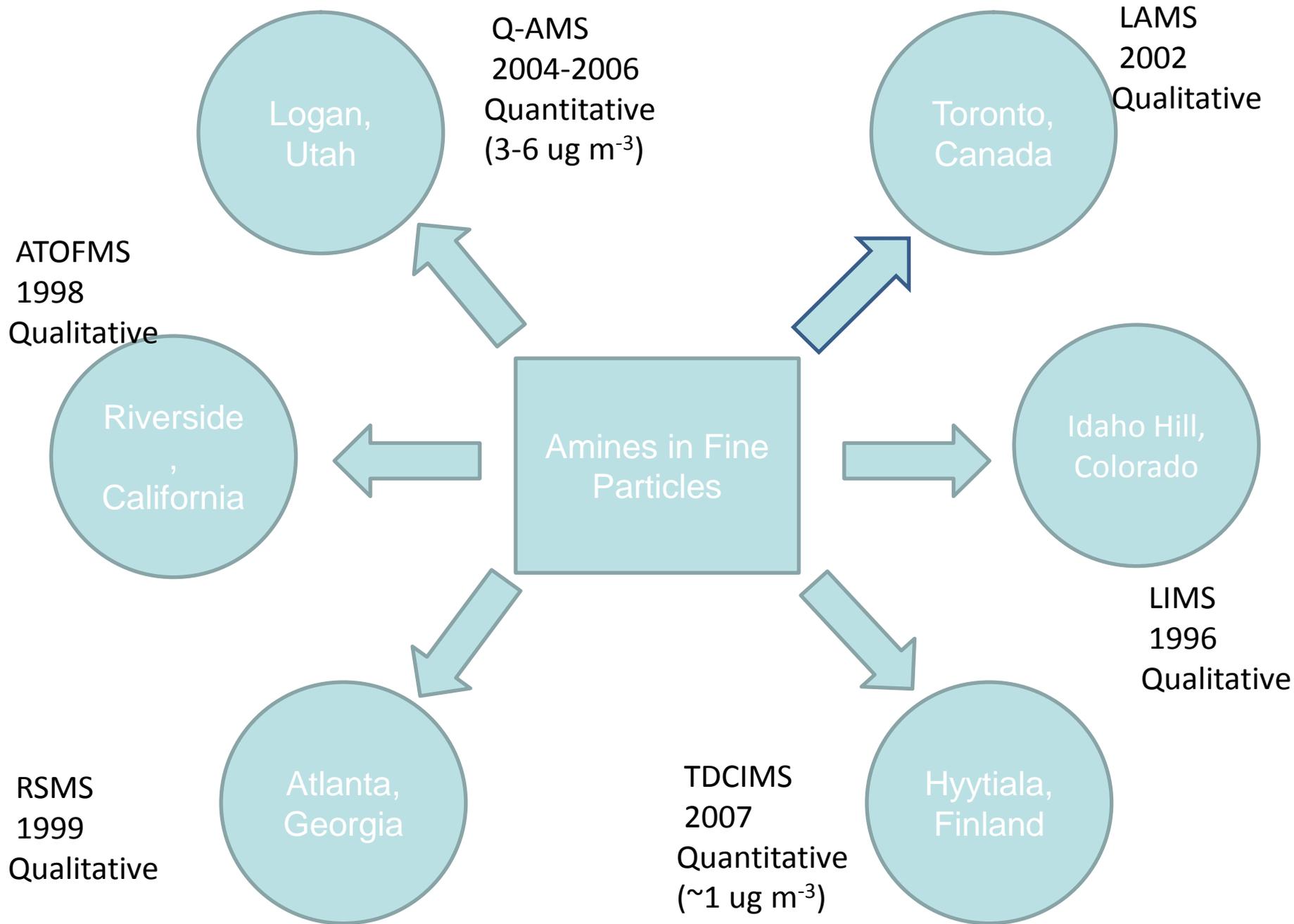
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**Quentin Malloy, Bethany Warren, Qi, Li, David R. Cocker III**

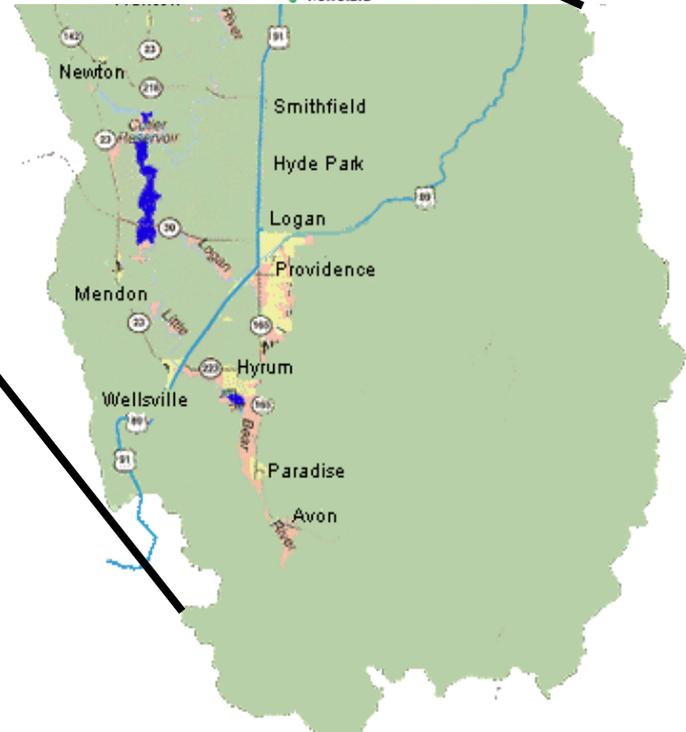
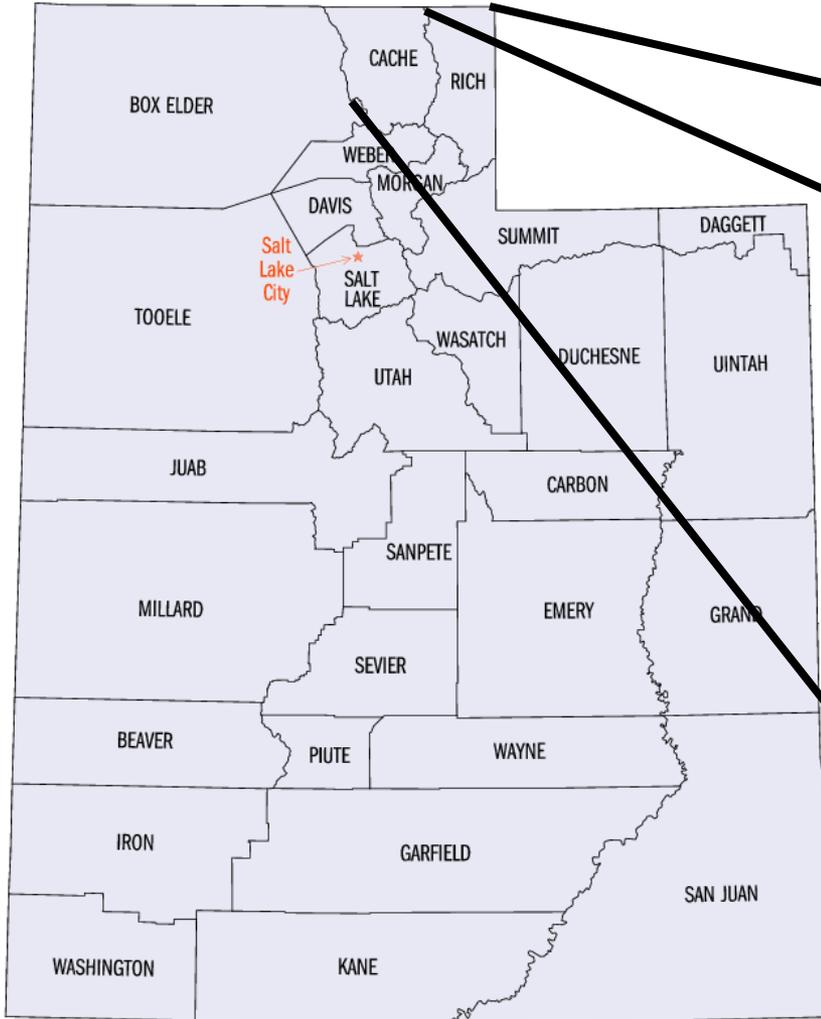
**CE-CERT, University of California Riverside**

