



Update on the Office of Research and Development's Monitoring and Methods Research Priorities

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Denver, CO**

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Ambient Measurement Methods Research in ORD's Air Climate and Energy (ACE) Research Program

- Renewed Focus on Ambient Methods Development
 - Increase in resources (despite reductions in most activities) - ~\$500K/FY
 - Clear on what we are going to deliver (and what we are not going to deliver)
- Methods to Inform Policy
 - ACE Task 176 – NAAQS Methods: Federal Reference Methods (FRMs) and Federal Equivalent Methods (FEMs)
 - FRM : Ozone, Lead, NO₂
 - Reference and Equivalent Methods Program: applications review
- Other Methods Research in ACE
 - ACE Task 135 – Innovative techniques for quantifying acrolein and other air toxics
 - ACE Task 245 – Use of satellite and aircraft remote sensing observations to diagnose aerosol and trace gas gradients and concentrations associated with National Ambient Air Quality Standards
 - ACE Task 071 – Development of low-cost, real-time sensors for fence line monitoring and community exposure assessment



Federal Reference Methods (FRMs) and Federal Equivalent Methods (FEMs)

Federal Reference Methods (FRM)

- A **FRM** is a method, sampler or analyzer that utilizes the measurement principles and calibration procedures specified in 40 CFR Part 50
- A candidate method (**CM**) must be shown to satisfy all applicable requirements of Part 53, Subparts **A** (documentation) and **B** (performance testing).

Federal Equivalent Methods (FEM)

- A **FEM** is an ambient air monitoring method that has been tested under 40 CFR Part 53 and designated by EPA as an FEM under Part 53.
- A **CM** must be shown to satisfy all applicable requirements of Part 53, Subparts **A** (documentation), **B** (performance testing), and **C** (testing for comparability to the FRM).

EPA AIRS Sampling Sites



Bendix 8002 Ozone
(future)

T265 Ozone

T700U Calibrator

200EUP
Photolytic NO₂

NO₂ FRM

Zero Air Generator

Not Shown

- 2B 202 & 205 Ozone
- CRDS & CAPS NO₂

Ambient air Innovative Research Site (AIRS)

- Site located on EPA RTP, NC campus
- Instruments calibrated according to operation manuals in accordance with FRM/FEM requirements
- Nightly, automated zero and span checks
- Glass inlet with sampling height @ 5 m above ground level and common sampling manifold



Update on Ozone Federal Reference and Equivalent Methods Research Activities

Research Managed by Dr. Russell Long
U.S. EPA, Office of Research and Development
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Ozone FRM/FEM

Federal Reference Method for Ozone

- An O₃ FRM (Federal Reference Method) is an *analyzer* that utilizes the measurement principle and calibration procedure specified in Part 50, Appendix D
 - Ethylene Chemiluminescence

Discussion

- Technical performance of existing FRM has proven to be very sound, no other ambient ozone measurement technique has emerged as clearly superior.
- FRM is currently unavailable commercially, instrument maintenance becoming increasingly difficult due to unavailability of components

Federal Equivalent Methods for Ozone

- An O₃ FEM (Federal Equivalent Method) is an ambient air monitoring method (usually an *analyzer*) that has been tested under 40 CFR Part 53 and designated by EPA as an FEM under Part 53.

Discussion

- UV Photometric – most widely used FEM for O₃
- FEMs based on other measurement methods also available

What Do You Do with an Old FRM?

