Air Monitoring Instrumentation
Nitrogen Oxides (NOy)

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What is NOy

- Total Reactive Nitrogen
  “Collective name for oxidized forms of *nitrogen* in the *atmosphere* such as *nitric oxide* (NO), *nitrogen dioxide* (NO$_2$), *nitric acid* (HNO$_3$), and *organic nitrates*; usually designated by NO$_y$,” - AMS

- Precursors in the formation of Ozone
- Definitions
  NOy = NOz + NOx
  NOx = NO + NO2
  NOz = HNO$_3$ + HONO + 2N$_2$O$_5$ + HO$_2$NO$_2$
    + PAN + NO$_3$ + Organic Nitrates – but **not** NH$_3$

- Some NOz compounds have short lifetimes
- NO$_2$ specific analyzer required to measure NOz
Technique

- Measurement using Nitric Oxide-Ozone Chemiluminescence analyzer
- Conversion of NOy species to NO
  - Molybdenum ~325°C
  - Gold with CO or H2 injection ~ 400°C
  - Vitreous Carbon ~ 350°C
  - Ferrous Sulfate
- Converter as near inlet as possible with no sample filter
- Requires trace level analyzer for useful measurement
- Minimizing residence time essential to good measurement
Simple Pneumatic Block Diagram

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## Analyzer Differences

<table>
<thead>
<tr>
<th>Specification or Characteristic</th>
<th>Standard NOx Analyzer</th>
<th>Premium NOx Analyzer</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDL</td>
<td>&lt;400 ppt</td>
<td>&lt;50 ppt</td>
<td></td>
</tr>
<tr>
<td>zero drift 24 hours</td>
<td>&lt;500 ppt</td>
<td>&lt;100 ppt</td>
<td></td>
</tr>
<tr>
<td>zero drift 7 days</td>
<td>&lt;1000 ppt</td>
<td>&lt;200 ppt</td>
<td></td>
</tr>
<tr>
<td>Propylene reject. Ratio</td>
<td>&gt;20,000:1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene reject. Ratio</td>
<td>&gt;40,000:1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMT Anode Sensitivity</td>
<td>2500 A/lm</td>
<td>3000 A/lm</td>
<td>More sensitivity, higher SNR</td>
</tr>
<tr>
<td>Reaction Cell</td>
<td>Non-plated</td>
<td>Gold Plated</td>
<td>Increased signal out</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>500 ccm</td>
<td>1000 ccm</td>
<td>Increased signal out</td>
</tr>
<tr>
<td>Nominal Cell Pressure</td>
<td>5&quot; HgA</td>
<td>2.5&quot; HgA</td>
<td>Increased sensitivity</td>
</tr>
<tr>
<td>Autoref scheme</td>
<td>Autozero stop sample flow</td>
<td>Autozero with prereactor</td>
<td>Improved hydrocarbon rejection</td>
</tr>
</tbody>
</table>
Inlet Materials
(or how can we keep “It” from sticking)

- “It” = gasses that readily stick to surfaces especially nitric acid and ammonia

- **Causes** memory effect leading to excessive rise and fall times:
  - Operation – over or under actual value, smear features
  - Calibration – Elevated zeros, reduced spans

- Exacerbated by long tubing, low temperatures
Inlet Materials

Standard: ¼” stainless tubing, adapters and fittings

Field Testing:
- SilcoSteel® (hydrogenated amorphous silicon) coated, stainless for inlet and other NOy wetted surfaces, including body and inlet tubing of converter
- PFA bulkhead, cross and tubing to within ½” of converter inlet; converter inlet and body SilcoSteel® coated
Calibration

- Gases: Nitric, iP, nP, NO₂, NO/GPT
  - No SRM
  - Nitric: very difficult to use
  - N-propyl nitrate: difficult to obtain & questionable analog for nitric
  - Iso-propyl nitrate: readily available
- Errors in verifying conversion efficiency using bottles
- Big cal gas flows required
- Can not run from common manifold
- Losses due to conditioning
- Must be VERY, VERY patient
Conditioning with 500 ppb NO$_2$
Checking Converter Efficiency

- Gas Phase Titration (GPT) golden standard
  - Auto-referencing - independent of NO or Ozone concentration
  - Independent of MFC calibrations and matching
- NO/NO$_2$, nPan or i-Pan bottles
  - Limited by accuracy of bottles
  - Limited by accuracy and linearity of MFCs
  - Best to maintain MFC flows use ratio of bottles
  - Check for contaminants in NO and other bottle
GPT vs. NO/NO2 gas Efficiency

<table>
<thead>
<tr>
<th>Method</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPT</td>
<td>99%</td>
</tr>
<tr>
<td>Gas Bottles</td>
<td>101%</td>
</tr>
</tbody>
</table>

**Efficiency with NO & NO2 Bottles**

<table>
<thead>
<tr>
<th>NO2</th>
<th>NO</th>
<th>Ratio</th>
<th>Converter Efficiency</th>
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</thead>
<tbody>
<tr>
<td>49.50</td>
<td>50.90</td>
<td>0.97</td>
<td>101%</td>
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</table>

**NOx NO Efficiency**

<table>
<thead>
<tr>
<th>NOx</th>
<th>NO</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>100.15</td>
<td>99.19</td>
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<tr>
<td>NO + O3</td>
<td>99.38</td>
<td>43.26</td>
</tr>
<tr>
<td>Delta</td>
<td>0.57</td>
<td>55.93</td>
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</tbody>
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iPan/nPan Efficiency

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Interferences

- Water: no effect at zero, ~ 3% quench at span
- \( \text{NH}_3 \): 1 – 5%
- Ammines ??
- Hydrocarbons

![Water Interference Data - Table 14](image)
Siting

- Be aware of nearby sources of:
  - Hydrocarbons – roofing materials
  - Ammonia – sewer vents
Pinnacle State Park NOy Comparison

Courtesy of Atmospheric Sciences Research Center
University at Albany - State University of NY

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- **Measurement of NO\textsubscript{y} During SCOS97-NARSTO**
  Dennis R. Fitz, University of California, Riverside, College of Engineering, Center for Environmental Research and Technology

- **Review of M200AU: NOY Converter Design Theory and Practice**
  Martin Buhr, Regional Air Quality Council, Denver, CO, 1997

- **AMS Glossary of Meteorology**
  American Meteorological Society
  [http://amsglossary.allenpress.com/glossary/acknowledge](http://amsglossary.allenpress.com/glossary/acknowledge)