# Amines in the Literature

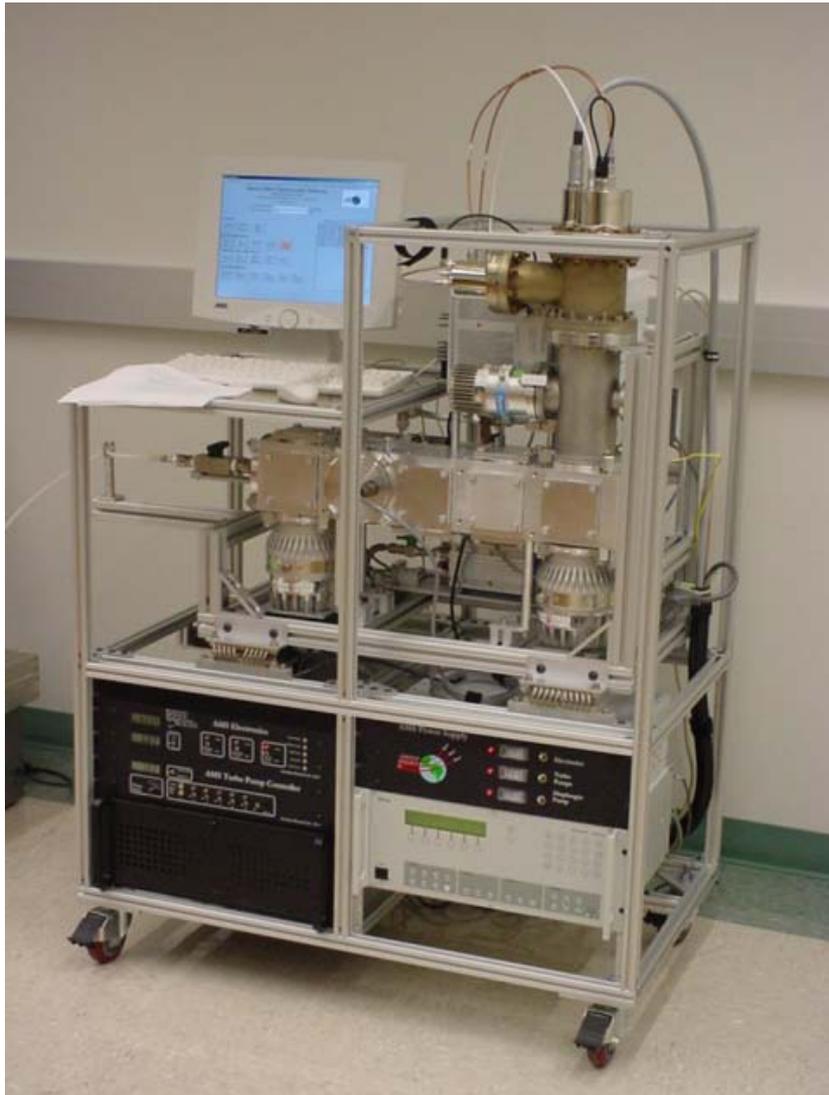
- Novakov: Particulate amines by XPS (1972, 1979)
- Pitts: Amines+NO<sub>x</sub> → Nitrosamines (1978)
- Gas-phase amines from catalyst equipped vehicles
  - Cadle (1980), Westerholm (1993)
- Gas-phase amines from dairies
  - Mosier (1973), Schade and Crutzen (1995)
- Amines in individual particles (LDI-MS)
  - Murphy (1997), Suess (2000), Tan (2002), Imre (2005)
  - Particle formation in smog chamber by acid-base reactions, photochemistry (Angelino, 2001)
- Dimethylamine in nucleation particles (Mäkelä, 2001)



# Cache County, Utah, USA



# Aerodyne Aerosol Mass Spectrometer



## Instrument Specs

### Physical

Power: *~600 watts*

Mass: *110 kg*

### • Performance

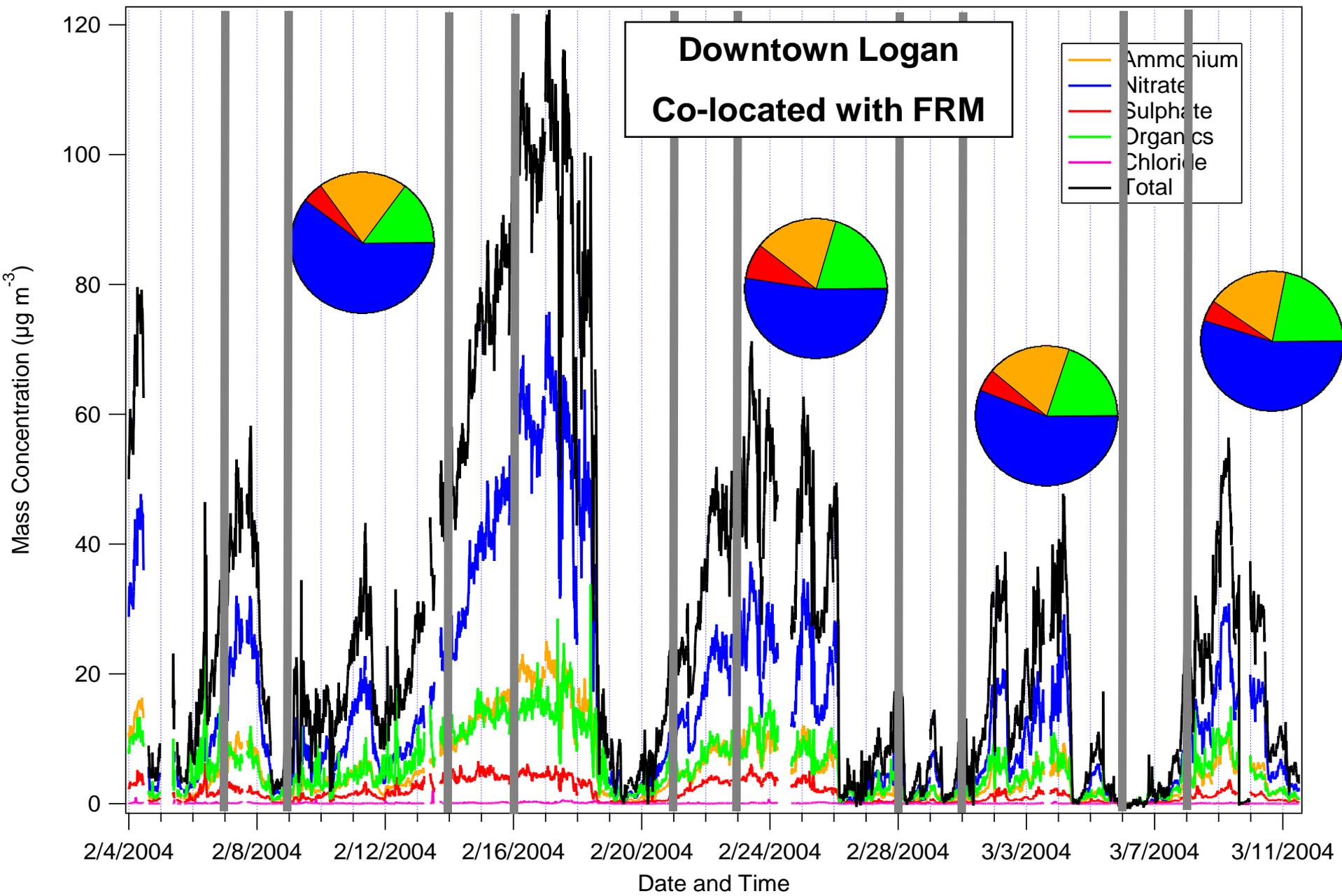
Measurement size range: *50 nm to 1  $\mu\text{m}$  for volatile and semi-volatiles*