FRM Analyzer Resurrection

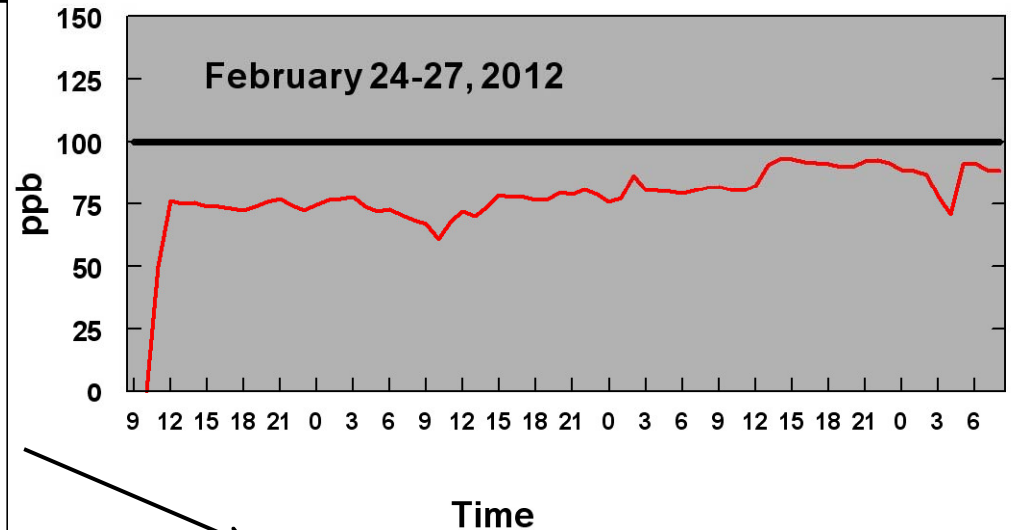
- 3 Bendix 8002 FRMs – all non-operational
- OK electronically
- Replaced PMTs – no longer available commercially from manufacturer
- Appeared to successfully zero and span instrument

- Source of noise and low span reading not yet identified

Result

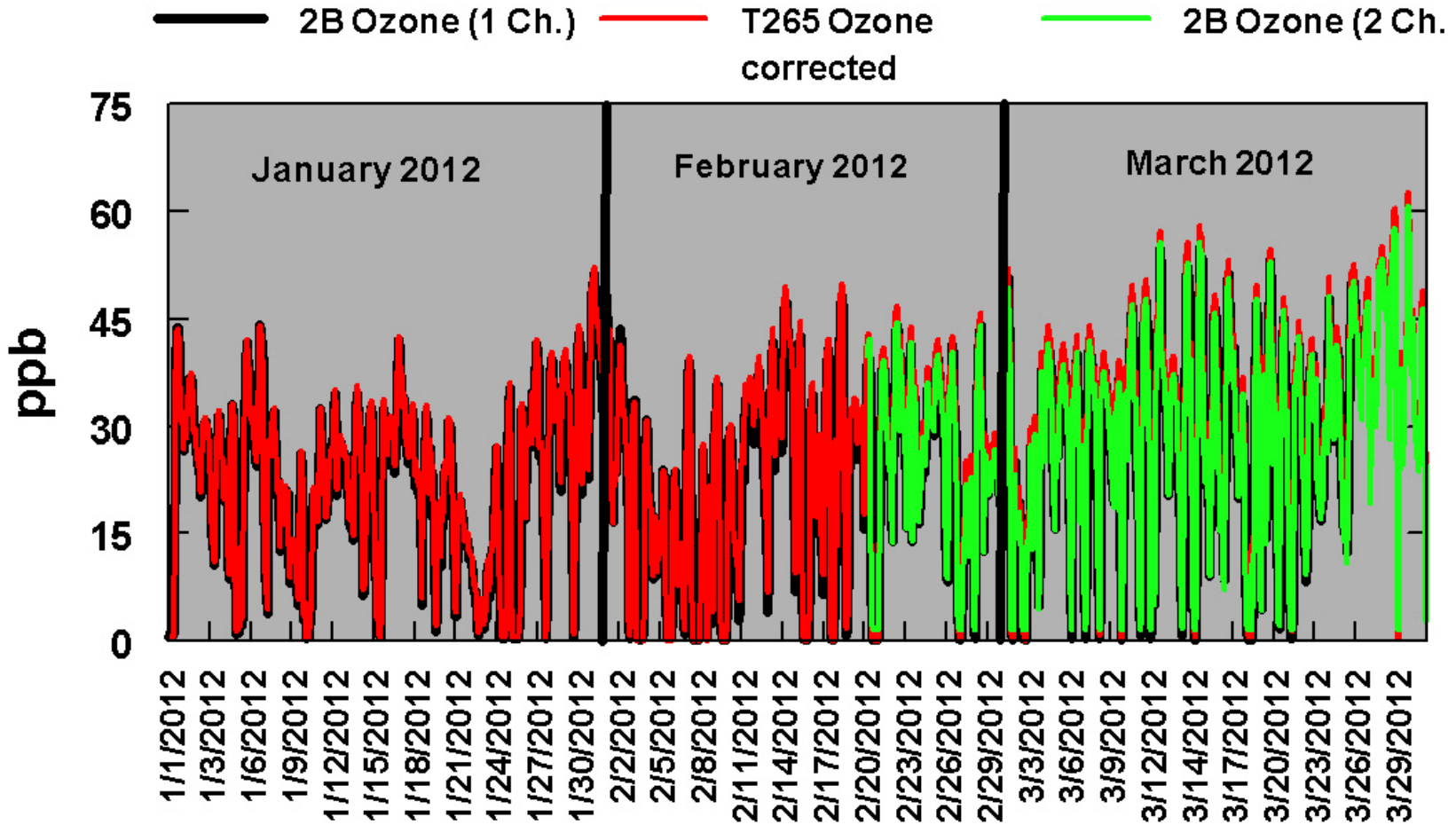
- 3 Bendix 8002 FRMs – all non-operational

