Ambient measurements of amines and related nitrogen-containing compounds in a rural environment using protonated ethanol chemical ionization high-resolution mass spectrometry

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Methods

Measurement Technique(s): Chemical-Ionization High-Resolution Time-of-Flight Mass Spectrometry

Tofwerk/Aerodyne HR-ToF-CIMS

Instrument specifications

- *Tofwerk/Aerodyne high-resolution mass spectrometer*
- *Resolution: up to 5000*
- *Measurement frequency 1 Hz*
- *Mass-to-charge range: 0-1000*

Ionization technique: Protonated Ethanol

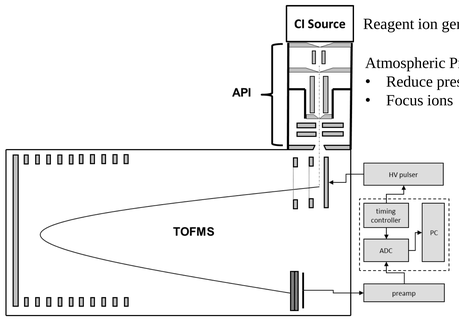
- ***Reagent ion production***

$n\ EtOH + H_2O \xrightarrow{^{210}Po} (EtOH)_nH^+,\ n=1\text{-}3$

- ***Analyte detection: clustering or proton transfer***

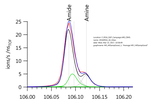
$(EtOH)_nH^+ + A \longrightarrow A(EtOH)H^+ \longrightarrow AH^+ \longrightarrow A(EtOH)_2H^+$

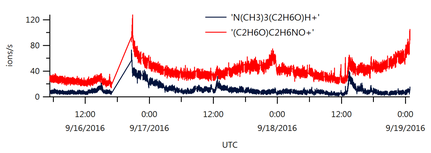
- ***Analytes***
  - *reduced nitrogen compounds*
  - *siloxanes*
  - *some organics*



Data Analysis: Tofware

- Precise mass-to-charge calibration
- Constrained peak fitting (predetermined peak width and shape)
- High-resolution data analysis separates isobaric compounds, e.g. amines and amides (acetamide at 106.0863 and C_3H_9N at 106.1226)

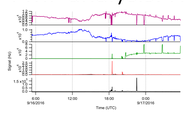


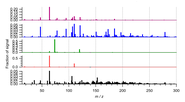


Time series shows different temporal behavior for isobaric compounds

Data Classification: Positive Matrix Factorization

PMF analysis: HISCALE, Oklahoma 2016-09-16, 5-factor solution





Preliminary results!

- Separate time series and spectra show potential for source apportionment and compound assignment

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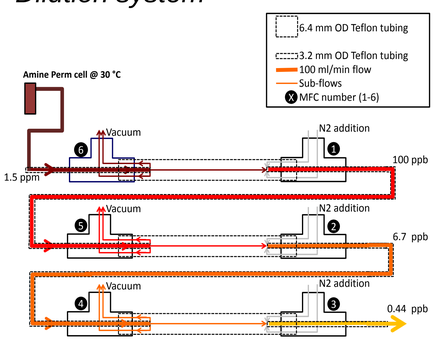
Take-home messages

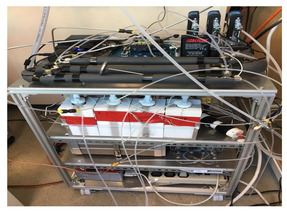
- Ethanol-CIMS detects ammonia, amines and many more reduced nitrogen compounds
- Time-of-flight mass spectrometry allows simultaneous detection
- High-resolution mass spectrometry allows specification and separation of individual compounds
- Laboratory and field calibrations give absolute concentrations
- Inlet design reduces residence times, but still needs improvement
- Sticky compounds difficult to measure
- Field measurements show temporal variation of most detected compounds before new particle formation events
- Strong changes in compounds not always correlated with new particle formation
- Frequent zeroing gives backgrounds and time-responses for individual compounds
- Statistical analysis (PMF) promises to specify sources and compound classes

Secure important "equipment" in Oooookla homa, where the wind comes sweepin' down the plain!