Maximum Data Rate: *100 Hz*

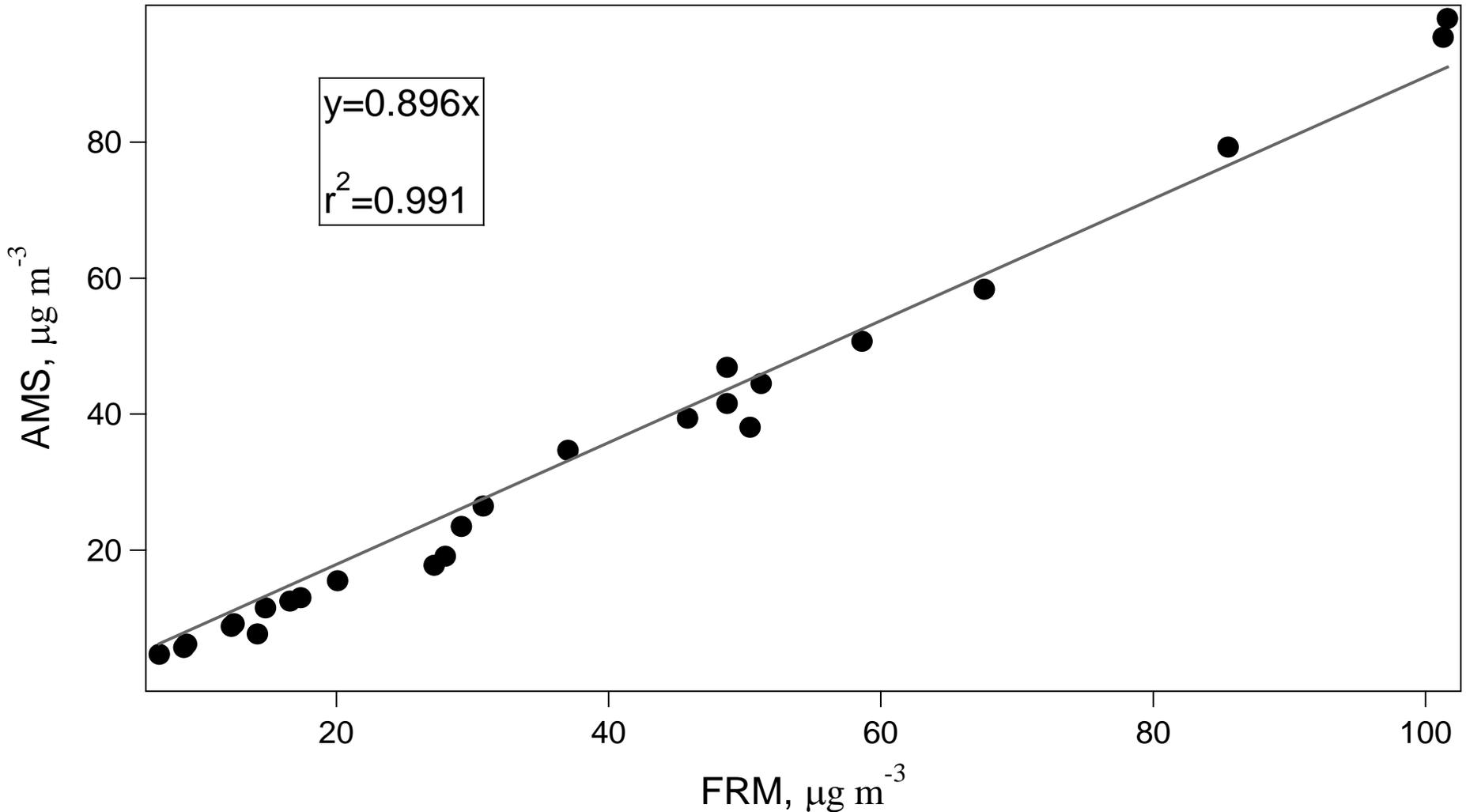
Sensitivity: *0.01  $\mu\text{g}/\text{m}^3$  (10 sec.)*