— Bendix 8002 Ozone — Reference Ozone



- Instrument supplied with 100 ppb ozone over 3 day period
- Analyzer did not reach span value
- Significant noise observed
- Calibrator/ozone generator eliminated as source of noise

O₃ Results from EPA AIRS Site



Wintertime 1-hr ozone FEM results from the EPA AIRS sampling site



Ozone Research Initiatives and Next Steps

- Obtain a working ozone FRM analyzer
- Continued collocated ambient monitoring with FRMs and FEMs
 - EPA AIRS site – ongoing
 - Houston, TX (Summer 2013) – NASA DISCOVER-AQ Study
- Laboratory based method evaluations
 - 40 CFR Part 53 performance testing for FRM and FEMs
 - Detailed interference testing
- Develop and document performance criteria including calibration and challenge procedures
- FRMs and FEMs use as reference analyzer for sensor/apps assessment



Update on Lead Federal Reference Method Research Activities

**Research Managed by Dr. Robert Vanderpool
U.S. EPA, Office of Research and Development
National Exposure Research Laboratory**

**Presented during Criteria Pollutant Methods Issues & Updates Session
Date/Time: Wednesday May 16, 2012, 3:30 PM
Room Colorado F**



Summary of Pb NAAQS: Sampling and Analytical Techniques

The two different sampling FRMs (Pb-TSP and Pb-PM₁₀) have correspondingly different analytical FRMs associated with them

Hi-Vol TSP Sampling (~ 50 cfm)

- Sampling at source-oriented sites
- Analytical FRM involves extraction of Pb on 8" x 10" glass fiber filters using acid extraction followed by flame AA analysis

PM₁₀ Sampling (16.7 Lpm)

- Sampling at non-source-oriented sites and at selected source-oriented sites where ultra-coarse emissions are expected to be minimal
- Analytical FRM involves XRF analysis of Pb on 46.2 mm diameter teflon filters

Source-oriented sites tend to produce high concentrations of large Pb-bearing particles



Design Features for a New Pb FRM Sampler

- New FRM designed to replace both the hi-vol and PM10 sampler with a single sampler and a single analytical method
- Fixed inlet dimensions, fixed flow rate, and omnidirectional inlet
- Acceptable variation in size selective performance as a function of ambient wind speeds (2 to 24 km/hr)
- Cutpoint in the 18 to 20 μm size range would quantify all Pb-bearing particles currently measured by the Pb-PM₁₀ FRM while accounting for a portion of Pb-bearing particles above 10 μm



