NOy Monitoring –
Moving Forward

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Objectives

- Review NOy monitoring network
- Review chronology of EPA guidance on NOy monitoring
- Discuss “current” guidance on operations and recommended QA/QC
- Future of NOy monitoring
- NOy operational issues discussion
EPA Guidance Chronology

• First EPA guidance on NOy monitoring was part of the “TAD for Sampling and Analysis of Ozone Precursors” issued September 1998 (http://www.epa.gov/ttn/amtic/pams.html)

  – NOy was ‘strongly encouraged’ as part of an enhanced ozone monitoring program (~PAMS) and data was to be used to evaluate and improve photochemical models

  – Detailed instructions on converting a NOx box to an NOy box, where changes in the location of the converter, particulate filter(s), flow control capillary, and the 3-way solenoid valve make the difference

  – All QA checks including converter efficiency were using NO$_2$; converter efficiency check suggested to be >96%

  – NPN and nitric acid are mentioned as challenge agents, but not elaborated upon
EPA Guidance Chronology

- NCore TAD Recommendations
  - External converter to be at 10 meters (primarily to reduce potential for HNO$_3$ loss)
  - Inlet to be made of PFA Teflon
  - Inlet to use part of a Teflon filter holder as a bug screen
  - Only a heated Molybdenum converter be used (versus Au) at 350°C
  - Use opaque lines and reduce residence times
EPA Guidance Chronology

- NCore TAD Recommendations (continued)
  - Quarterly multipoint NO calibrations (zero, 3 span levels)
  - Quarterly multipoint NO₂ calibrations (zero, 3 span levels, close to those used for NO)
  - Two week precision checks; with NO, target 20 ppb
  - Daily (Level 1) zero/span check; span gas unspecified, but target level to be 70 to 90 percent of scale
  - Detailed MDL determination procedures

- Monthly single-point converter efficiency tests --- TAD has two targets listed in different places: 95% and 96%
  - Converter efficiency test language suggests using NPN
EPA Guidance Chronology

- In the 2006 ‘Monitoring Rule’, NCore sites were required, which included requirements for NOy.

- NOy guidance resurfaced in 2007 as part of EPA – OAQPS’ Precursor Gas Training workshops (http://www.epa.gov/ttnamti1/precurtr.html)
  - Reiterates external converter at 10 meters
  - Initial Calibration and zero/span recommended using NO and NO₂
  - Converter efficiency checks recommended to use NPN or IPN (targeting 96% efficiency)
  - Recognized loss of NO₃ species within different inlet materials (SS, Teflon, silicon steel) – Teflon still preferred
EPA Guidance Chronology

• EPA issued an AQS Technical Note
  (http://www.epa.gov/ttn/amtic/files/NAAQSReportingUpdate11032010.pdf)

• Noted creation of new parameter code for use with NOy instruments: NOy – NO
  – NOy – NO has the parameter code 42612
  – Some submissions erroneously were labeling such data as NO$_2$
  – Document also listed method codes
EPA Guidance Chronology

• EPA gives advice on NOy operations issues and QA reporting in the December 2011 “QA Eye” - Issue 12 (http://www.epa.gov/ttn/amtic/qanews.html)

• For NO data from an NOy analyzer:
  – Daily zero/span (Level 1 check)
  – 1 – point QC check (a.k.a precision check) for NO, at least every two weeks (higher frequency suggested)

• For NOy:
  – 1 – point QC check (a.k.a precision check) every two weeks, using NPN or IPN (do not report NO 1 – point check data for these data)
  – Converter efficiency check: TAD suggested monthly check; however, MQO tables suggested every two weeks
  – Since we have a biweekly 1 – point QC check with NPN or IPN, converter efficiency check still recommended to be monthly
Summary & Discussion of Current NOy Guidance

• Instrument Set-up & Operation

  – Use PFA Teflon materials, opaque lines, and strive to reduce residence times

  – Molybdenum converter at 350° C

  – Inlet at 10 meters; use Teflon bug screen
### Summary & Discussion of Quality Control Procedures

<table>
<thead>
<tr>
<th>Data Channel</th>
<th>QC Function</th>
<th>Challenge Gas</th>
<th>Suggested Gas Level</th>
<th>Minimum Frequency</th>
<th>Is it Needed?</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>Zero/Span</td>
<td>NO</td>
<td>0 &amp; 70-90% of scale</td>
<td>Daily</td>
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<tr>
<td>NO</td>
<td>1-pt QC check (precision)</td>
<td>NO</td>
<td>~20 ppb</td>
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<tr>
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<td>1-pt QC check (precision)</td>
<td>NPN or IPN</td>
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<td>Biweekly</td>
<td>Yes</td>
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<tr>
<td>NOy</td>
<td>Converter Efficiency</td>
<td>NPN or IPN</td>
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<td>Monthly</td>
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<tr>
<td>NO</td>
<td>Multipoint Calibration</td>
<td>NO</td>
<td>Zero, 3 levels</td>
<td>Quarterly</td>
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<td>NPN or IPN or NO₂</td>
<td>Zero, 3 levels</td>
<td>Quarterly</td>
<td>?</td>
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<tr>
<td>NOy</td>
<td>MDL determination</td>
<td>NPN or IPN?</td>
<td>Annually?</td>
<td>?</td>
<td></td>
</tr>
</tbody>
</table>
NOy in the Secondary NOx/SOx Field Pilot


- One of the objectives of the pilot is to “Evaluate measurement methods for the ambient air indicators of NOy and SOX and consider designation of such methods as Federal Reference Methods (FRMs)”

- The EPA anticipates using CASTNET sites (possibly select NCore too) as a primary element in the pilot, supplementing the existing filter-pack samplers with NOy analyzers among other evaluative/complimentary methods
NOy as an FRM

- EPA is pursuing the potential designation of NOy analyzers as FRMs, pursuant to commitments made in the recent Secondary NOx/SOx NAAQS rulemaking.
- February 2011, EPA submitted evaluation plans to CASAC AMMS for NOy and other methods.
  - CASAC AMMS responded supportively.
- EPA – ORD is currently evaluating the commercially available NOy analyzers.

**Approach**

- Upon completion of the evaluation and compilation of the generated data and information on the NOy measurement method, ORD will be able to describe the accuracy, precision, and reliability of the NOy instruments and their applicability as FRM.
- ORD will provide a technical summary of the data and supporting information and develop the basis/rationale for adopting it as an FRM.
- ORD will prepare docket materials, proposal preambles, response to comments, and the FRM in regulatory text format.
NOy Operational Issues

- Think you’re seeing interferences?
- Low confidence in your data?
- Too much ‘down time’?
- Problems with calibrations/drift?

Let’s talk about it…