Sampling Rate: *100  $\text{cm}^3 \text{min}^{-1}$*

# February/March 2004

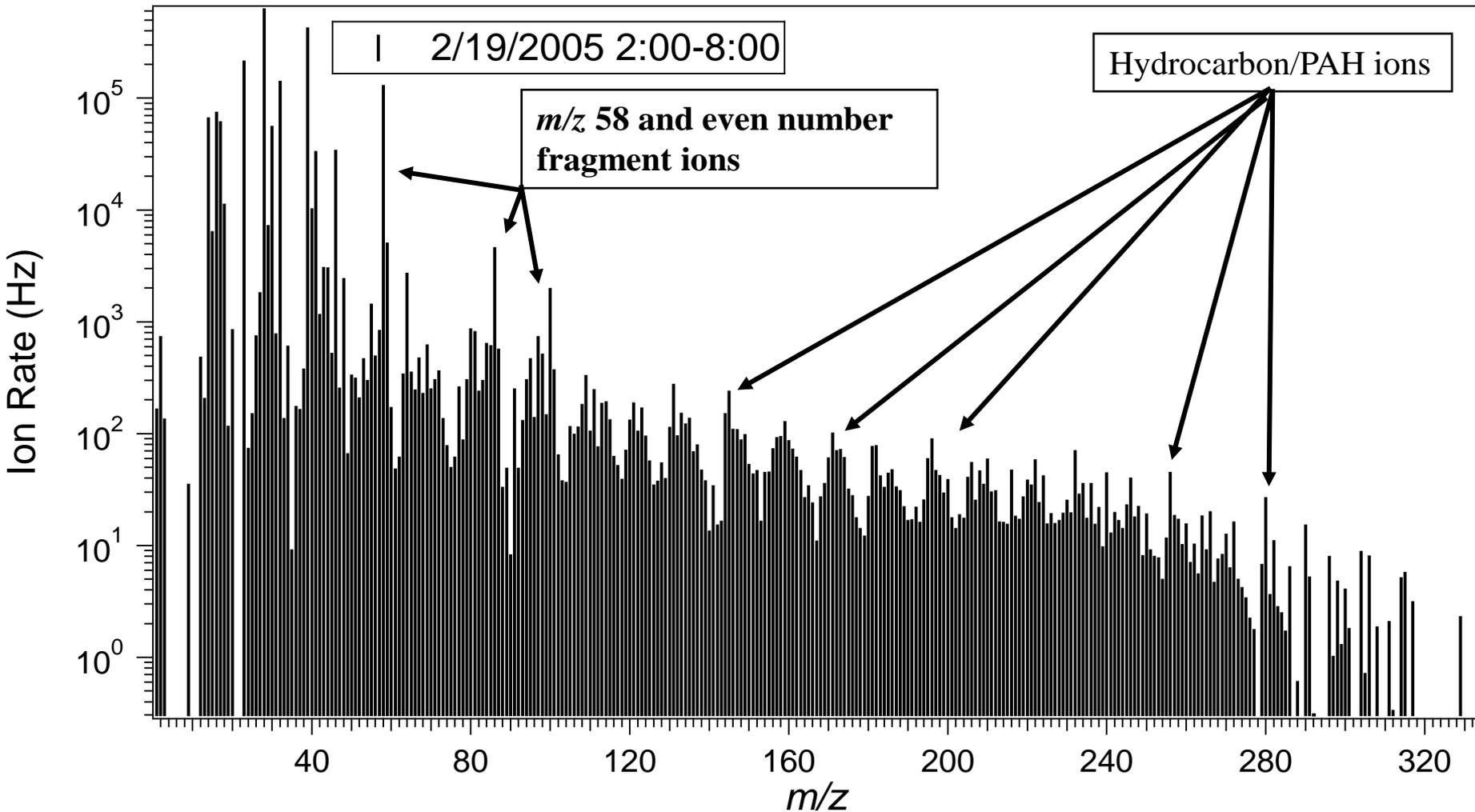


# AMS/ UDAQ FRM PM<sub>2.5</sub> Comparison (24-hour) Logan, Utah, February 2004

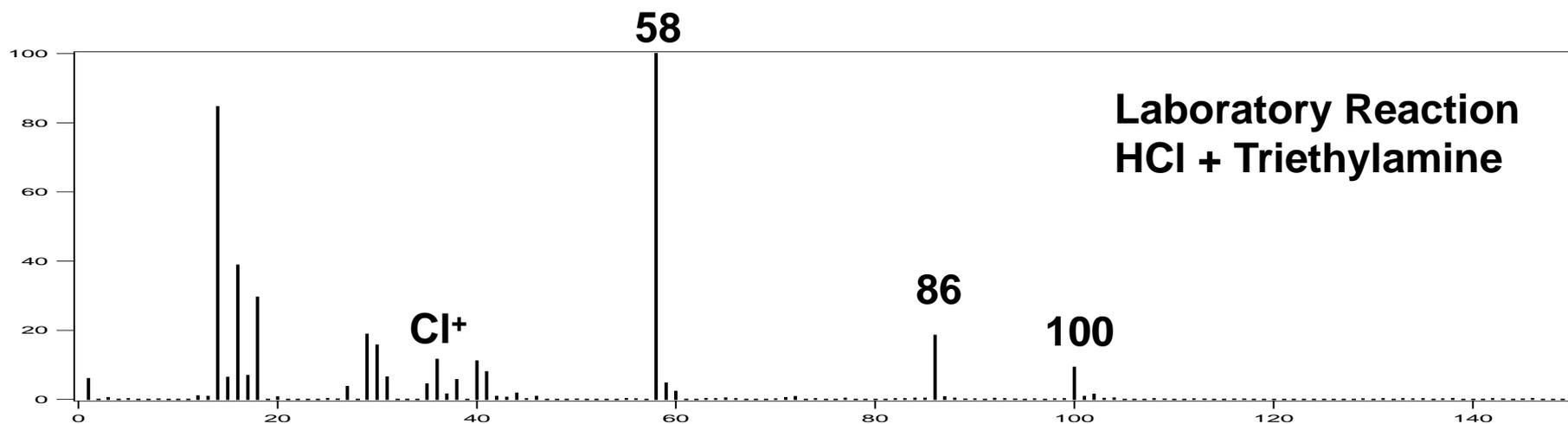
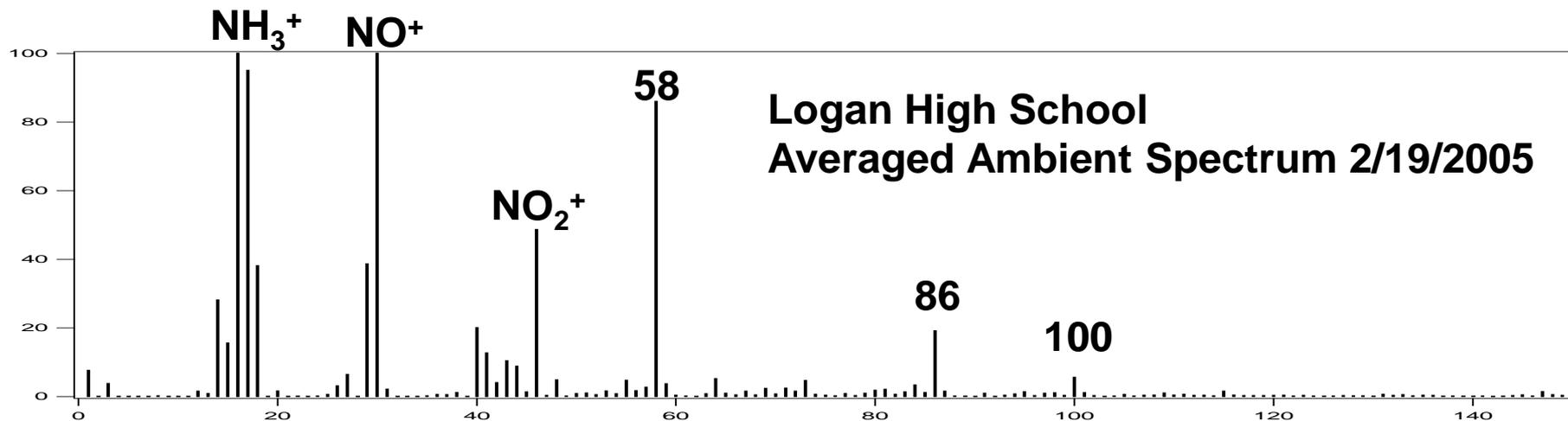


Silva, 2007, *Atmospheric Environment*

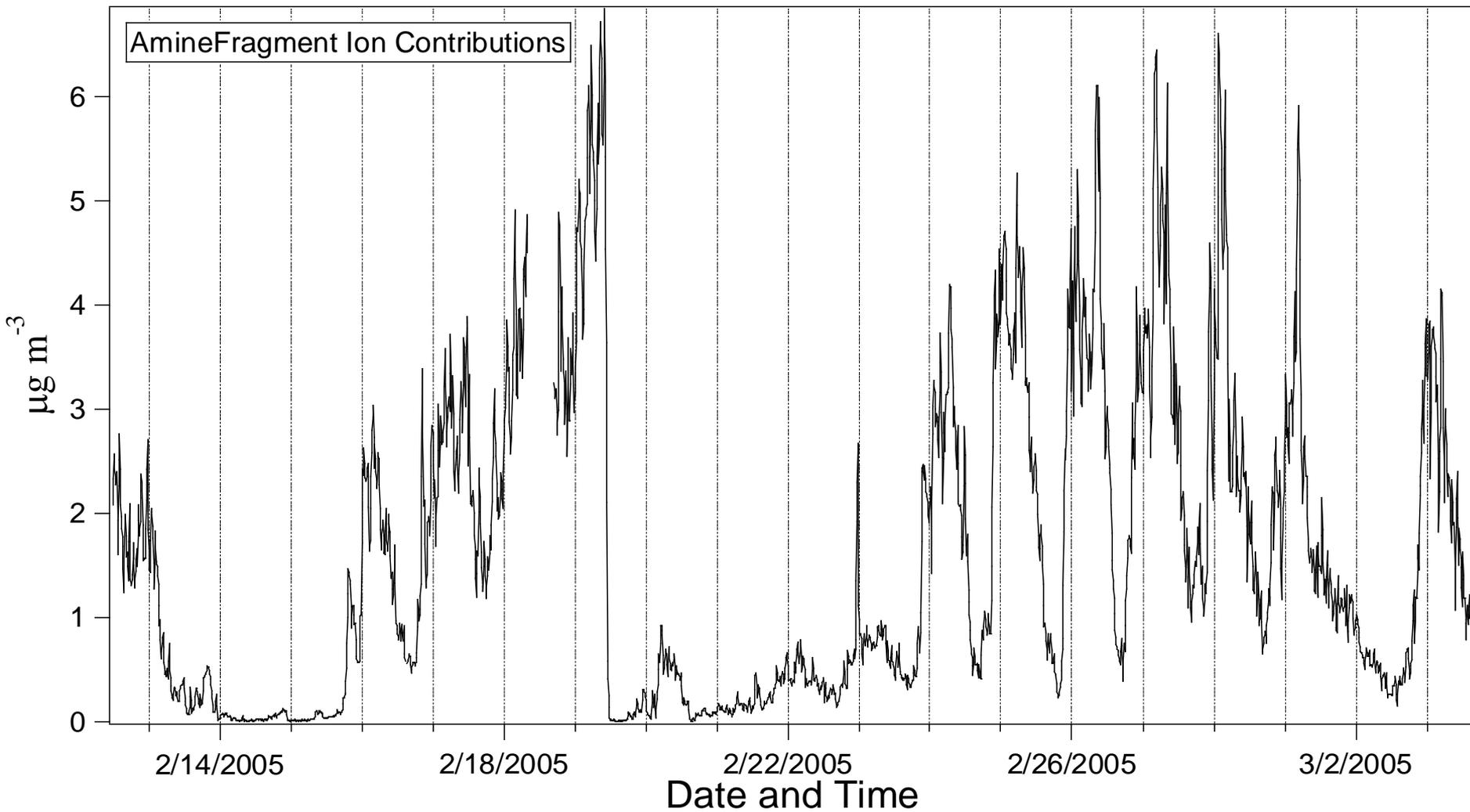
# Mass Spectrum of Particles (Logan)