Proposed New Analytical FRM for Pb in TSP – ICP-MS

- Designed to meet lower detection limit requirements of new Pb NAAQS
- Based on two recently designated FEMs (EQL-0510-191 and EQL-0710-192)
- Extraction options: Heated ultrasonic with HCl/HNO₃ or hot block with HNO₃
- Applicable to glass fiber, quartz, and teflon filters
- Interlaboratory results from RTI, ERG, ORIA, and ORD are favorable for precision and comparability

Lead Research Initiatives and Next Steps

- Develop generation and measurement techniques for wind tunnel calibration aerosols (ongoing)
- Optimization of EPA's aerosol wind tunnel for upcoming size selective tests (ongoing)
- Develop, wind tunnel evaluate, and finalize design of a new candidate inlet for the Pb FRM
- Conduct any necessary field evaluation of the proposed Pb FRM



Update on NO₂ Federal Reference and Equivalent Methods and “True” NO₂ Methods Research Activities

Research Managed by Dr. Melinda Beaver
U.S. EPA, Office of Research and Development
National Exposure Research Laboratory

Presented during Criteria Pollutant Methods Issues & Updates Session
Date/Time: Wednesday May 16, 2012, 3:30 PM
Room Colorado F

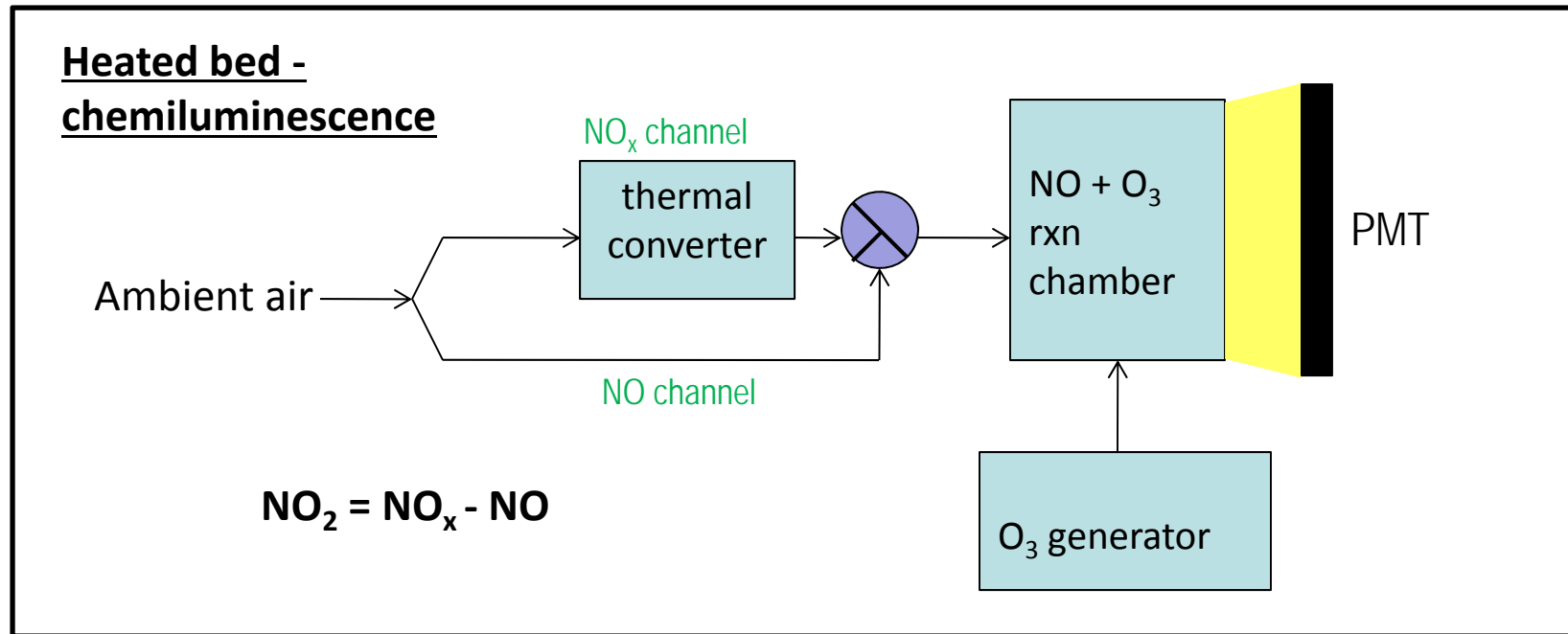
Current NO₂ Regulations

NO ₂ Primary Standards		
<i>level</i>	<i>averaging time</i>	<i>Year Finalized</i>
53 ppb	Annual mean	1971
100 ppb*	1 hr	2010

*** The monitoring locations for the new primary standard will be sited near roadways to capture areas of maximum concentration.**

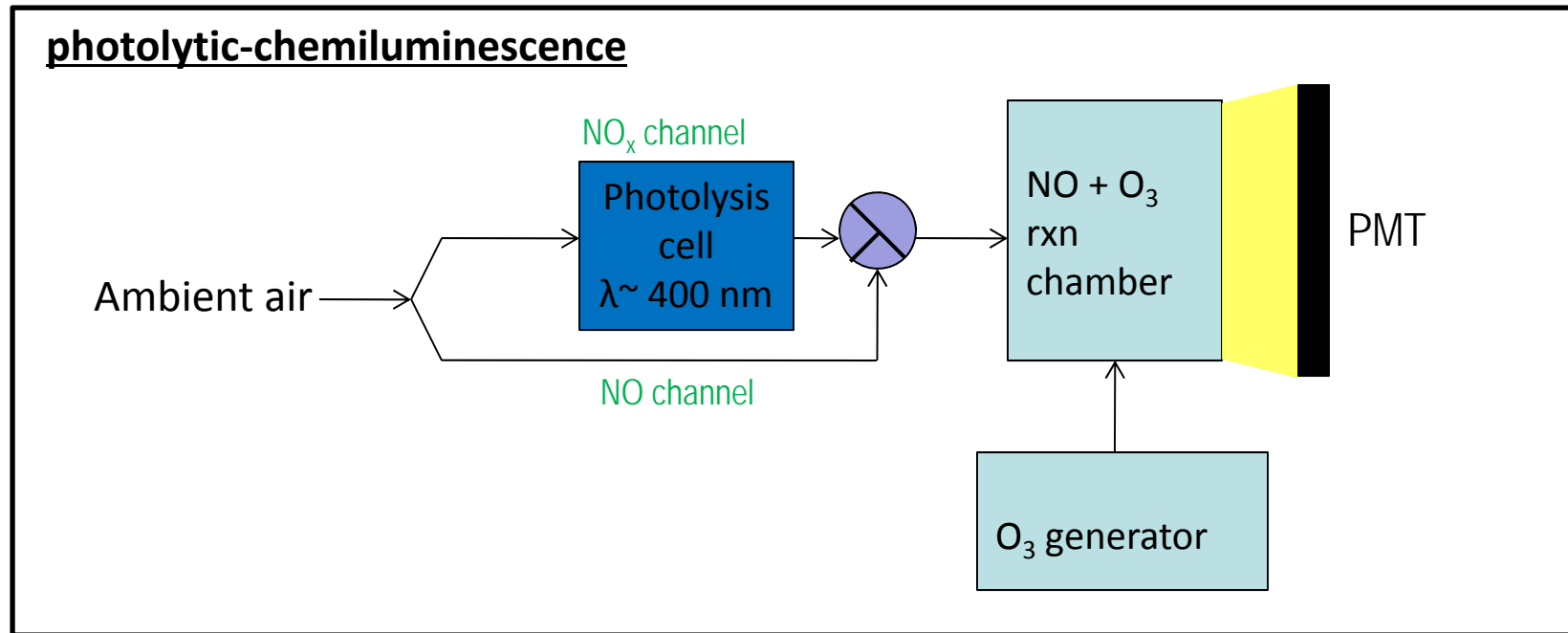
- Continuous monitors capable of hourly data are now necessary.**