Laboratory Characterization

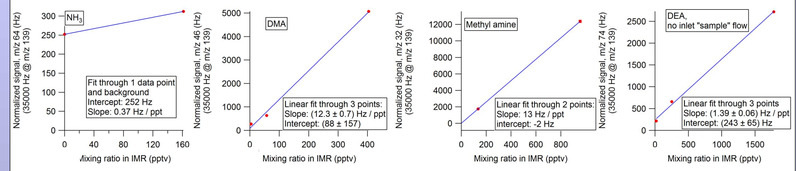
Dilution system





- No metal contact (fittings, flow controllers)
- Up to 1000 × dilution
- Calibration using CO_2 standard and optical detector
- 4 permeation tubes available
  - Ammonia
  - Methylamine
  - Dimethylamine
  - Diethylamine

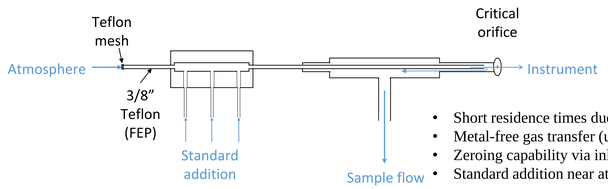
Calibrations



Compound	Sensitivity (Hz ppt^{-1})	Calibration factor (molec cm^{-3})
MA	13	6.52×10^{10}
MA, "sample"=0	16	5.29×10^{10}
DMA	12.3	6.89×10^{10}
NH_3	0.37	2.3×10^{12}
DEA	1.39	6.09×10^{11}

- Time-consuming calibrations due to long inlet residence times
- Only significant intercepts for ammonia and DEA, possible constant instrument, inlet, or dilution system background
- Less sensitive for ammonia
- Comparable sensitivity to bisulfate ion chemistry:
  - DMA: 26 Hz / ppt, 2.2×10^{10} molec cm^{-3}

Inlet design



- Short residence times due to large sample flow
- Metal-free gas transfer (up to instrument orifice)
- Zeroing capability via inlet overflow
- Standard addition near atmospheric input

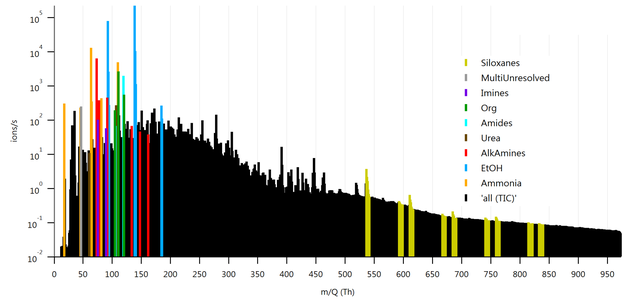
- 200 sec response times for sticky compounds
- Consider wall-less future inlet design using sheath flow design

Field Measurements

Campaign overview

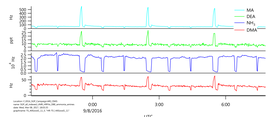
- August 25 – September 23, 2016
- Southern Great Plains ARM site, Oklahoma
- Rural environment
- Some influence from oil and gas extraction

Compound types present in mass spectra



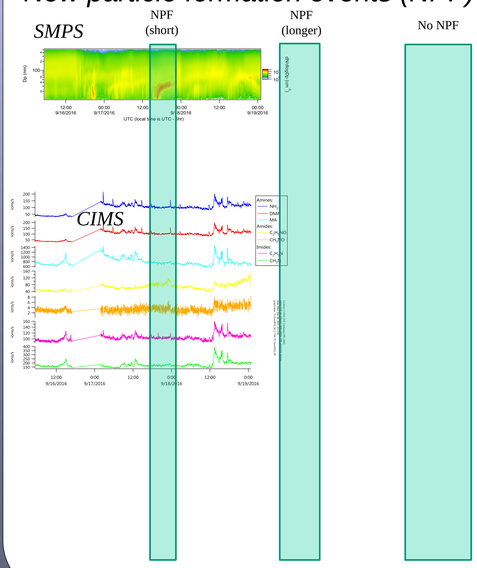
Calibrated amines

- Dilution system for ammonia, methyl amine (MA), dimethyl amine (DMA), diethyl amine (DEA)
- Frequent standard additions of around 500-1000 pptv
- Regular zeroing



- MA standard addition
- Slight increases for DEA and DMA during standard addition (impurities)
- Varying zero responses due to different residence times ("stickiness"):
  - NH3<MA<DMA<DEA

New particle formation events (NPF)



SMPS data courtesy of Chongai Kuang, Brookhaven National Laboratory

- Changes in most compounds slightly before events
- Strongest increase when no particles were formed:
  - gas phase compounds did not partition into particle phase