# Comparison of Mass Spectra



# “Amine” Mass Concentrations 2005



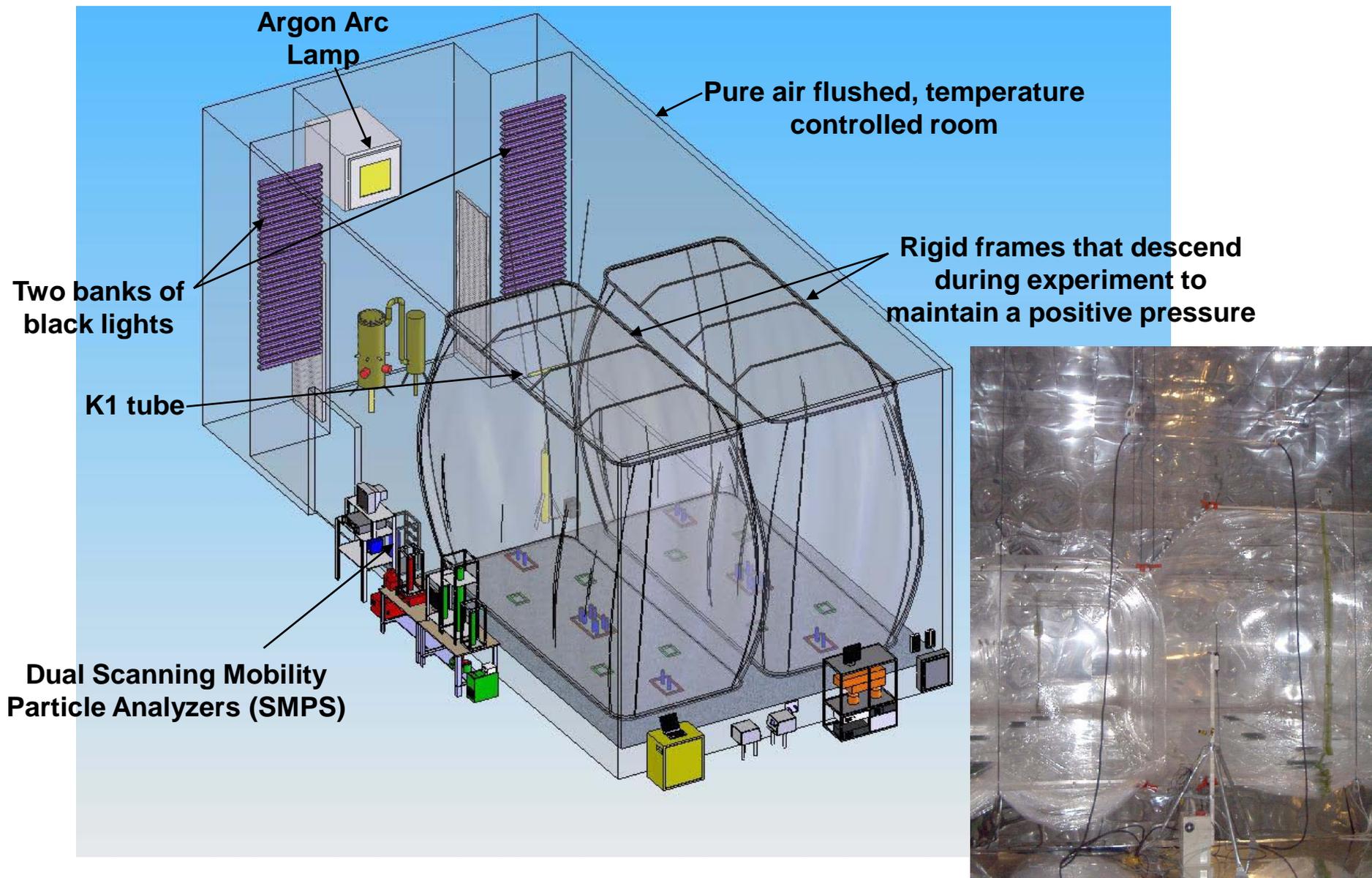
# Difficulties with Amines and the AMS

- Ionization Sensitivities
  - Amine salts yield high ionization efficiencies
    - Response factors vary from 5-10 relative to  $\text{NO}_3$
  - Oxidized amine compounds do not
    - Response factors  $\sim 1.4$
  - So, the mass concentration of “amines” depends on the state & chemical mechanism
- Fragmentation patterns
  - The molecule always breaks at C-C bond next to the nitrogen atom
    - Often no chain length information