NO₂ FRM



- Automated Federal Reference Method
 - Gas-phase chemiluminescence
 - Indirectly measure NO₂ by conversion to NO, then NO is detected by chemiluminescence (NO + O₃ → NO₂*)
 - Converter also capable of reducing other NO_y species to NO resulting in a positive artifact, NO₂ determination is considered an upper limit
 - Teledyne-API T200U, Thermo 42C

Photolytic-chemiluminescence



- Replace the molybdenum converter with a photolysis cell to photolyze NO_2 to NO ($\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$)
 - Use high-power light sources to maximize conversion to NO
- Advantage \rightarrow more specific to NO_2
- Disadvantages \rightarrow low, and variable (but stable) conversion efficiency; still indirect
- Teledyne-API 200EUP, T200UP, FEM designation imminent

Direct Optical Techniques

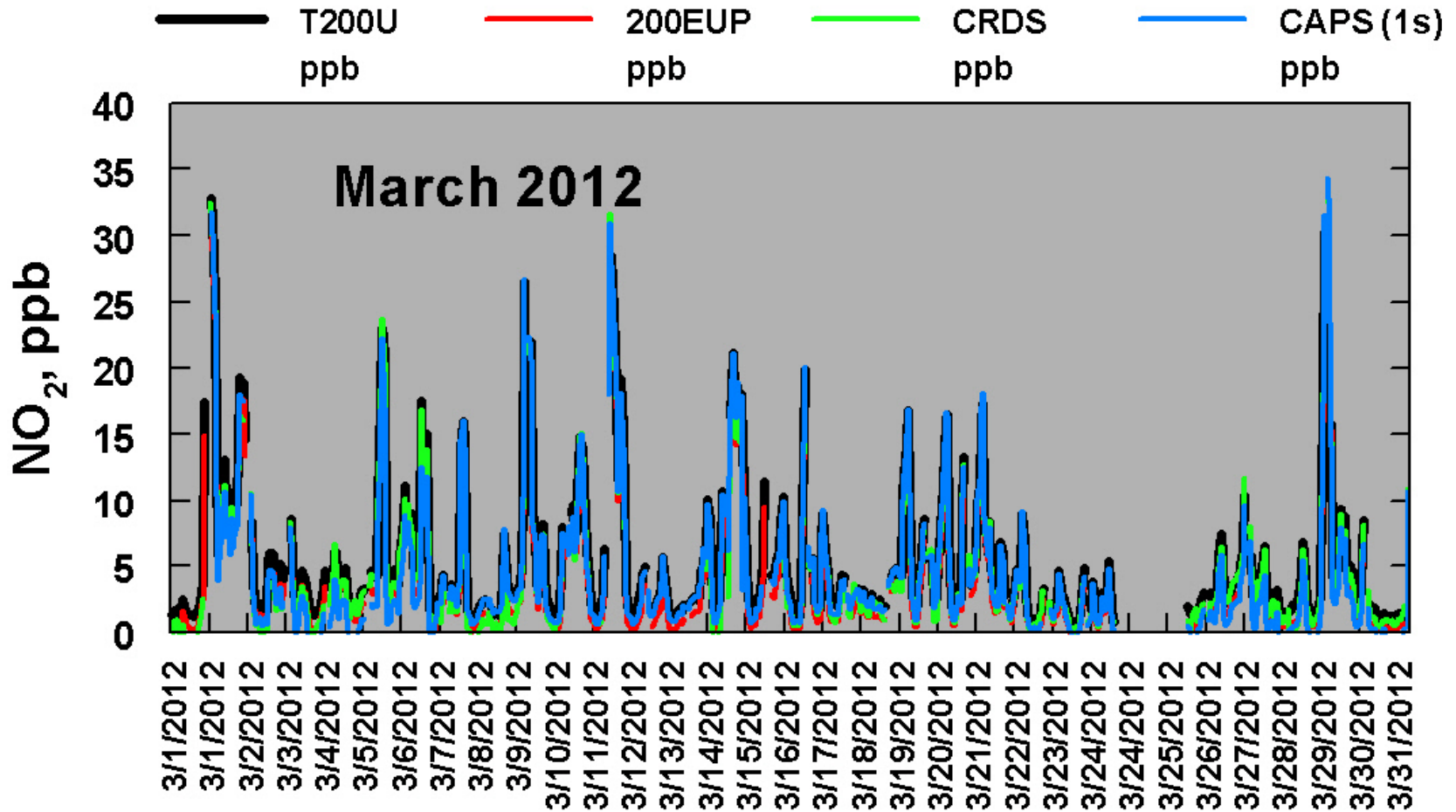
Cavity Ringdown Spectroscopy (CRDS)

