Detection of Novel Organic Nitrogen Compounds with Protonated Ethanol Cluster Chemical Ionization Mass Spectrometry

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Anthropogenic activities have radically altered the N cycle.

Adapted from Erisman et al, Curr. Opin. Environ. Sustain., 2011.
N cycle modifications have led to unintended consequences.

Organic N compounds account for a large fraction of dissolved Nr around the world.

Organic N measurement requirements:
- Sensitive
- Detection of multiple classes of compounds

Protonated Ethanol CIMS (EtOH-CIMS)

\[(C_2H_5OH)_nH^+ + B \rightarrow (C_2H_5OH)_yBH^+ + (n - y)C_2H_5OH\]

Ligand Switching
Proton Transfer
EtOH-CIMS provides sensitive measurement of organic N compounds.

Quad-MS for detection of amines and NH$_3$


<table>
<thead>
<tr>
<th>Compound</th>
<th>Sensitivity (Hz/ppt/MHz)</th>
<th>LOD (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl amine</td>
<td>4.0</td>
<td>25</td>
</tr>
<tr>
<td>Methyl amine</td>
<td>1.6</td>
<td>56</td>
</tr>
<tr>
<td>Diethyl amine</td>
<td>6.5</td>
<td>5.4</td>
</tr>
<tr>
<td>Pyridine</td>
<td>148</td>
<td>1.7</td>
</tr>
<tr>
<td>Imidazole</td>
<td>33</td>
<td>24</td>
</tr>
</tbody>
</table>

Ligand Switching
Proton Transfer
High resolving power MS is necessary for organic N measurement.

Also Yao et al., *Atmos. Chem. Phys.*, 2015.
Detection of multiple classes of compounds.

Ambient measurements
Boulder, CO
Application of EtOH CIMS

N, NO, NO$_2$, NO$_3$
C17-C29
DBE of 7+

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Are gas-phase organic nitrogen species formed?
Does the structure of the amine influence the observed products?
Ozonolysis of $\alpha$-pinene in the presence of NH$_3$, CH$_3$NH$_2$, (CH$_3$)$_2$NH, or (CH$_3$)$_3$N

Experimental Set-up

α-pinene 50 ppb
O₃ 100 ppb
Amine/NH₃ 5 ppb

Scanning Electrical Mobility Sizer
EtOH-CIMS
New particle formation is enhanced in the presence of bases.

Proton Affinity (kJ/mol)  
- None: 853.6
- Ammonia: 899
- MA: 929.5
- DMA: 948.9

Max Particle Concentration (#/cc)

Max Aerosol Volume (µm³/cc)
$\Sigma$ high intensity N ions is much larger for MA and DMA experiments.
Methyl amine + α-pinene
Dimethyl amine + α-pinene
Products of $\alpha$-pinene ozonolysis in the presence of amines

Dimethyl Amine

Methyl Amine

normalized ions/s

Elapsed Time (hr)

$C_{10}H_{17}NO_2H^+$

$C_{10}H_{17}NO_3H^+$

$C_{11}H_{19}NOH^+$

$C_{11}H_{19}NO_2H^+$

$C_{11}H_{19}NO_3H^+$

$C_{12}H_{21}NOH^+$

$C_{12}H_{21}NO_2H^+$

$C_{12}H_{21}NO_3H^+$
Proposed Pathways

Rapid oxidation of imines/enamines

Formation of stable amides
Products of $\alpha$-pinene ozonolysis in the presence of amines

Dimethyl Amine

Methyl Amine

![Graph showing the normalized ion counts over elapsed time for Dimethyl Amine and Methyl Amine with various molecules and their respective ion concentrations over time.](image)
Summary

• EtOH-CIMS
  • Sensitive
  • Measure multiple classes of organic N compounds

• Multiphase chemical reaction of amines results in the formation of gas-phase organic N
  • Imines/enamines
  • Amides