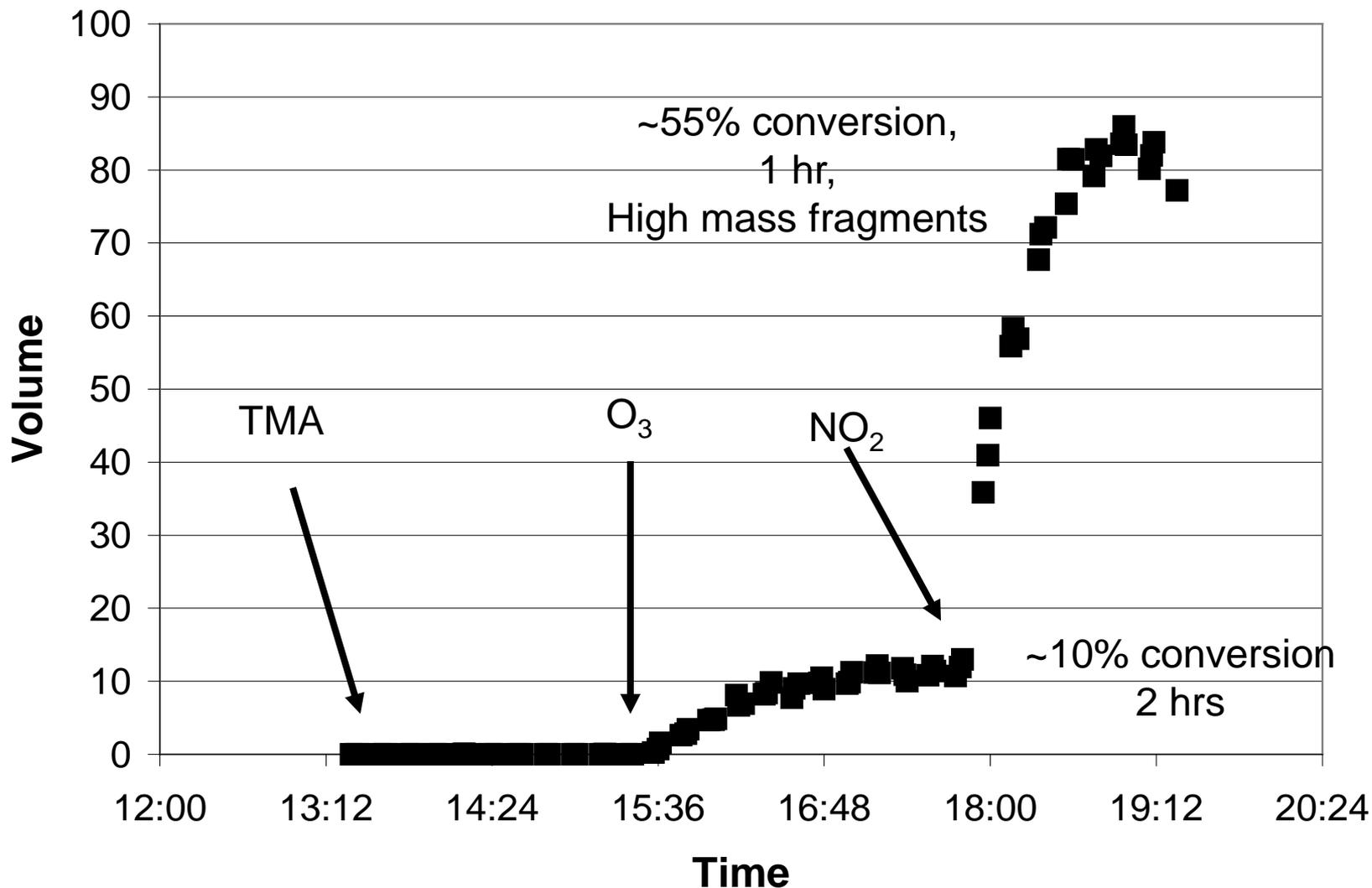
# UCR Chamber



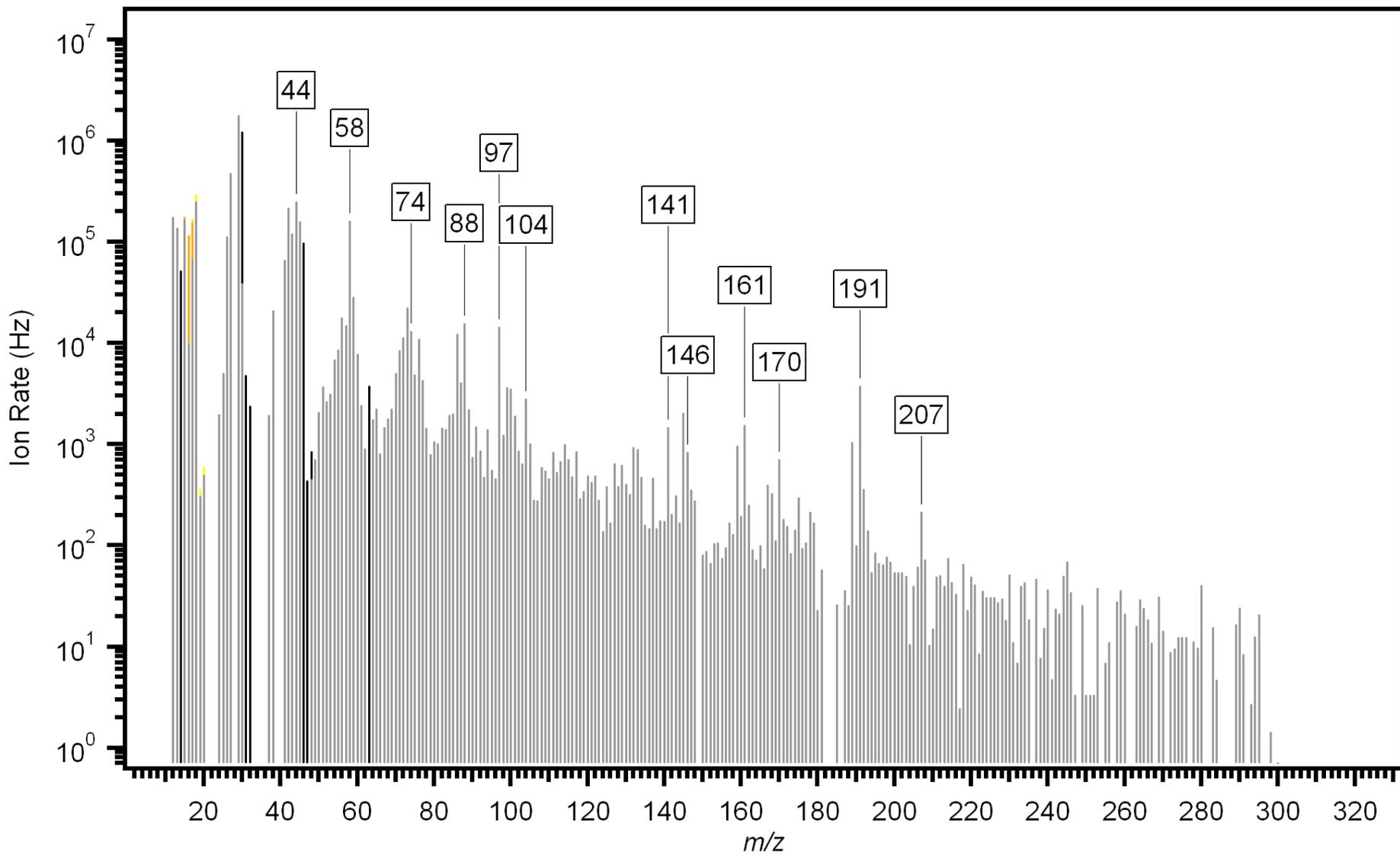
# Schematic of the Chamber



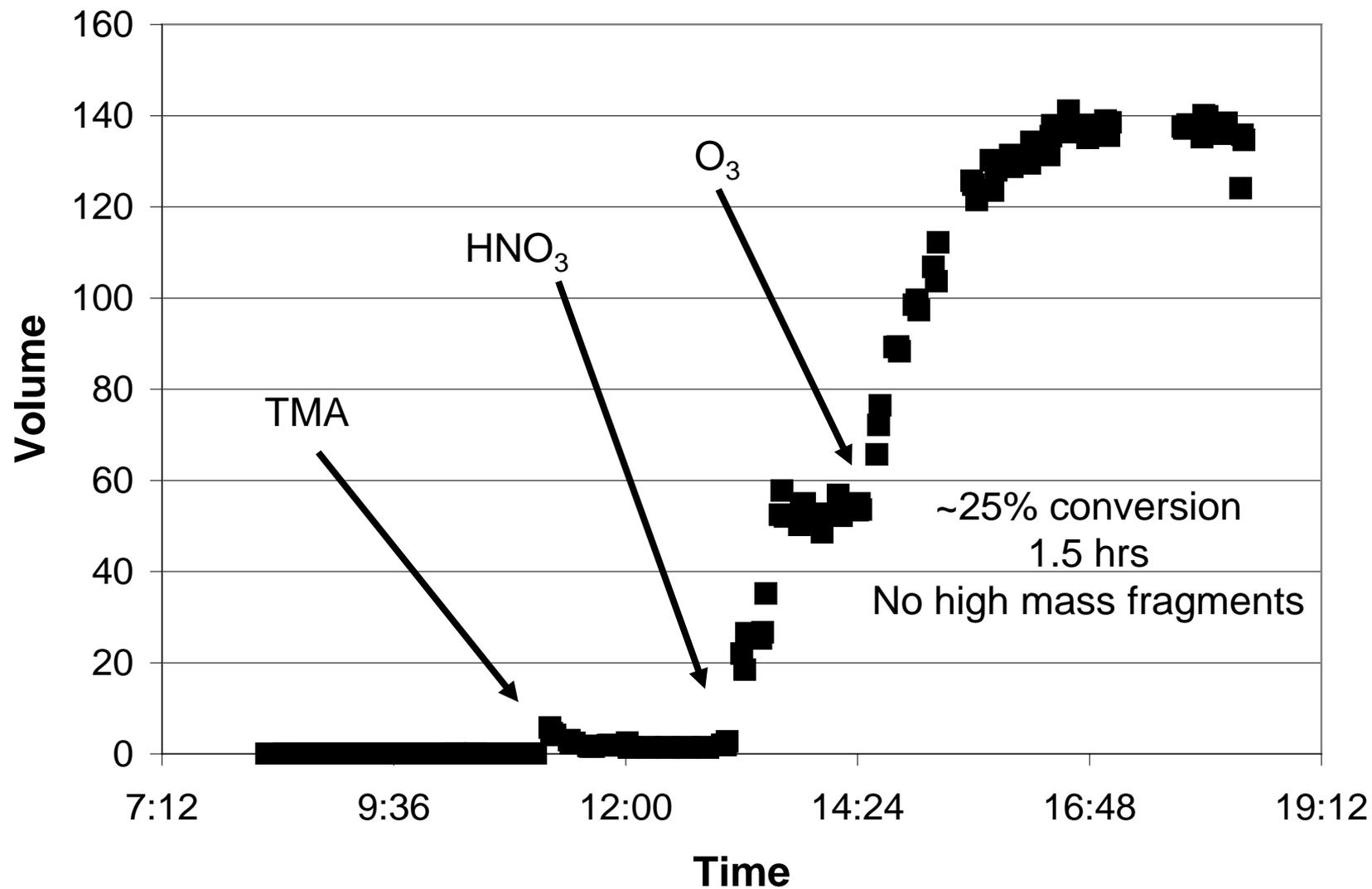
# Trimethylamine+O<sub>3</sub>+NO<sub>x</sub>