- Instrument manufactured by Los Gatos Research, Inc.
- 10 s time resolution
- Advantage → DIRECT measurement
- Disadvantages → not-necessarily specific to NO₂, but to any molecule that absorbs light at 407 nm

Cavity Attenuated Phase Shift spectroscopy (CAPS)

- Instrument manufactured by Aerodyne Research, Inc.
- 2 versions: fast response (1 s) and ambient (10 s)
- Advantage → DIRECT measurement
- Disadvantage → not-necessarily specific to NO₂, but to any molecule that absorbs light at ~450 nm

Results from EPA's AIRS site, NC



Wintertime FRM, photolytic, and direct measurement method 1-hr NO_2 results



NO₂ Research Initiatives and Next Steps

- Ambient method inter-comparison through the summer
- Develop and document calibration and challenge procedures for direct measurement techniques
 - NO₂ cylinder vs GPT
- Detailed laboratory based assessments
 - Interference testing
 - 40 CFR part 53 subpart B performance testing
- Evaluate optical monitors in a near-roadway environment
- New NO₂ methods as reference analyzer for sensor/apps assessment



FRM/FEM Applications Review

- The most recent (Oct. 12, 2011) list of designated Reference and Equivalent Methods can be found at the AMTIC site:

<http://www.epa.gov/ttn/amtic/files/ambient/criteria/reference-equivalent-methods-list.pdf>

- 5 new designations were made during the past year
 - Class III PM_{2.5} (1) - Grimm Model 180 PM_{2.5} monitor
 - PM₁₀ (2) - Thermo 2000-D PM₁₀ sampler and Thermo 2025-D PM₁₀ sampler,
 - Lead (1) - US EPA/OAQPS TSP Pb by ICP-AES
 - Ozone (1) - Teledyne API Model T265 ozone analyzer
- 27 modification requests to existing designations were reviewed and approved in the past year.
- 11 new applications are currently undergoing review (2 for Class III PM_{2.5}, 2 for Class III PM_{10-2.5}, 2 for PM₁₀, 2 for Pb, 1 for CO, 1 for O₃, and 1 for NO₂)

Summary

- **EPA is currently performing research on methods for the measurement of ozone, lead, and NO₂ in ambient air.**
- **Further research is needed both in laboratory and field settings to develop and assess methods for NAAQS criteria pollutants including the identification of potential sampling interferences and/or challenges and to evaluate their use in routine monitoring.**
- **The results of this research may serve an informative role in the NAAQS review process for the corresponding criteria pollutants including the measurement methods used for its regulatory determination.**



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Disclaimer

Although this work was reviewed by EPA and approved for presentation, it may not necessarily reflect official Agency policy.