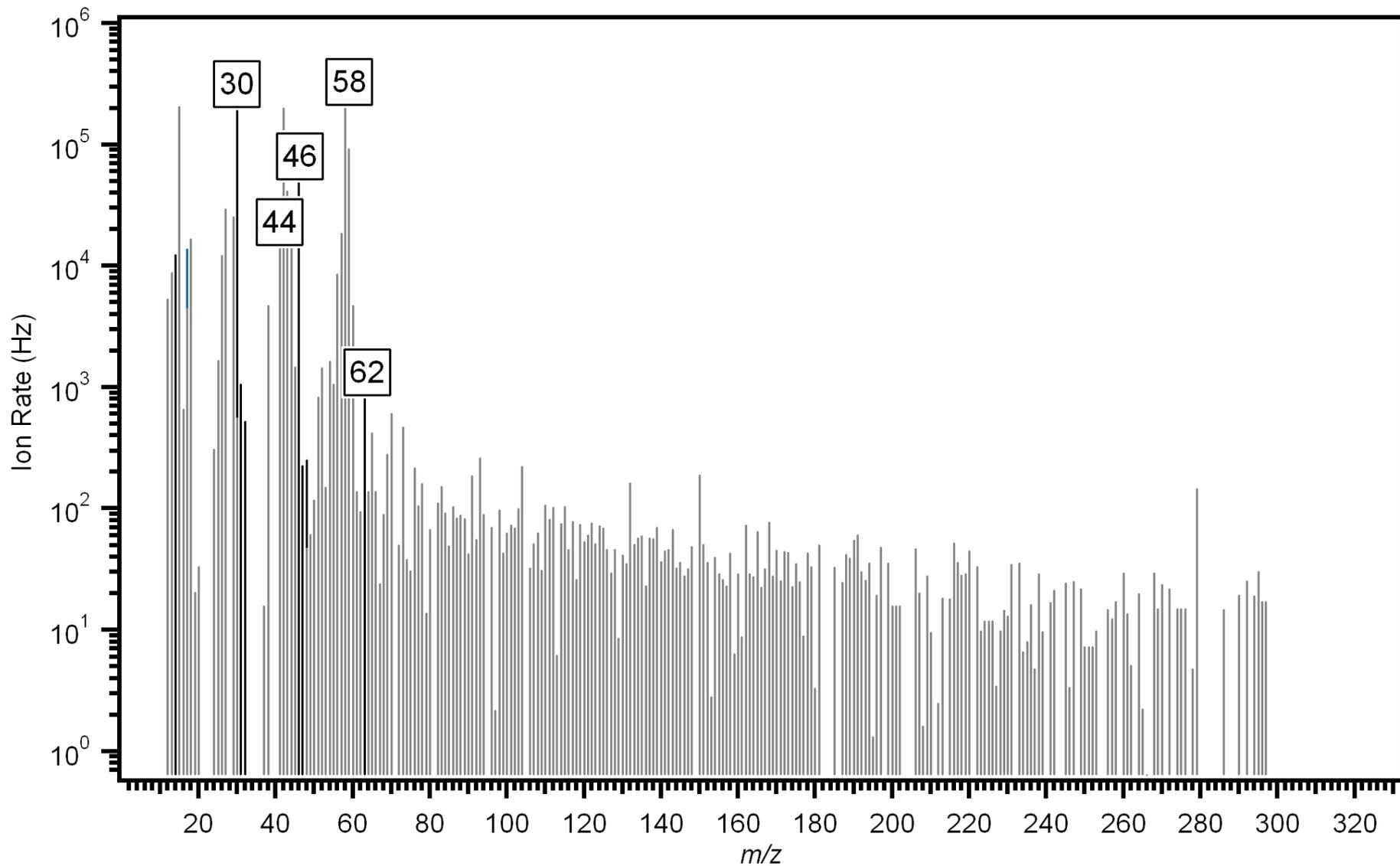
# TMA/O<sub>3</sub>/NO<sub>x</sub>



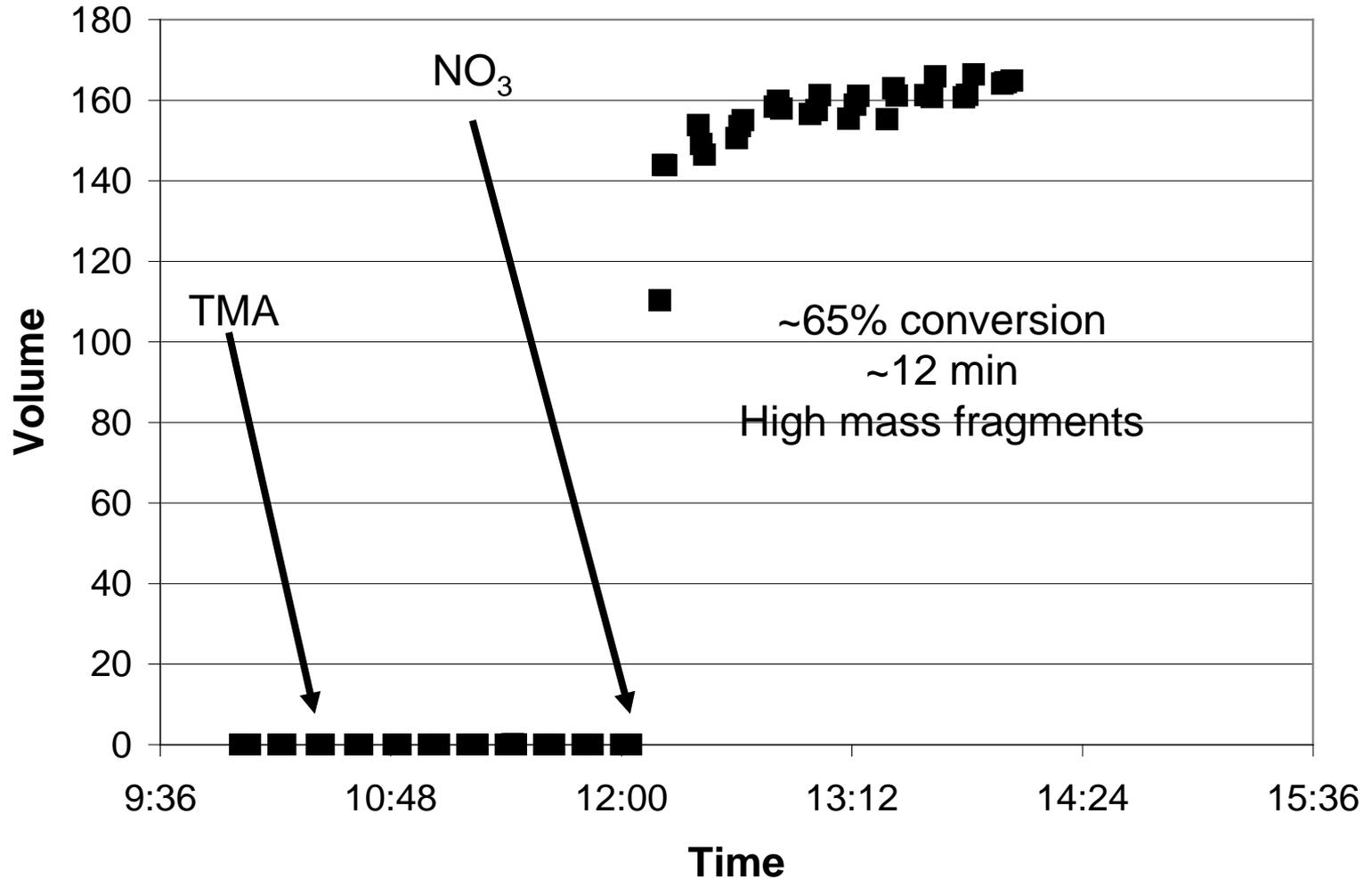
# Trimethylamine+HNO<sub>3</sub>



# TMA/HNO<sub>3</sub>

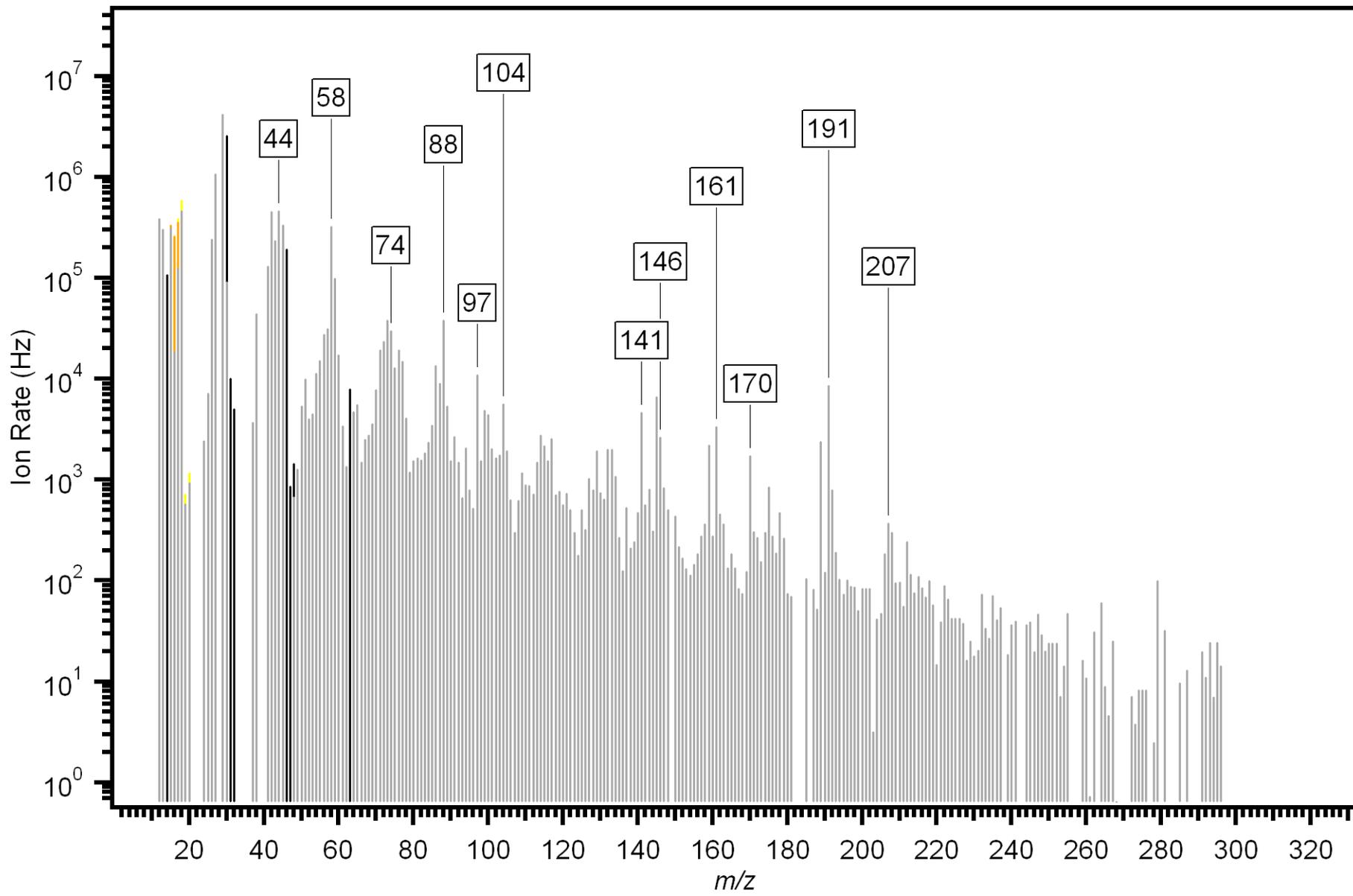


# Trimethylamine + $\cdot\text{NO}_3$

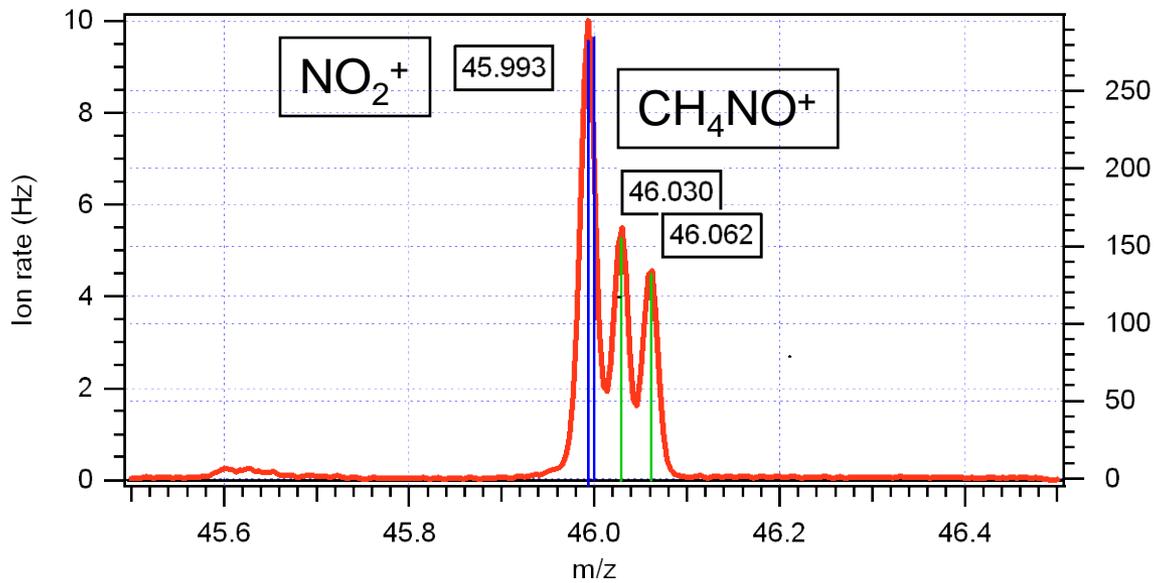
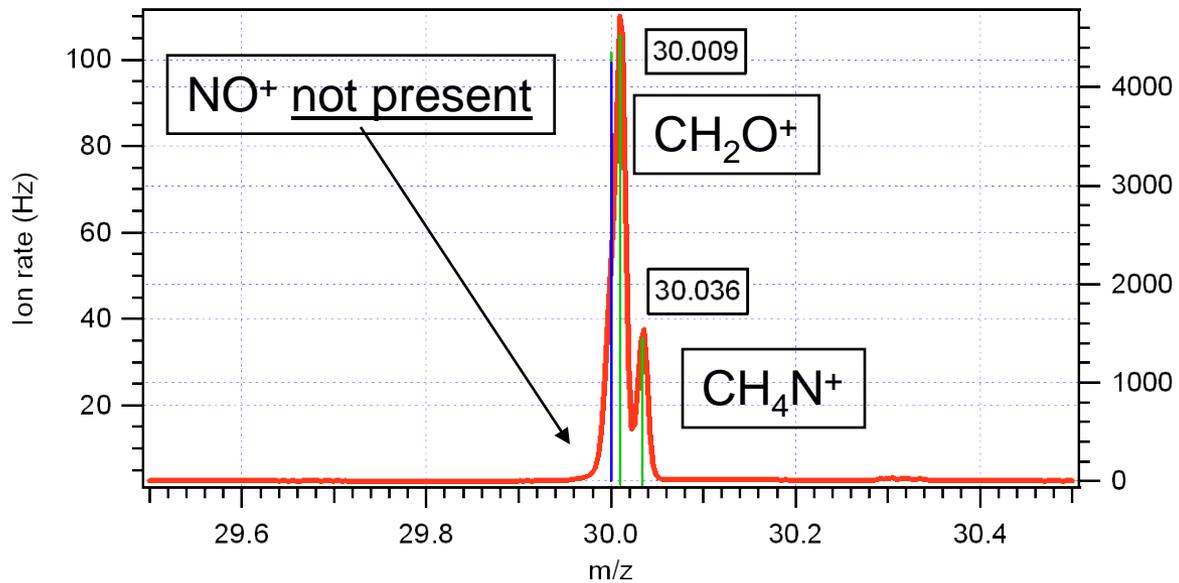


$\text{NO}_3$  chemistry with amines: VERY fast, produces significant condensed phase species

# TMA-NO<sub>3</sub>/NO<sub>2</sub>



# HR-ToF-AMS “Nitrate”





# Implications

- Even small amines form SOA readily
- Very rapid chemistry with  $\text{NO}_3$ 
  - Fast secondary aerosol formation
  - Appears to be mostly oxidation chemistry, not acid-base chemistry
- Reactions not accounted for in local or global models of atmospheric chemistry
  - Particle source
  - Nitrogen sink

# Funding and People

- \$\$\$

- State of Utah (Ambient Data)
- NSF (Smog Chamber Experiments)



Derek Price (USU '08)  
Mark Erupe (Current Grad)

Ambient:  
Eric Vawdrey (USU '06)

Amines:  
John Elias (Rice '09)  
Amanda Bingham (USU '09)

- David Cocker and group at UCR